

# Synthesis and Characterization of PMMA/SiO<sub>2</sub> Nanocomposites by *In Situ* Suspension Polymerization

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**ABSTRACT:** Poly(methyl methacrylate) (PMMA)/SiO<sub>2</sub> nanocomposites were prepared by *in situ* suspension polymerization. Two types of modified methods were used to modify nano-SiO<sub>2</sub>: one was modification by  $\gamma$ -methacryloxypropyl trimethoxy silane (KH570) and lauryl alcohol (12COH) while the other was grafting PMMA onto the surface of KH570 treated SiO<sub>2</sub>. Transmission electron microscopy (TEM) and Fourier transformed infrared (FTIR) were used to characterize the structures of the nanocomposites. The influence of synthetic conditions, for instance, surface modification, initial SiO<sub>2</sub> contents and reaction temperature, on the microsphere's size and molecular weight of the extracted PMMA were studied by gel permeation chromatograph (GPC) and optical microscopy

(OM) in details. Thermal property of the nanocomposites was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results indicate that the presence and content of SiO<sub>2</sub> have a vital effect on the shape and size of the nanocomposite microspheres, as well as molecular weight of the extracted PMMA. Grafting polymer to the surface of SiO<sub>2</sub> is an effective way for the purpose of effective *in situ* suspension polymerization. Compared to pure PMMA, the thermal properties of the nanocomposites were improved. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1975–1981, 2010

**Key words:** PMMA; SiO<sub>2</sub>; nanocomposites; suspension polymerization; thermal properties

## INTRODUCTION

Polymer–matrix nanocomposites represent an attractive family of composite materials in which the nanometer-size reinforcing fillers are uniformly dispersed in the polymer matrix on a nanometer scale as compared to conventional phase-separated composites.<sup>1–3</sup> Nanocomposites often exhibit physical and chemical properties that are dramatically different from conventional microcomposites. Poly(methyl methacrylate) (PMMA) is an important member in the family of polyacrylic and methacrylic esters. PMMA has several desirable properties, including exceptional optical clarity, good weatherability, high strength, and excellent dimensional stability. PMMA/SiO<sub>2</sub> nanocomposites have been extensively prepared by bulk polymerization,<sup>4</sup> emulsion polymerization,<sup>5,6</sup> microemulsion polymerization,<sup>7</sup> solution polymerization,<sup>8</sup> sol-gel method.<sup>9</sup> The mechanical and thermal properties of the nanocomposites were improved. However, to the best of our knowledge, no investigation on preparation of PMMA/SiO<sub>2</sub> nanocomposites via suspension polymerization has been reported. Only PMMA micro-

spheres prepared via suspension polymerization can be widely used for bone cements and dental materials.

Polymer microspheres have been applied in chromatographic separations, biochemistries, and bioengineering, especially in dental materials and prosthetic replacement operations.<sup>10–13</sup> As for PMMA suspension system, several inorganic materials have been introduced to improve the mechanical and thermal properties of PMMA. For instance, Huang and Brittain<sup>14</sup> firstly reported the synthesis of PMMA/montmorillonite nanocomposites by suspension polymerization, and followed by other researchers.<sup>15,16</sup> PMMA/ZnO and PMMA/TiO<sub>2</sub> nanocomposites prepared by suspension polymerization have been reported.<sup>17,18</sup>

As there is no systematic investigation of suspension polymerization for the PMMA/SiO<sub>2</sub> system, in this article, we use SiO<sub>2</sub> nanoparticles and PMMA for *in situ* suspension polymerization. The structure and the dispersion of SiO<sub>2</sub> in the nanocomposites were characterized by FTIR and TEM. Some influencing parameters such as surface modification and initial SiO<sub>2</sub> contents, reaction temperature on the nanocomposites, and the thermal properties were also investigated in details.

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## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA) was purchased from Da-Mao Institute of Chemical Agents (Tianjin,

China) and purified by the standard treatment with aqueous NaOH followed by distillation at a normal pressure and then stored at low temperature before use. SiO<sub>2</sub> nanoparticles with an average diameter of around 20 nm were purchased from Zhoushan Mingri Nanomaterial Co. (Zhejiang, China). KH570 was supplied by Nanjing Crompton Shuguang Organosilicon Co. (Nanjing, China) and used as received. All other reagents were all of analytical grade. Distilled water was used throughout.

