

# Preparation and Characterization of Polystyrene/Titanium Dioxide Composite Particles Containing Organic Ultraviolet-Stabilizer Groups

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**ABSTRACT:** Polystyrene/titanium dioxide ( $\text{TiO}_2$ ) composite particles containing organic ultraviolet (UV)-stabilizer groups were prepared by the emulsion copolymerization of styrene and 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone with sodium sulfopropyl lauryl maleate as a surfactant in the presence of rutile  $\text{TiO}_2$  modified with 3-(trimethoxysilyl) propyl methacrylate, and the product was poly[styrene-co-sodium sulfopropyl lauryl maleate-co-2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone] [poly(St-co-M12-co-BPMA)]/ $\text{TiO}_2$  composite particles. The structures of the composite particles were characterized with Fourier transform infrared spectroscopy, ultraviolet-visible (UV-vis) absorption spectroscopy, thermogravimetric analysis, and differential scanning calorimetry. The Fourier transform infrared and UV-vis

measurements showed that poly(St-co-M12-co-BPMA) was grafted from the surface of  $\text{TiO}_2$ , and this copolymer possessed a high absorbance capacity for UV light, which is very important for improving the UV resistance of polystyrene. The thermogravimetric analysis measurements indicated that the percentage of grafting and the grafting efficiency could reach 513.9 and 59.9%, respectively. The differential scanning calorimetry measurement indicated that the glass-transition temperature of the poly(St-co-M12-co-BPMA)/ $\text{TiO}_2$  composite particles was higher than that of poly(St-co-M12-co-BPMA). These research results are very important for preparing polystyrene with high UV resistance.  
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**Key words:** composites; emulsion polymerization

## INTRODUCTION

Polystyrene is a widely used plastic, but it can be easily photolyzed by ultraviolet (UV) light (190–400 nm). One way to protect polystyrene from UV destruction is to add UV stabilizers to the matrix. Inorganic UV stabilizers and organic UV stabilizers are two kinds of UV stabilizers that are used widely. However, inorganic UV stabilizers, such as titanium dioxide ( $\text{TiO}_2$ ), silicon dioxide, and zinc oxide, usually cannot be evenly distributed in the polystyrene matrix; organic UV stabilizers, such as hydroxyl benzophenone and benzotriazoles, generally have poor extraction resistance, which makes them easily migrate from polystyrene during processing.

To resolve such problems, the introduction of an organic UV stabilizer and  $\text{TiO}_2$  into polystyrene

chains by covalent bonding is put forward by our group. The use of a reactive UV stabilizer and modified  $\text{TiO}_2$  can combine the organic UV stabilizer and  $\text{TiO}_2$  with polystyrene by covalent bonding. As a result, the problems of evaporation, migration, and distribution of the UV stabilizers will be solved; furthermore, the service life of polystyrene can be prolonged effectively. In the past decades, there have been a lot of works on reactive UV stabilizers<sup>1–5</sup> and organic/inorganic composite particles,<sup>6–8</sup> and they supply a good foundation for preparing polystyrene with high UV resistance, as discussed previously.

With the advantages of high reaction rates and good heat dispersion, emulsion polymerization is a good method for preparing organic/inorganic composite particles. However, there are some adverse effects of surfactants on emulsion polymerization, such as foaming, and when mixed with other products in paints, surfactants can migrate to the pigment phase and cause destabilization of the latex particles. To overcome these disadvantages, a reactive surfactant<sup>9–11</sup> containing a polymerizable double bond is introduced. When the surfactant is anchored to the surface of the latex particles in an emulsion polymerization, it cannot migrate to the pigment phase and hence can continue to stabilize the particles.

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In this study, the reactive UV stabilizer 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone (BPMA) and the reactive surfactant sodium sulfopropyl lauryl maleate (M12) were copolymerized with styrene (St) in the presence of modified TiO<sub>2</sub> via emulsion polymerization to obtain polystyrene/TiO<sub>2</sub> composite particles containing organic UV stabilizer groups, that is, poly[styrene-co-sodium sulfopropyl lauryl maleate-co-2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone] [poly(St-co-M12-co-BPMA)]/TiO<sub>2</sub> composite particles. This is very important for enhancing the UV resistance of polystyrene.

