

# Preparation of Calcium Carbonate/Poly(methyl methacrylate) Composite Microspheres by Soapless Emulsion Polymerization

Xiaokun Ma, Bing Zhou, Ye Sheng, Chengyu Wang, Yan Pan, Shanshan Ma, Ye Gao, Zichen Wang

College of Chemistry, Jilin University, Changchun, 130023, China

Received 31 March 2006; accepted 26 January 2007

DOI 10.1002/app.26486

Published online 16 May 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Calcium carbonate ( $\text{CaCO}_3$ )/poly(methyl methacrylate) (PMMA) composite microspheres were synthesized in a soapless emulsion polymerization process.  $\text{CaCO}_3$  nanoparticles were pretreated with oleic acid to improve the compatibility between  $\text{CaCO}_3$  and the monomer methyl methacrylate, and this effectively enhanced the mass fraction of  $\text{CaCO}_3$  in the composite. The results of the thermogravimetric analysis showed that the thermal stability of the composite microspheres was better than that of PMMA. X-ray diffraction and Fourier transform infrared were applied to investigate the chemical and physical properties of the composite microspheres, and the

results proved that the composites were composed of  $\text{CaCO}_3$  and PMMA. Scanning electron microscopy and transmission electron microscopy pictures showed that the morphology of the composite microspheres was uniform, and the  $\text{CaCO}_3$  nanoparticles could be well dispersed in the polymeric matrix. The soapless emulsion polymerization process effectively increased the filling amount of  $\text{CaCO}_3$  in the composite microspheres. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2925–2929, 2007

**Key words:** compatibility; composites; emulsion polymerization; fillers; matrix

## INTRODUCTION

As nanotechnology has developed, composite microspheres have attracted increasing interest for both fundamental research and industrial applications.<sup>1,2</sup> Composite microspheres often exhibit properties completely different from those of polymeric systems in which an inorganic component has been added to a polymeric matrix at a micrometer level.<sup>3</sup> Some unexpected properties of composite microspheres, such as superconductivity, magnetism, nonlinear optics, thermal stability,<sup>4–6</sup> and dynamic mechanical properties, have been observed because of the enormous interfacial adhesion area of nanoparticles.

Several methods have been used to produce polymer composite microspheres, such as miniemulsion polymerization,<sup>7</sup> intercalative polymerization,<sup>8</sup> emulsion polymerization,<sup>9</sup> and hybrid latex polymerization.<sup>10</sup> Soapless emulsion polymerization has been frequently used to synthesize nanoparticle/polymeric composite microspheres. Few surfactants or no surfactants have been used in such systems, which provide advantages for the synthesis of monodisperse latex. In soapless emulsion polymerization systems, polymer particles have been stabilized by ion-

ized initiators.<sup>12</sup> When inorganic fillers without participation in the polymerization process [e.g., calcium carbonate ( $\text{CaCO}_3$ )] have been added, the locus and velocity of the polymerization have been changed to stabilize the emulsion system.

Yang et al.<sup>13</sup> obtained  $\text{CaCO}_3$ /polystyrene (PS) composites by soapless polymerization. The encapsulating ratio was about 60%, and the morphology of the composites was not uniform. Yu et al.<sup>14</sup> pretreated  $\text{CaCO}_3$  with  $\gamma$ -methacryloxypropyltrimethoxysilane to introduce polymerizable groups onto its surface and prepared  $\text{CaCO}_3$ /PS composites through an emulsion polymerization process. Avella et al.<sup>15</sup> prepared  $\text{CaCO}_3$ /poly(methyl methacrylate) (PMMA) nanocomposites and studied the abrasion-resistant behavior of the materials. However, the content of  $\text{CaCO}_3$  in the nanocomposites was reasonably low (<6%).

$\text{CaCO}_3$  is the cheapest commercially available inorganic material and is extensively used as a particulate filler in the manufacture of paint, paper, rubber, plastics, and so forth.<sup>16</sup>  $\text{CaCO}_3$  can be modified with different surfactants such as fatty acids, phosphonate, and titanate through the reaction of adsorbed hydroxy on the particle surface. In this study,  $\text{CaCO}_3$  nanoparticles were pretreated with oleic acid (OA), which provided them with high compatibility between the nanofillers and methyl methacrylate (MMA) monomer.

Correspondence to: Z. Wang (wangzc@mail.jlu.edu.cn).