### Characterization

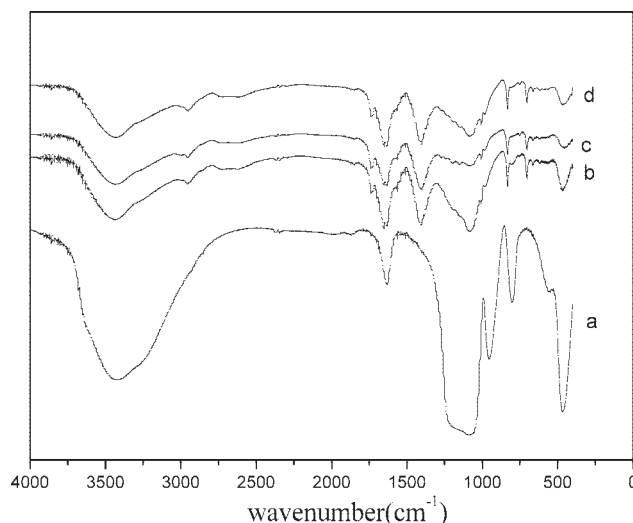
Before the FTIR measurements, the PMMA/SiO<sub>2</sub> nanocomposite microspheres were Soxhlet extracted with refluxing acetone for 48 h and dried at 60°C to remove the acetone. The FTIR spectra of the samples were taken with a Nicolet Magna Nicolet-5DX FTIR spectrophotometer using KBr pellets. The nanostructure features were characterized by TEM, using Hitachi H-800 TEM with 200 kV accelerating voltage. The molecular weight of the extracted PMMA from the nanocomposites was examined by GPC. The morphology and size of the nanocomposite microspheres were observed by OM. TGA was performed on a NETZSCH TG 209 instrument over the temperature range 25–800°C at a heating rate of 10°C/min. DSC was performed on DSC 2910 differential scanning calorimeter (DuPont Instruments) in N<sub>2</sub> atmosphere range from 25 to 300°C at a heating rate of 10°C/min.

### Modification of the SiO<sub>2</sub> nanoparticles

Before suspension polymerization, the SiO<sub>2</sub> nanoparticles were modified. A typical modified process was carried out as follows: a mixture of xylene (150 mL) and SiO<sub>2</sub> (5 g) was ultrasonically dispersed, and then the dispersion was added to a 100 mL three-neck flask followed by adding modifying agents (12COH, KH570) dropwise under continuous agitation. The mixture was stirred for 8 h in boiling state to obtain the modified SiO<sub>2</sub> nanoparticles named as SiO<sub>2</sub>-12COH and SiO<sub>2</sub>-KH570, standing for 12COH and KH570 modified SiO<sub>2</sub> nanoparticles, respectively.

### Grafting PMMA onto the modified SiO<sub>2</sub> nanoparticles

Xylene (150 mL) was mixed with the SiO<sub>2</sub>-KH570 nanoparticles (5 g) and then the mixture was ultrasonically dispersed. The mixture was changed into four-neck flask equipped with mechanical stirrer under a slow stream of N<sub>2</sub> and then heated to 80°C, followed by adding benzoyl peroxide (BPO) initiator (0.4 g). The system was maintained for 30 min to



**Figure 1** FTIR spectra of original SiO<sub>2</sub> and PMMA/SiO<sub>2</sub> nanocomposites (a) original SiO<sub>2</sub>, (b) PMMA/SiO<sub>2</sub>-12COH, (c) PMMA/SiO<sub>2</sub>-KH570, (d) PMMA/SiO<sub>2</sub>-KH570-PMMA.

obtain a homogeneously dispersed system and then MMA (40 g) was added dropwise into the mixture system. After the addition was completed, the reaction was performed for 5 h under stirring, and then cooled to room temperature to obtain modified SiO<sub>2</sub> nanoparticles named as SiO<sub>2</sub>-KH570-PMMA, standing for PMMA-grafted SiO<sub>2</sub>-KH570.

### *In situ* suspension polymerization of PMMA/SiO<sub>2</sub> nanocomposite microspheres

PMMA/SiO<sub>2</sub> nanocomposite microspheres were prepared by *in situ* suspension polymerization. A typical synthetic process was described as follows: the mixture of modified SiO<sub>2</sub> and MMA monomer (60 mL) were ultrasonically dispersed and then diluted with distilled water (180 mL) containing hydroxyethyl cellulose (HEC, 1.8 g) and sodium dodecyl sulfate (SDS, 0.072 g), stirred until obtaining homogeneous suspension system. The mixture was poured into the suspension polymerization reactor and then heated to the designated temperature under a nitrogen atmosphere for 30 min. After BPO (0.6 g) was employed to the system, the reaction was performed for 12 h. The result was repeatedly washed with water, followed by filtered and then dried in a vacuum oven overnight at 60°C to obtain PMMA/SiO<sub>2</sub>-12COH, PMMA/SiO<sub>2</sub>-KH570 and PMMA/SiO<sub>2</sub>-KH570-PMMA, standing for the nanocomposites of PMMA and SiO<sub>2</sub>-12COH, SiO<sub>2</sub>-KH570, as well as SiO<sub>2</sub>-KH570-PMMA, respectively.