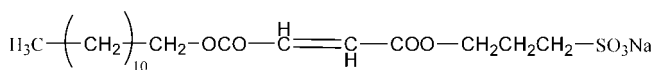
## EXPERIMENTAL

### Materials

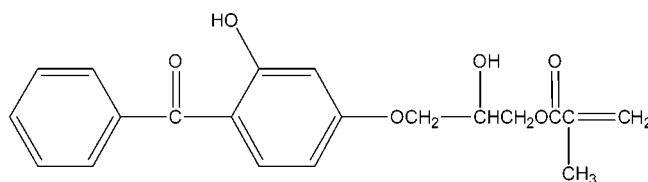
St, from the Chengdu Kelong Chemical Reagent Factory (Chengdu, China), was washed with a 10 wt % NaOH aqueous solution and distilled *in vacuo* before use. The initiator, potassium peroxydisulfate (KPS), was supplied by the Beijing Chemical Reagent Factory (Beijing, China). TiO<sub>2</sub> in a rutile form was acquired from PanGang Group Corp. of China (Panzhuhua, China). 3-(Trimethoxysilyl) propyl methacrylate ( $\gamma$ -MPS), used for modifying the surface of TiO<sub>2</sub>, was obtained from the Ha'erbin Chemical Research Institute (Ha'erbin, China). BPMA and M12 were synthesized according to patents.<sup>12,13</sup> The molecular structures of M12 and BPMA are shown in Schemes 1 and 2. Calcium chloride (CaCl<sub>2</sub>) came from the Tianjin Tanggudeng Chemical Factory (Tianjin, China). Deionized water was used in the experiments. Trichloromethane (CHCl<sub>3</sub>; analytical reagent) and tetrahydrofuran (THF; analytical reagent) were purchased from the Kelong Chemical Reagent Factory (Chengdu, China).

### Modification of TiO<sub>2</sub>

The TiO<sub>2</sub> particles were dispersed in an ethanol solution of 5 wt %  $\gamma$ -MPS (based on the content of TiO<sub>2</sub>) for 10 min via ultrasonic vibrations with an SC-I ultrasonic apparatus supplied by Chengdu Jiuzhou Ultrasonic Technology Co., Ltd. (Chengdu, China). The mixture was heated at 70–75°C for 6 h, dried at 70–80°C, and then extracted with ethanol to remove  $\gamma$ -MPS adsorbed physically on the surface of the TiO<sub>2</sub> particles. At last, the product was dried at 70–80°C to remove the solvent.



Scheme 1 Molecular structure of M12.



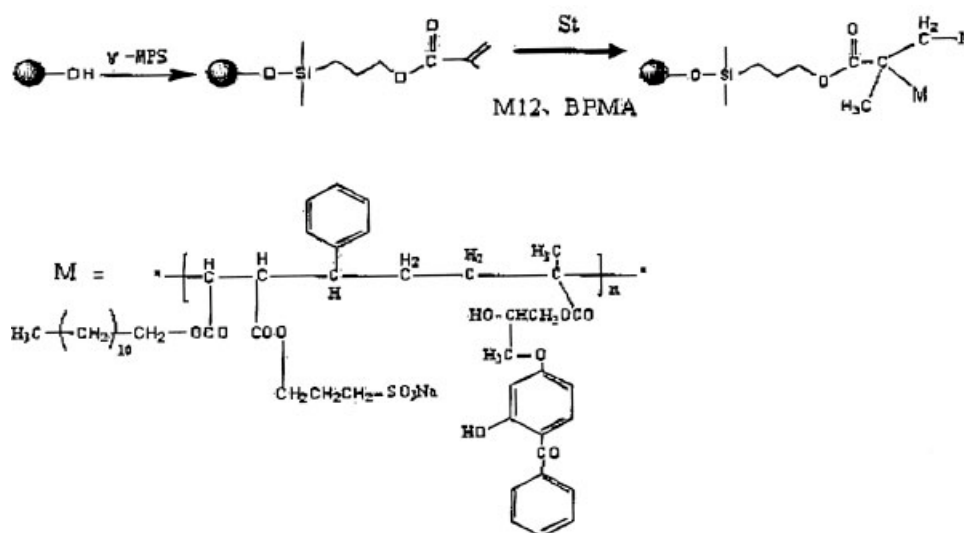
Scheme 2 Molecular structure of BPMA.