**TABLE I**  
Different Quantities of CaCO<sub>3</sub> in the Soapless Emulsion Process

Sample	CaCO <sub>3</sub> content (g)	Yield (%)	Encapsulating ratio (%)
1	0.47	78.9	6.7
2	0.75	77.6	7.2
3	1.10	85.4	18.2
4	1.45	83.1	23.3
5	2.00	84.7	28.1
6	2.35	64.2	17.6

In this work, we obtained CaCO<sub>3</sub>/PMMA composite microspheres through a soapless emulsion polymerization process. The scanning electron microscopy (SEM) photographs showed that the morphology of the composite microspheres was uniform and that the size of the composite microspheres was about 350 nm. The encapsulating ratios of CaCO<sub>3</sub> in the composite microspheres could be controlled in this soapless emulsion polymerization process.

## EXPERIMENTAL

### Materials

The MMA monomer, with a density of 0.943 g/cm<sup>3</sup>, was obtained from Tianjin Chemicals Factory (China) and was not distilled. The ammonium persulfate (APS) initiator and OA surfactant were analytical-grade and were used without further purification. Distilled and deionized water was used throughout the work.

### Preparation of the CaCO<sub>3</sub> latex

Calcium oxide (CaO) was put into boiling deionized water, and then a saturated Ca(OH)<sub>2</sub> slurry was diluted after the impurity deposit was removed. The gas of CO<sub>2</sub> was aerated into the slurry to prepare a nanometer CaCO<sub>3</sub> latex through the control of the flux of CO<sub>2</sub> until the pH of the solution was down to 7. OA was dissolved in ethanol to be well dispersed in water and was added dropwise into the flask at 60°C for 1 h. The CaCO<sub>3</sub> latex was self-prepared with particle sizes of 40–100 nm.

### Preparation of the CaCO<sub>3</sub>/PMMA composite microspheres

A 500-mL, four-necked flask equipped with a thermometer, mechanical stirrer, reflux condenser, and N<sub>2</sub> inlet was charged with deionized water (100 g) and an OA-modified nanometer CaCO<sub>3</sub> latex. APS (0.100 g), as an initiator, and MMA (5 mL) were added dropwise to the flask at 60°C, and the amounts of the CaCO<sub>3</sub> nanoparticles are listed in Table I. The mixture was maintained at this tempera-

ture for 0.5 h and then at 80°C for 4 h. The product was collected by suction filtration and then dried at 70°C for 6 h. CaCO<sub>3</sub> nanoparticles unencapsulated in PMMA were eliminated from the composite microspheres after 1 h of dipping in 0.01M HCl. In contrast to the quantities of the composite microspheres, the encapsulated ratio of the CaCO<sub>3</sub> nanofiller could be calculated.

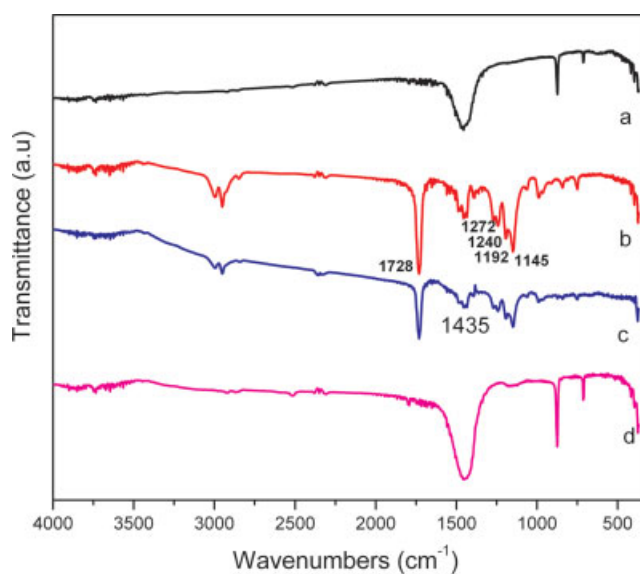
### Characterization

Fourier transform infrared (FTIR) was recorded with an Ominic System 2000 (USA), which employed a KBr pellet method. X-ray diffraction (XRD) patterns of the products were taken on a Shimadzu (Japan) model XRD-6000 that filtered Cu K $\alpha$  radiation. Thermogravimetric analysis (TGA) was conducted with a Mettler-Toledo (USA) 825<sup>e</sup> instrument at a heating rate of 20°C/min in an air atmosphere. The morphology of the CaCO<sub>3</sub>/PMMA composite microspheres was investigated by SEM with a Shimadzu SSX-55 electron microscope and by transmission electron microscopy (TEM) with a Hitachi (Japan) H-8100 electron microscope.