## RESULTS AND DISCUSSION

### Morphology characterization

The FTIR spectra of original SiO<sub>2</sub> and a series of nanocomposites after extraction are shown in

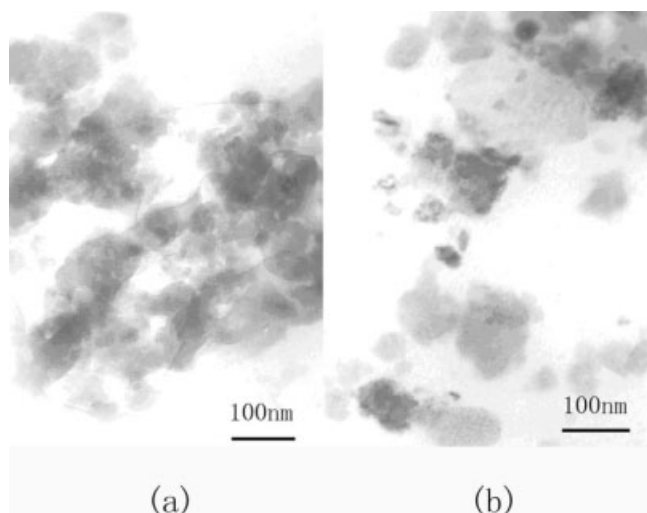
Figure 1. There is no product of pure PMMA after extraction. However, the spectra of the nanocomposites displays both the characteristic absorption bands at 1100 and 810 cm<sup>-1</sup> of Si—O stretching vibration of SiO<sub>2</sub> and the carbonyl group absorption band at 1735 cm<sup>-1</sup> of PMMA. The results reveal that PMMA strongly interacts with the modified SiO<sub>2</sub>. Therefore, the formation of the PMMA/SiO<sub>2</sub> nanocomposites was confirmed.

Figure 2 presents the TEM images of the PMMA/SiO<sub>2</sub> nanocomposites. The bright field represents the PMMA matrix and the dark field stands for the SiO<sub>2</sub> particles. The TEM micrograph of the PMMA/SiO<sub>2</sub>-12COH nanocomposite [Fig. 2(a)] shows the aggregation of the SiO<sub>2</sub> particles. On the other hand, the PMMA/SiO<sub>2</sub>-KH570-PMMA nanocomposite [Fig. 2(b)] shows much better SiO<sub>2</sub> dispersion, though slight aggregation can still be observed in some regions. Figure 3 shows the TEM images of PMMA/SiO<sub>2</sub> nanocomposites when the SiO<sub>2</sub> content is 1 and 4%, respectively. Serious agglomeration of SiO<sub>2</sub> particles can also be detected for that with 4 wt % SiO<sub>2</sub>. The FTIR results and TEM images indicate that a series of PMMA/SiO<sub>2</sub> nanocomposites were prepared by *in situ* suspension polymerization.

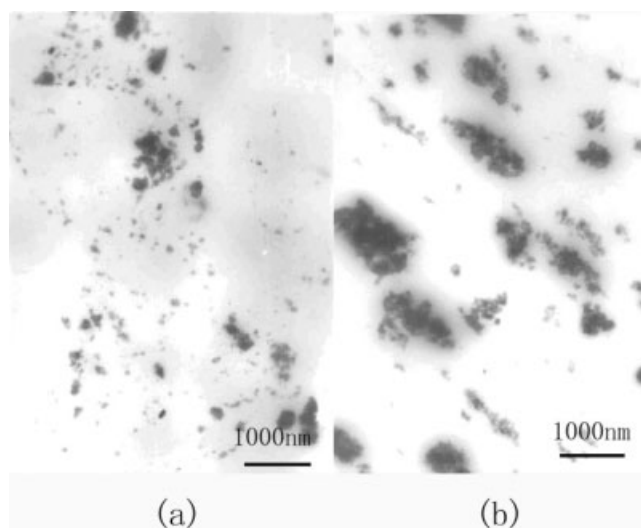
### Molecular weight of the extracted PMMA and morphology of the PMMA/SiO<sub>2</sub> microspheres

#### Effect of SiO<sub>2</sub> surface modification

Suspension polymerization of PMMA have been reported a lot,<sup>19,20</sup> but there is no report on PMMA/SiO<sub>2</sub> suspension polymerization system. And the articles about free radical type polymer/SiO<sub>2</sub> nanocomposites are seldom reported.<sup>3</sup> This phenomenon



**Figure 2** TEM images of PMMA/SiO<sub>2</sub> nanocomposites (SiO<sub>2</sub> content: 1 wt %) (a) PMMA/SiO<sub>2</sub>-12COH, (b) PMMA/SiO<sub>2</sub>-KH570-PMMA.