### Synthesis of poly(St-co-M12-co-BPMA)

Poly(St-co-M12-co-BPMA) was prepared via the emulsion copolymerization of St with M12 and BPMA. First, 45 mL of a 1 wt % M12 aqueous solution (based on the amount of deionized water) was added to a 250-mL, three-necked flask equipped with an N<sub>2</sub> flow, mechanical stirrer, and drop funnel. When the temperature rose to 60–70°C, 5 mL of a 0.5 wt % KPS aqueous solution (based on the amount of St) was added to the three-necked flask with mechanical stirring. A few minutes later, 9 g of St and 0.45 g of a BPMA mixture were trickled slowly into the three-necked flask. The polymerization was carried out at 70–80°C for about 4 h, and then the poly(St-co-M12-co-BPMA) latex was obtained. The latex was precipitated with a CaCl<sub>2</sub>-water solution, and the precipitation was filtered, washed, dried at 60°C, pulverized, and then Soxhlet-extracted with refluxing deionized water for 72 h to get purified poly(St-co-M12-co-BPMA).

### Preparation of the poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles and poly(styrene-co-sodium sulfopropyl lauryl maleate) [poly(St-co-M12)]/TiO<sub>2</sub> composite particles

The poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles were obtained through the emulsion polymerization of St with M12 and BPMA in the presence of modified TiO<sub>2</sub>. First, 1 g of modified TiO<sub>2</sub> was dispersed in 45 mL of a 1 wt % M12 aqueous solution (based on the amount of deionized water) via ultrasonic vibrations under 150–200 W for 10 min. Then, the TiO<sub>2</sub> slurry was diverted into a 250-mL, three-necked flask equipped with an N<sub>2</sub> flow, mechanical stirrer, and drop funnel. Then, 5 mL of a 0.5 wt % KPS aqueous solution (based on the amount of St) was added to the three-necked flask with mechanical stirring when the temperature rose to 60–70°C. After 10 min, 9 g of St and 0.45 g of a BPMA mixture trickled slowly into the three-necked flask. Emulsion polymerization was carried out at 80°C for about 6 h. Then, the obtained latex was coagulated with the CaCl<sub>2</sub> aqueous solution, filtered, washed, dried at 60°C, and pulverized to get the poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles. With the help of a Soxhlet extractor, the composite particles were extracted with refluxing deionized water



**Scheme 3** Preparation of poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles.

for 72 h and with refluxing chloroform for 10 days to remove the unreacted M12, BPMA, and poly(St-co-M12-co-BPMA) that adsorbed onto the surfaces of the modified TiO<sub>2</sub> particles. At last, the purified poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles were obtained. The poly(St-co-M12)/TiO<sub>2</sub> composite particles were prepared with the same method without BPMA in the feed.

### Measurements and characterization

#### Fourier transform infrared (FTIR) measurements

Before the FTIR measurements, poly(St-co-M12-co-BPMA) was Soxhlet-extracted with refluxing deionized water for 72 h, and the poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles and modified TiO<sub>2</sub> were Soxhlet-extracted with refluxing CHCl<sub>3</sub> at 70°C for 10 days to remove the free M12, BPMA, poly(St-co-M12-co-BPMA), and  $\gamma$ -MPS. During the extraction, the chloroform solution was replaced with fresh chloroform (99.0%) after a time interval. The purified poly(St-co-M12-co-BPMA), poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles, and modified TiO<sub>2</sub> were prepared in the form of potassium bromide pellets. FTIR measurements of all the samples were carried out on a Nicolet 560 FTIR spectrometer (Thermo Nicolet Corp.).

#### Ultraviolet-visible (UV-vis) measurements

Before the measurements, the extracted poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> and poly(St-co-M12)/TiO<sub>2</sub> composite particles were treated with hydrofluoric acid (HF) to remove the TiO<sub>2</sub> particles. The UV-vis absorption spectra of poly(St-co-M12-co-BPMA) grafted from the surface of TiO<sub>2</sub>, pure poly(St-co-M12-co-

BPMA), and poly(St-co-M12) grafted from the surface of TiO<sub>2</sub> were characterized with a UV-240 UV-vis spectrophotometer (Shimadzu Corp., Japan) in the range of 200–450 nm with THF as the solvent.