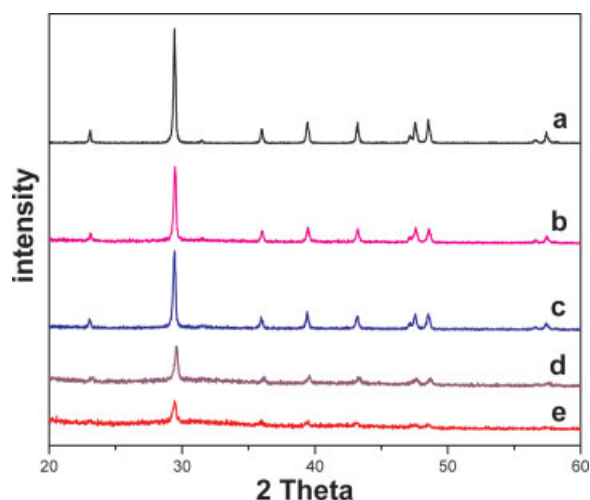
## RESULTS AND DISCUSSION

### Synthesis of the CaCO<sub>3</sub>/PMMA composite microspheres

The components of the CaCO<sub>3</sub>/PMMA composite microspheres were determined through FTIR and



**Figure 1** IR spectra of (a) CaCO<sub>3</sub> before emulsion polymerization, (b) pure PMMA, (c) CaCO<sub>3</sub>/PMMA composite microspheres, and (d) the composites after calcination. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 2** XRD plots of (a)  $\text{CaCO}_3$  pretreated with OA, (b)  $\text{CaCO}_3/\text{PMMA}$  composites with 28.1 wt %  $\text{CaCO}_3$ , (c)  $\text{CaCO}_3/\text{PMMA}$  composites with 23.2 wt %  $\text{CaCO}_3$ , (d)  $\text{CaCO}_3/\text{PMMA}$  composites with 18.2 wt %  $\text{CaCO}_3$ , and (e)  $\text{CaCO}_3/\text{PMMA}$  composites with 7.1 wt %  $\text{CaCO}_3$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

XRD investigations. Figure 1(a–d) shows FTIR spectra of  $\text{CaCO}_3$ , pure PMMA,  $\text{CaCO}_3/\text{PMMA}$  composites, and composites calcined at  $550^\circ\text{C}$  for 4 h, respectively. As shown in Figure 1(b), typical bands of PMMA were found at 1728, 1145, 1192, 1272, and  $1240\text{ cm}^{-1}$  and were assigned to the stretching vibrations of C=O and C–O (symmetric and asymmetric). Compared with pure PMMA and  $\text{CaCO}_3$ , the composites showed an adsorption band at  $1435\text{ cm}^{-1}$  that was broadened by the interaction between PMMA and  $\text{CaCO}_3$ .<sup>17</sup> Through a comparison with the curve of  $\text{CaCO}_3$ , as shown in Figure 1(a), an adsorption band at  $1728\text{ cm}^{-1}$  was found in the IR spectrum of the composites, indicating the presence of an ester group that came from PMMA. As shown in Figure 1(d), the IR spectrum of the calcined composites well agreed with that of  $\text{CaCO}_3$ , and this provided proof of the existence of  $\text{CaCO}_3$  in PMMA.