**Figure 3** TEM images of PMMA/SiO<sub>2</sub>-KH570-PMMA nanocomposites with different SiO<sub>2</sub> contents (a) 1 wt % (b) 4 wt %.

is because of the fact that the presence of SiO<sub>2</sub> particles will terminate free radical reaction as reported by Percy and coworkers,<sup>21</sup> which will result in only oily low-molecular-weight oligomers. To overcome this problem, the modification of the SiO<sub>2</sub> surface with an appropriate surface modifier is considered the best approach to solve this problem. Since the SiO<sub>2</sub> surface will be covered with modifier after treatment, it will not hurt the further polymerization of monomers. However, the introduction of SiO<sub>2</sub> to the system of suspension polymerization of PMMA should have some effects on the molecular weight and polydispersity indices (PDI) of the extracted PMMA of the obtained nanocomposites. The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and PDI of pure PMMA and extracted PMMA from the three nanocomposites are shown in Table I. The extracted PMMA from the three nanocomposites of PMMA/SiO<sub>2</sub>-12COH, PMMA/SiO<sub>2</sub>-KH570 and PMMA/SiO<sub>2</sub>-KH570-PMMA are named PMMA 1, PMMA 2 and PMMA 3, respectively. The data show the modified SiO<sub>2</sub> has some effect on the molecular weight of PMMA. Both

**TABLE I**  
 $M_n$ ,  $M_w$ , PDI of the Pure PMMA and the Extracted PMMA from the Three Nanocomposites<sup>a</sup>

| Sample    | $M_n$ ( $\times 10^{-4}$ ) | $M_w$ ( $\times 10^{-4}$ ) | PDI ( $M_w/M_n$ ) |
|-----------|----------------------------|----------------------------|-------------------|
| Pure PMMA | 32.2                       | 84.6                       | 2.63              |
| PMMA 1    | 22.9                       | 59.1                       | 2.58              |
| PMMA 2    | 46.3                       | 90.3                       | 1.95              |
| PMMA 3    | 29.3                       | 84.7                       | 2.89              |

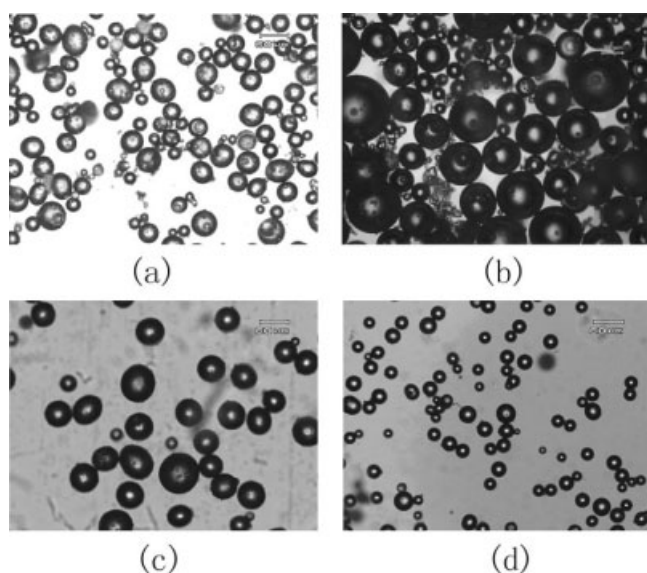
<sup>a</sup> The extracted PMMA from the three nanocomposites of PMMA/SiO<sub>2</sub>-12COH, PMMA/SiO<sub>2</sub>-KH570 and PMMA/SiO<sub>2</sub>-KH570-PMMA are named PMMA 1, PMMA 2 and PMMA 3, respectively.

$M_n$  and  $M_w$  decrease for PMMA1 and increase for PMMA2, but almost have no change for PMMA3. An explanation is that, in the presence of SiO<sub>2</sub>-KH570 and SiO<sub>2</sub>-KH570-PMMA, the inhibited polymerization is not pronounced, and especially for the system of PMMA2, SiO<sub>2</sub>-KH570 even plays a role in promoting and enhancing the propagation of the suspension polymerization. As a result, the modification of PMMA/SiO<sub>2</sub>-KH570-PMMA is the best, as the molecular weight of PMMA3 is most consistent with that of pure PMMA.