#### Thermogravimetric analysis (TGA) measurements

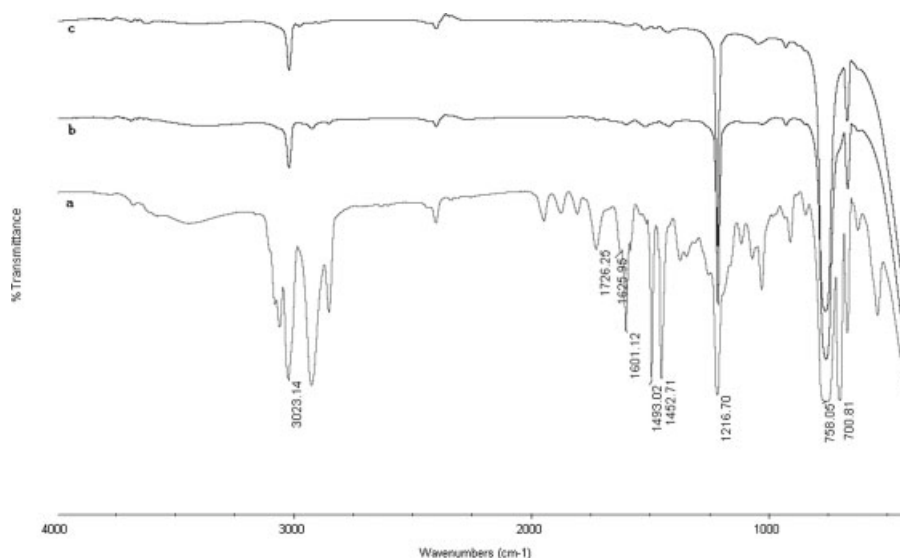
TGA measurements were performed with a Dupont 2100 thermal analysis apparatus (Dupont Corp.) over the temperature range of 30–500°C at the rate of 10°C/min. The samples were heated in a nitrogen atmosphere, and the rate of N<sub>2</sub> was 50 mL/min.

#### Differential scanning calorimetry (DSC) measurements

The DSC measurements were as carried out on a Netzsch DSC 204 apparatus (Netzsch Corp., Germany). An extracted sample (5 mg) was heated from 50 to 200°C to detect the glass-transition temperature ( $T_g$ ) of the poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles. The heating rate was 10°C/min, and the test was under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

It is well known that there are lots of hydroxyl groups on the surface of TiO<sub>2</sub> that can react with organic compounds. In this study, surface-modified TiO<sub>2</sub> was first prepared via the reaction between the silane coupling agent  $\gamma$ -MPS and TiO<sub>2</sub>. Then, modified TiO<sub>2</sub> containing carbon-carbon double bonds reacted with St, the reactive UV stabilizer BPMA, and the reactive surfactant M12 via emulsion copolymerization. The polymerization process can be simulated as shown in Scheme 3.



**Figure 1** FTIR spectra of (a) a chloroform solution after a sample was extracted for 24 h, (b) a chloroform solution after a sample was extracted for 240 h, and (c) fresh chloroform (99.0%).