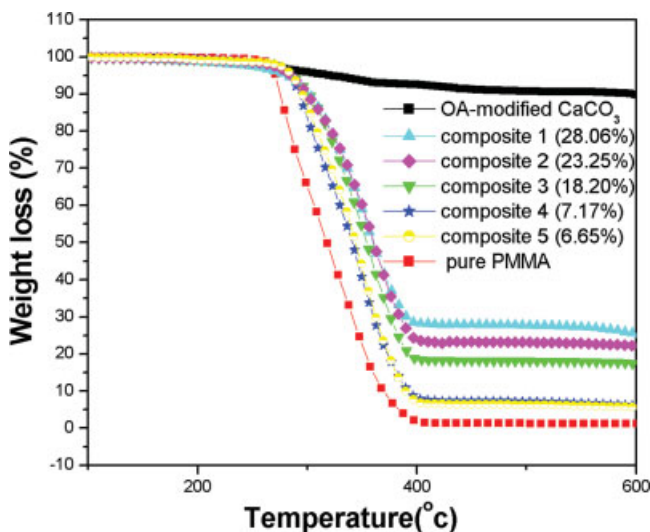
The presence of  $\text{CaCO}_3$  nanoparticles in the  $\text{CaCO}_3/\text{PMMA}$  composite microspheres was confirmed by XRD analysis, and the spectra are shown in Figure 2. In the pattern, the diffraction peaks were observed at  $2\theta$  values of 29.35, 48.62, 39.42, and  $47.50^\circ$ , which corresponded to  $\text{CaCO}_3$  crystals as calcite. Figure 2(b–e) shows the XRD peaks of composite samples 5–2 and were according to the order of samples listed in Table I (5–2). All the characteristic XRD peaks of the fillers could be observed, and this indicated that the  $\text{CaCO}_3$  nanoparticles were encapsulated in the PMMA matrix. On the other hand, the intensity of the characteristic XRD peaks of the fillers became weaker with a decreasing amount of  $\text{CaCO}_3$ . The difference in the inten-

sity was ascribed to the thickness of the PMMA layer on the surface of  $\text{CaCO}_3$  particles.

#### Encapsulating ratio of the $\text{CaCO}_3/\text{PMMA}$ composite microspheres

Table I lists the yields and encapsulating ratios of the different composite microspheres. The yields and encapsulating ratios of the  $\text{CaCO}_3/\text{PMMA}$  composite microspheres gradually increased with an increasing amount of  $\text{CaCO}_3$  when the filler mass fraction was below 2.00 g. A further increase in the filler decreased both the yield and encapsulating ratio. More  $\text{CaCO}_3$  could cause more coagulation, decreasing the stability of the latex. As a result, the appropriate concentration of  $\text{CaCO}_3$  was below 30 wt % in this case.

Figure 3 shows TGA plots of  $\text{CaCO}_3$ , pure PMMA, and  $\text{CaCO}_3/\text{PMMA}$  composite microspheres with different amounts of  $\text{CaCO}_3$ . Redundant  $\text{CaCO}_3$  was removed with a 0.01M HCl solution before testing, so the amounts of  $\text{CaCO}_3$  in the composites could be regarded as encapsulating ratios. Figure 3(a) shows that  $\text{CaCO}_3$  did not decompose below  $600^\circ\text{C}$ , and the weight loss was 8.6%, which was derived from the removal of water absorbed onto the particles surface and the decomposition of OA. The pure PMMA synthesized under the same polymerization conditions decomposed from 260 to  $400^\circ\text{C}$ , as shown in Figure 3(f). The weight loss between 260 and  $600^\circ\text{C}$  in the composites was used to calculate the amount of  $\text{CaCO}_3$  in the composite microspheres. Figure 3 (b–e) shows that the concentrations of  $\text{CaCO}_3$  in the composites were 28.1, 23.3, 18.2, 7.2, and 6.7 wt %, respectively.



**Figure 3** TGA plots of  $\text{CaCO}_3$  pretreated with OA, pure PMMA, and  $\text{CaCO}_3/\text{PMMA}$  composite microspheres. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



respectively. In this work, such a soapless emulsion polymerization process was effective for increasing the filling amount of  $\text{CaCO}_3$  in the composite microspheres. The decomposition temperature of the composite microspheres was higher than that of PMMA, and the decomposition temperature increased with increasing filler content. As a result, it was suggested that the nanoparticles could improve the thermal stability of the PMMA matrix.