Figure 4 shows optical micrographs of PMMA and PMMA/SiO<sub>2</sub> nanocomposite microspheres. Compared to pure PMMA, the size of PMMA/SiO<sub>2</sub>-12COH microspheres [Fig. 4(b)] markedly increases and distributes more unevenly, while the size of PMMA/SiO<sub>2</sub>-KH570 microspheres [Fig. 4(c)] just increases slightly. On the other hand, the size of PMMA/SiO<sub>2</sub>-KH570-PMMA microspheres is the smallest and closest to that of pure PMMA microspheres, with a diameter of 40–60 μm. The diameter of the microspheres is dependent on the modifying agents and treated methods of the initial used SiO<sub>2</sub> nanoparticles.

#### Effect of SiO<sub>2</sub> contents

The suspension polymerization was performed with different contents of SiO<sub>2</sub> nanoparticles to evaluate the effect of SiO<sub>2</sub> contents on the molecular weight and PDI of PMMA/SiO<sub>2</sub>-KH570-PMMA nanocomposite, as summarized in Table II. Compared to pure PMMA, when the SiO<sub>2</sub> content is 1 wt %, the  $M_n$  of the extracted PMMA from the nanocomposite tends

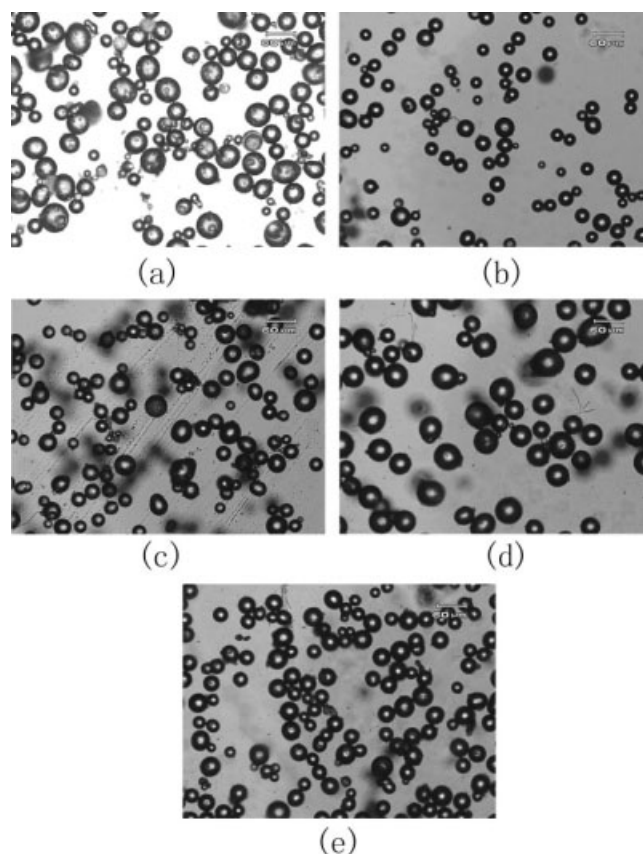


**Figure 4** Optical micrographs of PMMA and PMMA/SiO<sub>2</sub> nanocomposite microspheres (a) pure PMMA, (b) PMMA/SiO<sub>2</sub>-12COH, (c) PMMA/SiO<sub>2</sub>-KH570, (d) PMMA/SiO<sub>2</sub>-KH570-PMMA.