#### FTIR analysis of the poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles

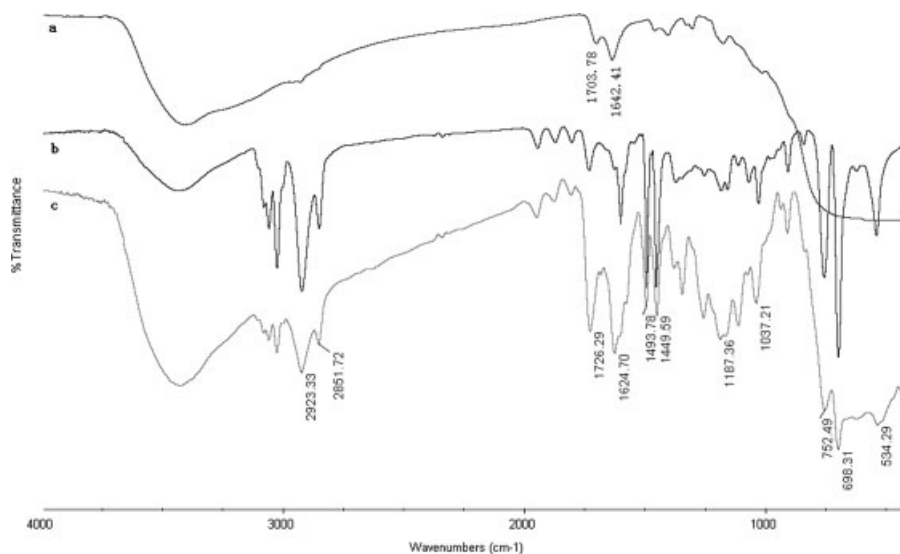
To confirm the polymerization of St, M12, and BPMA from the surface of TiO<sub>2</sub>, FTIR measurements were used. Before the measurements, the products were extracted with chloroform (99.0%) for 24 h. Then, the chloroform solution was replaced with fresh chloroform (99.0%) at a time interval during the extraction of the products. The free M12, BPMA, poly(St-co-M12-co-BPMA), and coupling agent could be moved. The FTIR spectra of fresh chloroform (99.0%) and chloroform solutions after the extraction of samples for 24 and 240 h are shown in Figure 1. The FTIR spectrum of the chloroform solution after extraction for 24 h [Fig. 1(a)] shows the characteristic absorption of the benzene ring of poly(St-co-M12-co-BPMA) at 1493, 1452, 758, and 700 cm<sup>-1</sup> and the absorption of the C=O group of poly(St-co-M12-co-BPMA) at 1726 cm<sup>-1</sup>, whereas these absorptions cannot be found in the spectrum of fresh chloroform [99.0%; Fig. 1(c)]. This result indicates that some free poly(St-co-M12-co-BPMA) may be still on the surface of poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles. Figure 1(b,c) shows that there is no difference between the spectra of the chloroform solution after extraction for 240 h and the fresh chloroform (99.0%); only the characteristic absorption bands of CH<sub>2</sub> at about 3023.14 cm<sup>-1</sup> and that of C—Cl from chloroform at about 1216.70 and 758.05 cm<sup>-1</sup> can be found. In other words, in Figure 1(b), the band centered at about 1730 and 1300–1190 cm<sup>-1</sup> due to the ester group stretching and the characteristic absorption of the benzene ring and ketone group cannot be observed, and this indicates that poly(St-co-M12-co-BPMA) blending with poly(St-co-M12-co-BPMA)/

TiO<sub>2</sub> composite particles was removed completely by extraction for 240 h.

Figure 2 shows the FTIR spectra of modified TiO<sub>2</sub>, poly(St-co-M12-co-BPMA), and extracted poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles. Figure 2(a) shows that there is a characteristic absorption at about 1703.78 cm<sup>-1</sup>, which is due to the stretching vibration of the carbonyl group in  $\gamma$ -MPS. In the FTIR spectrum of the poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles [Fig. 2(c)], we can find an absorption band at 1726.29 cm<sup>-1</sup> attributable to the carbonyl group (C=O), absorption bands at 2923.33 and 2851.72 cm<sup>-1</sup> assignable to the asymmetric and symmetric stretching of methylene (CH<sub>2</sub>) bands, and absorption bands at 1187.36 and 1037.21 cm<sup>-1</sup> attributable to sulfonic (S—O) bands. These are the characteristic absorptions of M12. The absorption at 1624.70 cm<sup>-1</sup> can be attributed to the ketone carbonyl group (C=O) of BPMA. The absorption bands at 1493.78, 1449.59, 752.49, and 698.31 cm<sup>-1</sup> can be assigned to the benzene ring of St. These characteristic absorptions are the same as those of poly(St-co-M12-co-BPMA) [Fig. 2(b)]. The absorption at 500–600 cm<sup>-1</sup> is the characteristic absorption of Ti—O belonging to TiO<sub>2</sub>. According to the analysis of FTIR, it can be concluded that poly(St-co-M12-co-BPMA) was successfully grafted onto the surface of TiO<sub>2</sub>.