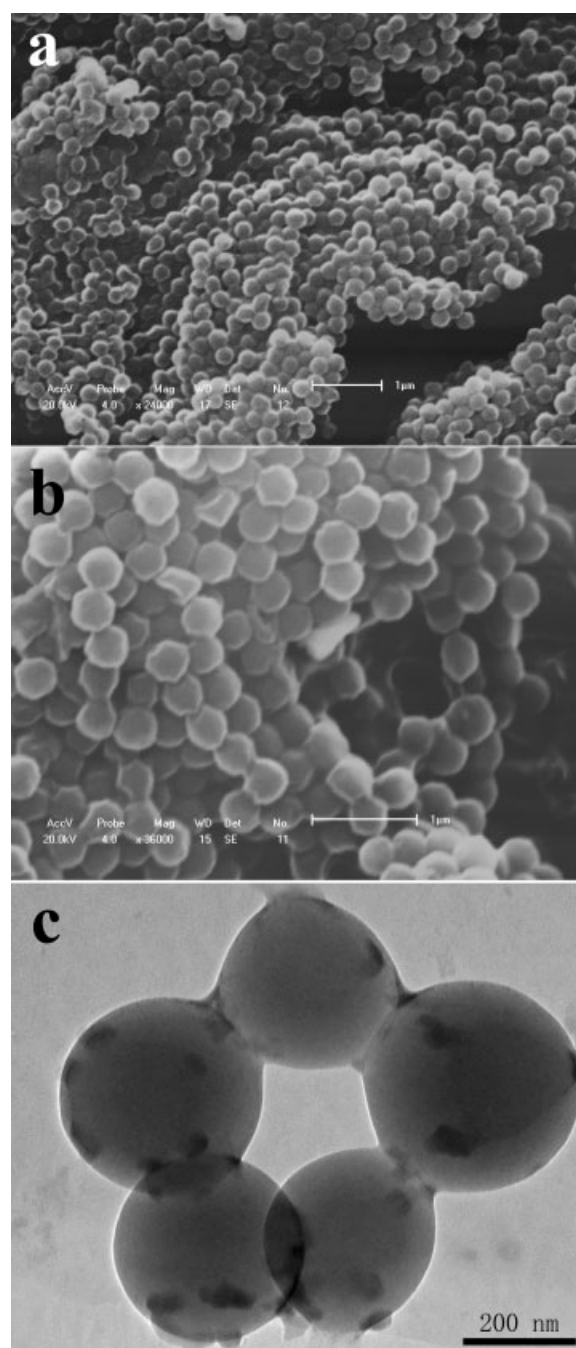
### Morphology of the $\text{CaCO}_3$ /PMMA composite microspheres

Figure 4(a,b) shows the SEM pictures of pure PMMA and  $\text{CaCO}_3$ /PMMA composite microspheres. Both the pure PMMA and  $\text{CaCO}_3$ /PMMA composite microsphere particles were uniform. The diameters were about 200 and 350 nm, respectively. The morphology of  $\text{CaCO}_3$ /PMMA was not smooth as that of PMMA. In addition,  $\text{CaCO}_3$  nanoparticles could not be observed in the  $\text{CaCO}_3$ /PMMA composite samples anywhere. The result allowed us to assume that  $\text{CaCO}_3$  nanoparticles were located in the PMMA polymer microspheres and made the polymer particles become larger. Shim et al.<sup>18</sup> prepared zinc oxide/PMMA composite microspheres by *in situ* suspension polymerization. In their work, they studied the influence of the amount of ZnO on the morphology of the composites and proved that ZnO nanoparticles were in the PMMA polymer spheres. A similar conclusion also could have been obtained for the  $\text{CaCO}_3$ /PMMA composite microspheres; however, the morphology of the  $\text{CaCO}_3$ /PMMA was uniform and was unchanged when the concentration of  $\text{CaCO}_3$  nanoparticles increased up to 30 wt %.

Figure 4(c) shows the TEM pictures of the  $\text{CaCO}_3$ /PMMA composite microspheres (sample 5) taken from the emulsion system. The size of the polymer spheres was in good agreement with the results of the SEM pictures. The  $\text{CaCO}_3$  nanoparticles were encapsulated or embedded in the PMMA matrix. In addition, the  $\text{CaCO}_3$  nanoparticles were apt to disperse at the edge of the PMMA polymer spheres. Therefore, a possible mechanism for the formation of the  $\text{CaCO}_3$ /PMMA composite microspheres in a soapless emulsion polymerization process could be proposed as follows.

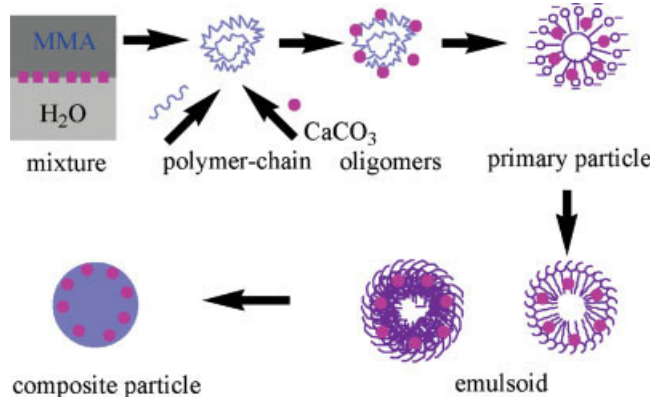
For the soapless emulsion polymerization of MMA with APS as the initiator, the particle generation was certified to follow the mechanism of homogeneous nucleation. In the aqueous phase, the APS initiator decomposed and propagated with the monomer to form oligomers.