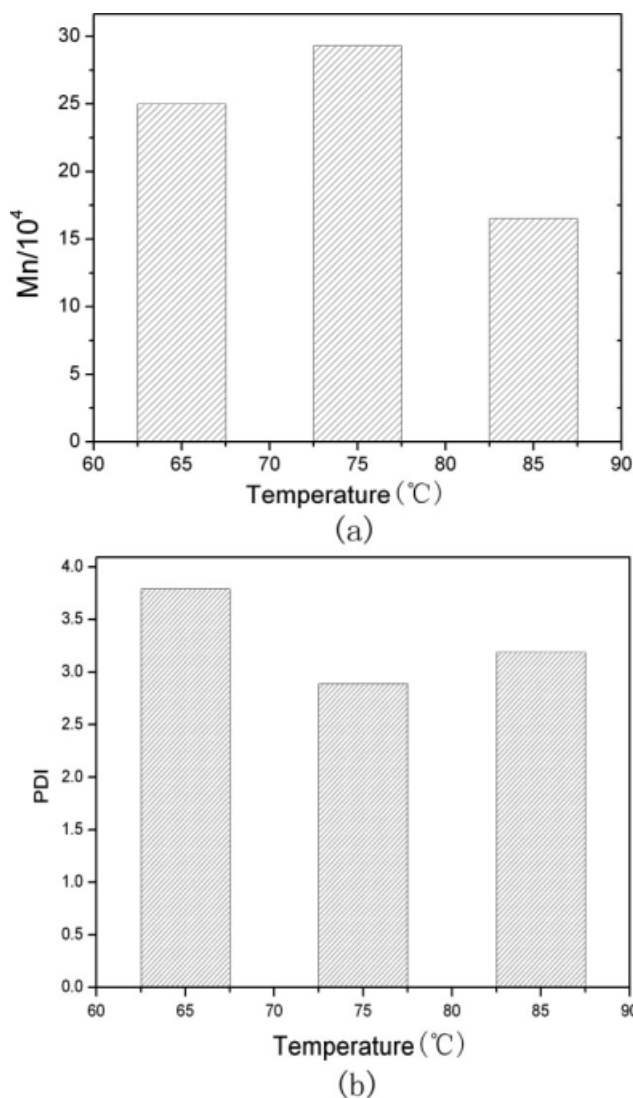
**TABLE II**  
 $M_n$ ,  $M_w$ , PDI of the Pure PMMA and the Extracted PMMA from PMMA/SiO<sub>2</sub>-KH570-PMMA Nanocomposites

| SiO <sub>2</sub> content (wt %) | $M_n$ ( $\times 10^{-4}$ ) | $M_w$ ( $\times 10^{-4}$ ) | PDI ( $M_w/M_n$ ) |
|---------------------------------|----------------------------|----------------------------|-------------------|
| 0                               | 32.2                       | 84.6                       | 2.63              |
| 1                               | 29.3                       | 84.7                       | 2.89              |
| 2                               | 45.6                       | 98.2                       | 2.15              |
| 3                               | 45.6                       | 98.5                       | 2.16              |
| 4                               | 46.0                       | 98.2                       | 2.14              |

to decrease. When the SiO<sub>2</sub> content is 2 wt %, both the  $M_n$  and  $M_w$  sharply increases, followed by remaining consistent with increasing SiO<sub>2</sub> contents; and PDI decreases compared to that of pure PMMA. It suggests that the introduction and the contents of SiO<sub>2</sub> have a certain effect on the molecular weight of the extracted polymer. When the SiO<sub>2</sub> content is 1 wt %, SiO<sub>2</sub> nanoparticles can inhibit the polymer chains from free radical polymerization; but when SiO<sub>2</sub> nanoparticles were coated by PMMA molecular chains, the inhibition effect is not obvious and with the increasing of SiO<sub>2</sub> content, the viscosity of the system increased, resulting in the increase of the

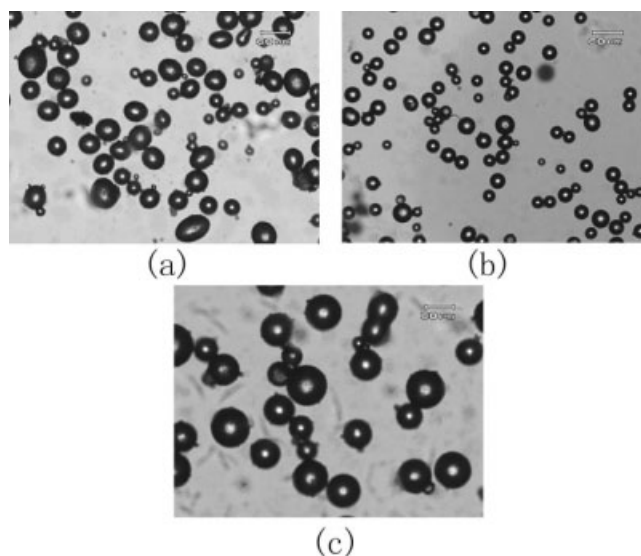


**Figure 5** Optical micrographs of PMMA/SiO<sub>2</sub>-KH570-PMMA microspheres with different SiO<sub>2</sub> contents (a) pure PMMA, (b) 1 wt %, (c) 2 wt %, (d) 3 wt %, (e) 4 wt %.



**Figure 6** Effect of reaction temperature on the molecular weight and PDI of the extracted PMMA from PMMA/SiO<sub>2</sub>-KH570-PMMA nanocomposites (SiO<sub>2</sub> content: 1 wt %). (a) molecular weight, (b) PDI.