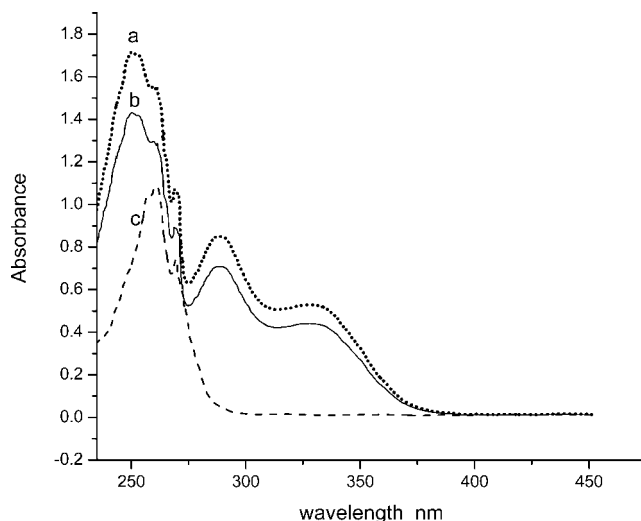
#### UV-vis absorption spectroscopy analysis

The UV absorption spectra of poly(St-co-M12-co-BPMA), poly(St-co-M12-co-BPMA) grafted from the surface of TiO<sub>2</sub>, and poly(St-co-M12) grafted from the surface of TiO<sub>2</sub> are shown in Figure 3. Figure 3(a) shows absorption peaks of BPMA at 332 and 284 nm



**Figure 2** FTIR spectra of (a) modified TiO<sub>2</sub>, (b) poly(St-co-M12-co-BPMA), and (c) extracted poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles.

that are due to the  $n \rightarrow \pi^*$  transition and  $\pi \rightarrow \pi^*$  transition,<sup>14</sup> respectively. The UV absorption spectrum of poly(St-co-M12-co-BPMA) grafted from the surface of TiO<sub>2</sub> [Fig. 3(b)] is the same as that of poly(St-co-M12-co-BPMA) [Fig. 3(a)]. However, the peaks at 284 and 332 nm do not exist in the UV absorption spectrum of poly(St-co-M12) grafted from the surface of TiO<sub>2</sub> [Fig. 3(c)]. The peaks at 284 and 332 nm in the spectrum of poly(St-co-M12-co-BPMA) grafted from the surface of TiO<sub>2</sub> further illuminate that BPMA successfully reacted with St and M12 grafted from TiO<sub>2</sub>. Poly(St-co-M12-co-BPMA) grafted from the surface of

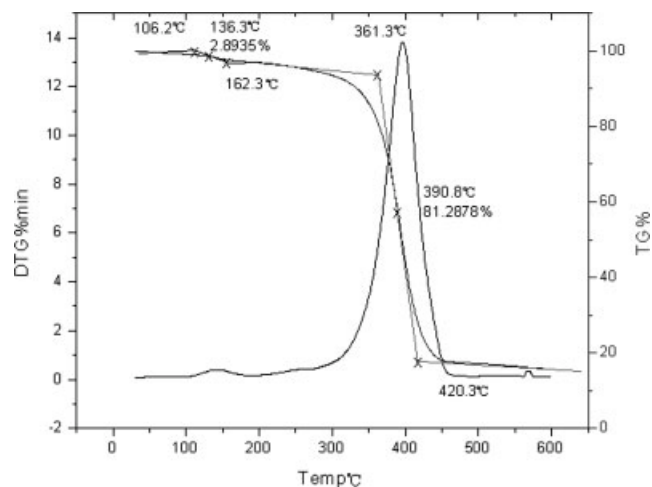


**Figure 3** UV-vis absorption spectra of (a) poly(St-co-M12-co-BPMA), (b) poly(St-co-M12-co-BPMA) grafted from the surface of TiO<sub>2</sub>, and (c) poly(St-co-M12) grafted from the surface of TiO<sub>2</sub> in THF.