Because of the interfacial compatibility of the OA-modified  $\text{CaCO}_3$  nanoparticles and the monomers,  $\text{CaCO}_3$  nanoparticles could be adsorbed around the oligomers during the stage of MMA growing from



**Figure 4** (a) SEM micrograph of pure PMMA, (b) SEM micrograph of  $\text{CaCO}_3$ /PMMA composite microspheres, and (c) TEM photograph of  $\text{CaCO}_3$ /PMMA composite microspheres.

the monomers to the MMA oligomers. When the oligomers reached their critical chain length, the composites precipitated from the aqueous phase and then formed as primary particles, and the  $\text{CaCO}_3$  nanoparticles could be encapsulated in the primary particles. These primary particles were unstable during the reaction; the coagulation between the primary particles proceeded strenuously at the begin-



**Scheme 1** Schematic illustration of the formation process of CaCO<sub>3</sub>/PMMA composite spheres. [Color scheme can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ning of the reaction until the polymer particles received enough surface charge, which led the composites to become uniform spheres, as shown in Scheme 1.

### CONCLUSIONS

In this work, CaCO<sub>3</sub>/PMMA composite microspheres were synthesized by soapless emulsion polymerization. This method was effective in increasing the filling amount of CaCO<sub>3</sub> in the composite microspheres. CaCO<sub>3</sub> pretreated with OA was encapsulated in the PMMA organic matrix because of the good compatibility between the nanofillers and the

polymeric matrix. The encapsulating structures are possibly interesting for the generation of water-borne hybrid coatings, which show the ability of the polymer for high mechanical scratch resistance provided by inorganic nanoparticles.

### References

- Li, Z.; Zhu, Y. *Appl Surf Sci* 2003, 211, 315.
- Fellahi, F. *Polym Compos* 2000, 21, 2.
- Lu, Y.; McLellan, J.; Xia, Y. *Langmuir* 2004, 20, 3464.
- Tojo, C.; Blanco, M. C.; Lopez-Quintela, M. A. *Langmuir* 1997, 13, 4527.
- Xi, Q.; Zhao, C.; Yuan, J.; Yuan, C. S. *J Appl Polym Sci* 2004, 91, 2739.
- Saito, R.; Ni, X. Y.; Ichimura, A.; Ishizu, K. *J Appl Polym Sci* 1998, 69, 211.
- Tiarks, F.; Landfester, K.; Antonietti, M. *Langmuir* 2001, 17, 5775.
- Avella, M.; Errico, M. E.; Martelli, S.; Martuscelli, E. *Appl Organomet Chem* 2001, 15, 435.
- Liu, P.; Liu, W. M.; Xue, Q. J. *Eur Polym J* 2004, 40, 267.
- Tissot, I.; Novat, C.; Bourgeat-Lami, E. *Macromolecules* 2001, 34, 5737.
- Espiard, P.; Guyot, A. *Polymer* 1995, 36, 4391.
- Chen, Y.-C.; Chia, F.; Chiu, W.-Y. *J Appl Polym Sci* 1996, 61, 2235.
- Yong, Y.; Xiang, Z. K.; Cheng, Y. K.; Chang, G. S. *Adv Polym Technol* 1999, 10, 54.
- Yu, J.; Yu, J.; Guo, Z.-X.; Gao, Y.-F. *Macromol Rapid Commun* 2001, 22, 1261.
- Avella, M.; Errico, M. E.; Martuscelli, E. *Nano Lett* 2001, 1, 4213.
- Leong, Y. W.; Abu Bakar, M. B.; Mohd Ishak, Z. A.; Ariffin, A.; Pukanszky, B. *J Appl Polym Sci* 2004, 91, 3315.
- Li, Z.; Zhang, J.; Du, J.; Mu, T.; Liu, Z.; Chen, J.; Han, B. *J Appl Polym Sci* 2004, 94, 1643.
- Shim, J.-W.; Kim, J.-W.; Han, S.-H.; Chang, I.-S.; Kim, H.-K.; Kang, H.-H.; Lee, O.-S.; Suh, K.-D. *Colloid Surf A* 2002, 207, 105.