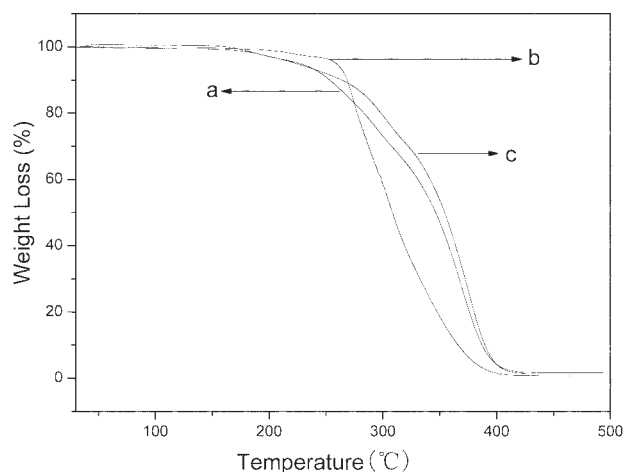
molecular weight. Within the SiO<sub>2</sub> content ranging from 2 wt % to 4 wt %, the  $M_n$ ,  $M_w$  and PDI almost remain the same. However, high molecular weight polymer could still be polymerized with the introduction of SiO<sub>2</sub> nanoparticles. Figure 5 shows the optical micrographs of the microspheres prepared with modified SiO<sub>2</sub> ranging from 1 to 4 wt %. The diameter of the nanocomposite microspheres tends to increase followed by decrease with increasing SiO<sub>2</sub> contents and the maximum size appears when the SiO<sub>2</sub> content is 3 wt %. However, with increasing SiO<sub>2</sub> contents, the size of the microspheres is kept within 30 to 60  $\mu\text{m}$  for all, which is consistent with that of pure PMMA. It suggested that the introduction of SiO<sub>2</sub>-KH570-PMMA had little effect on suspension polymerization of PMMA. The microspheres with proper size and size distribution were achieved.



**Figure 7** Optical micrographs of PMMA/SiO<sub>2</sub>-KH570-PMMA nanocomposite microspheres prepared at different reaction temperature (SiO<sub>2</sub> content: 1 wt %) (a) 65°C, (b) 75°C, (c) 85°C

#### Effect of reaction temperature

The effect of reaction temperature on the molecular weight and PDI of extracted PMMA from PMMA/SiO<sub>2</sub>-KH570-PMMA nanocomposites (SiO<sub>2</sub> content: 1 wt %) are illustrated in Figure 6. The data in Figure 6(a) show that with the increase of reaction temperature, the molecular weight of extracted PMMA from nanocomposites increases followed by markedly decreases and the high-point is visualized at 75°C. Figure 6(b) presents the effect of reaction temperature on PDI of extracted PMMA from the nanocomposites. The extracted PMMA has a rather narrow distribution when the temperature is 75°C. The possible reason can be explained as follows: (1) the



**Figure 8** TGA curves of PMMA and PMMA/SiO<sub>2</sub> nanocomposites (a) Pure PMMA, (b) PMMA/SiO<sub>2</sub>-12COH, (c) PMMA/SiO<sub>2</sub>-KH570-PMMA.

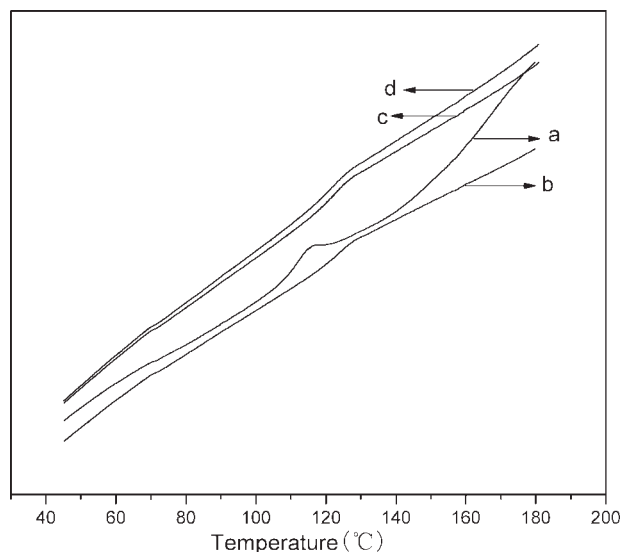
**TABLE III**  
TGA Results of PMMA and the Nanocomposites  
(SiO<sub>2</sub> Content: 1 wt %)

| Samples                           | T <sub>10</sub> (°C) | T <sub>50</sub> (°C) |
|-----------------------------------|----------------------|----------------------|
| PMMA                              | 252                  | 346                  |
| PMMA/SiO <sub>2</sub> -12COH      | 269                  | 308                  |
| PMMA/SiO <sub>2</sub> -KH570-PMMA | 263                  | 354                  |