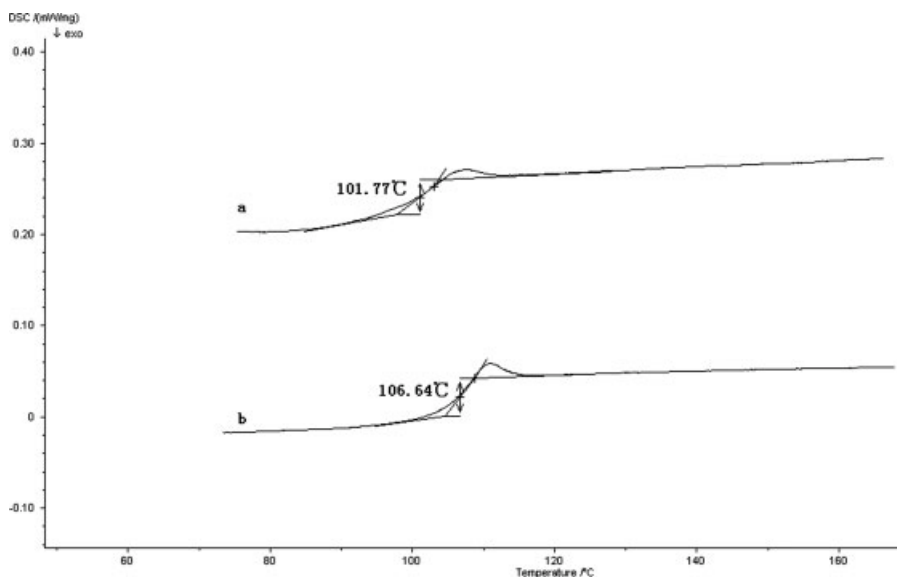
TiO<sub>2</sub> keeps the excellent character of BPMA, which possesses a high absorbance capacity for UV light. This result is very important for improving the UV resistance of polystyrene.

#### TGA of the poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles

Furthermore, to determine the percentage of the polymers grafted from the surface of the TiO<sub>2</sub> particles, TGA was used. Figure 4 presents the TGA curve of poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles. In this figure, the loss mass is 84.18%, and this attests that poly(St-co-M12-co-BPMA) is grafted from the TiO<sub>2</sub> particles; the percentage of the remains is



**Figure 4** TGA curves of poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles.



**Figure 5** DSC curves of (a) poly(St-co-M12-co-BPMA) and (b) extracted poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles.

15.81%, so the grafting percentage is 513.9% according to eq. (1). Because the conversion of the monomers, measured by the gravity method, is 86.64%, the grafting efficiency, calculated by eq. (2), is 59.9%:

$$\text{Grafting (\%)} = \frac{\text{Grafted polymer (g)}}{\text{Modified TiO}_2\text{(g)}} \times 100\% \quad (1)$$

$$\begin{aligned} & \text{Grafting efficiency (\%)} \\ = & \frac{\text{Grafted polymer (g)}}{\text{Monomers (g)} \times \text{Conversion of the monomers}} \\ & \times 100\% \quad (2) \end{aligned}$$

Poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles with higher grafting percentages were prepared, but the grafting efficiency was not as high. The lower grafting efficiency might be ascribed to the low mass ratio of TiO<sub>2</sub> to St. The content of TiO<sub>2</sub> was so low that the reactive point on the surface of the particle was not enough. Therefore, many of the monomers were copolymerized without the reaction of TiO<sub>2</sub>.

#### DSC analysis of the poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles

Figure 5 presents the DSC curves of poly(St-co-M12-co-BPMA) and poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles. Poly(St-co-M12-co-BPMA) exhibits only one  $T_g$  at 101.77°C, and this further proves that BPMA and M12 are copolymerized with St.  $T_g$  of poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles is 106.64°C, which is higher than that of poly(St-co-M12-co-BPMA). The increase in  $T_g$  is mainly ascribable to the confinement of the intercalated polymer

chains within TiO<sub>2</sub>, which prevent the segmental motions of the polymer chains. The DSC study also implies good thermal stability of the composite particles and successful bonding of the organic and inorganic components in the composite particles.

#### CONCLUSIONS

Polystyrene/TiO<sub>2</sub> composite particles containing organic UV absorbent groups, that is, poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles, were successfully prepared via the *in situ* emulsion copolymerization of the reactive UV stabilizer BPMA and the reactive surfactant M12 with St in the presence of TiO<sub>2</sub>. Poly(St-co-M12-co-BPMA), grafted from the surface of TiO<sub>2</sub>, retained the excellent character of BPMA, which possesses a high absorbance capacity for UV light. The percentage of grafting and the grafting efficiency could reach 513.9 and 59.9%, respectively.  $T_g$  of poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles was higher than that of copolymer poly(St-co-M12-co-BPMA). These research results are very important for preparing polystyrene that can resistant to UV light. The UV resistance of the poly(St-co-M12-co-BPMA)/TiO<sub>2</sub> composite particles are being studied by our group and will be published in the near future.

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