increase of reaction temperature improve the decomposed rate of the initiator, the free radical concentration become increased within a short period of time, and the average polymerization degree decreases. So, the extracted PMMA has a rather small molecular weight when the temperature is 85°C. (2) the increase of reaction temperature make the polymerization rate become faster and the conversion rate increase, hence the viscosity of the system increase. Obviously, when the temperature is below 75°C, the decomposed rate of the initiator was not fast enough ( $t_{1/2} = 10$  h at 73°C for the initiator), the second reason contribute to the increase of the molecular weight. As Figure 7 presents, the size of obtained nanocomposite microspheres at 75°C is the smallest and most homogenous, suggesting that the reaction temperature has a certain influence on the size and morphology of the microspheres and 75°C is the optimum reaction temperature.

#### Thermal properties

An enhanced thermal stability of the PMMA/SiO<sub>2</sub> nanocomposites with 1 wt % SiO<sub>2</sub> content is observed by TGA. As shown in Figure 8 and Table III, different surface modified methods play different roles in thermal stability of PMMA/SiO<sub>2</sub> nanocompo-



**Figure 9** DSC curves of PMMA and PMMA/SiO<sub>2</sub>-KH570-PMMA nanocomposites with different SiO<sub>2</sub> contents (a) PMMA, (b) 1 wt %, (c) 2 wt %, (d) 3 wt %.

**TABLE IV**  
DSC Results of PMMA/SiO<sub>2</sub>-KH570-PMMA  
Nanocomposites with Different SiO<sub>2</sub> Contents

| SiO <sub>2</sub> content<br>(wt %) | T <sub>g</sub> (°C) |
|------------------------------------|---------------------|
| 0                                  | 111                 |
| 1                                  | 124                 |
| 2                                  | 122                 |
| 3                                  | 122                 |

sites. The data include the temperature at which 10% mass is lost ( $T_{10}$ ), indicative of the onset temperature of the decomposition, and the temperature at which 50% mass is lost ( $T_{50}$ ), a measure of the course of the decomposition. PMMA/SiO<sub>2</sub>-12COH exhibits a higher  $T_{10}$  but much lower  $T_{50}$  than those of pure PMMA, whereas PMMA/SiO<sub>2</sub>-KH570-PMMA exhibits higher  $T_{10}$  and  $T_{50}$ , showing an enhanced thermal stability than pure PMMA.

DSC curves of pure PMMA and PMMA/SiO<sub>2</sub>-KH570-PMMA nanocomposites are shown in Figure 9 and the results are listed in Table IV. The endothermic peak near 111°C is related to  $T_g$  of pure PMMA, while the PMMA/SiO<sub>2</sub>-KH570-PMMA nanocomposites exhibit elevated  $T_g$  values ranging from 122 to 124°C. When the SiO<sub>2</sub> content is 1 wt %, the nanocomposite shows the highest  $T_g$  with 13°C higher compared to that of pure PMMA. An explanation is that strong interfacial bonding between the functionalized nanofiller and polymer matrix leads to an increase of the  $T_g$  by impeding chain flexibility.<sup>18</sup> Further research work about the mechanical properties of these nanocomposites will be carried out.

#### CONCLUSIONS

PMMA/SiO<sub>2</sub> nanocomposites were successfully prepared via *in situ* suspension polymerization. FTIR analysis indicated that there existed interactions between modified SiO<sub>2</sub> and polymer segments. TEM results confirmed the morphology and dispersed behavior of modified SiO<sub>2</sub> in the obtained PMMA/SiO<sub>2</sub> nanocomposites, the best of which was observed for PMMA/SiO<sub>2</sub>-KH570-PMMA with 1 wt % SiO<sub>2</sub> content. GPC and OM results showed the introduction and the content of SiO<sub>2</sub> nanoparticles, as well as the reaction temperature had a certain effect on the molecular weight of extracted PMMA and the size of the nanocomposite microspheres. The molecular weight of extracted PMMA from PMMA/SiO<sub>2</sub>-KH570-PMMA is the most consistent to that of pure PMMA, and the size of PMMA/SiO<sub>2</sub>-KH570-PMMA microspheres is the closest to that of pure PMMA. Compared to pure PMMA, the thermal properties of the PMMA/SiO<sub>2</sub>-KH570-PMMA

nanocomposite improved, and the  $T_{10}$ ,  $T_{50}$ , and  $T_g$  increased 11°C, 8°C, and 13°C, respectively.

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