

# Modification of Halloysite Nanotubes with Poly(styrene–butyl acrylate–acrylic acid) via *In Situ* Soap-Free Graft Polymerization

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**ABSTRACT:** Halloysite nanotubes (HNTs) were grafted with poly(styrene–butyl acrylate–acrylic acid) (P-SBA) via an *in situ* soap-free emulsion polymerization. To introduce double bonds into the HNTs, *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyl trimethoxysilane was first used to modify the HNTs and render amino groups, and then, the double bonds were anchored through an amidation reaction between acryloyl chloride and amino groups. P-SBA chains were grafted onto HNTs because of participating of double bonds in the copolymerization of styrene, butyl acrylate, and acrylic acid. Fourier transforms infrared spectroscopy, transmission electron microscopy, specific surface area measurements, and thermogravimetric analysis

were used to characterize the HNTs grafted with P-SBA. The results indicate that 25.21% of P-SBA was grafted onto the outer walls of the HNTs and filled into the inner spaces of the HNTs. The modification dramatically decreased the surface area of the HNTs. The property study of the HNTs grafted with P-SBA focused on the dispersion behavior in the biphasic system. The results show that the grafted HNTs dispersed stably in the water/cyclohexane biphasic system and were a potential emulsifier. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3054–3059, 2010

**Key words:** copolymerization; emulsion polymerization; nanotechnology; stabilization; structure

## INTRODUCTION

Nanotubes, such as carbon nanotubes (CNTs), have been widely applied in materials, electronics, sensors, catalysts, and drug carriers because of their large aspect ratio, special tube structure, and properties since Ijima first reported CNTs in 1991.<sup>1–4</sup> How to solve the dispersion of nanotubes at the nanometer level is the key step in achieving desired chemical and physical characteristics. At this point, various methods, including chemical and physical functionalization, have been applied to modify CNTs.<sup>5,6</sup> Among these, graft polymerization is one of most versatile techniques.<sup>7</sup> Grafted polymers include poly(ethylene glycol),<sup>4</sup> polystyrene,<sup>8</sup> poly( $\epsilon$ -caprolactone),<sup>9</sup> poly(4-vinylpyridine),<sup>10</sup> and other copolymers.<sup>11</sup> For example, poly(aminobenzene sulfonic acid) and poly(ethylene glycol) were covalently attached to single-walled CNTs to enhance the

hydrophilic properties of CNTs.<sup>12</sup> The dispersion of CNTs grafted with poly(4-vinylpyridine) were stable in DMF, methanol, and 2-propanol for at least 8 months.<sup>13</sup> However, the precondition of graft polymerization is the rendering of functional groups onto the inert wall of CNTs through various methods.<sup>14</sup>

Halloysite nanotubes (HNTs), which are a kind of naturally deposited aluminosilicate chemically similar to kaolin, have a predominantly hollow tubular structure in the submicrometer range with a high aspect ratio.<sup>15</sup> Unlike the inert wall of CNTs, HNTs possess numerous hydroxyl groups, which provide anchoring sites for further modification. At this point, HNTs have been substituted for CNTs in some fields, such as nanotemplates.<sup>16,17</sup> Particularly, HNTs as a new type of nanotubes have been used to modify polymers such as polyaniline,<sup>18</sup> polystyrene,<sup>19</sup> and epoxy resins.<sup>20</sup>

In this study, double bonds as functional groups were anchored onto HNTs, and then, these anchored double bonds participated in the copolymerization of acrylic acid (AA), styrene (St), and butyl acrylate (BA). Because AA as a hydrophilic monomer could be incorporated into the copolymer chains and these copolymer chains helped stabilize the polymerization system, the copolymerization was conducted via an *in situ* soap-free emulsion polymerization. During the procedure of anchoring the double bonds, an amidation reaction between acryloyl

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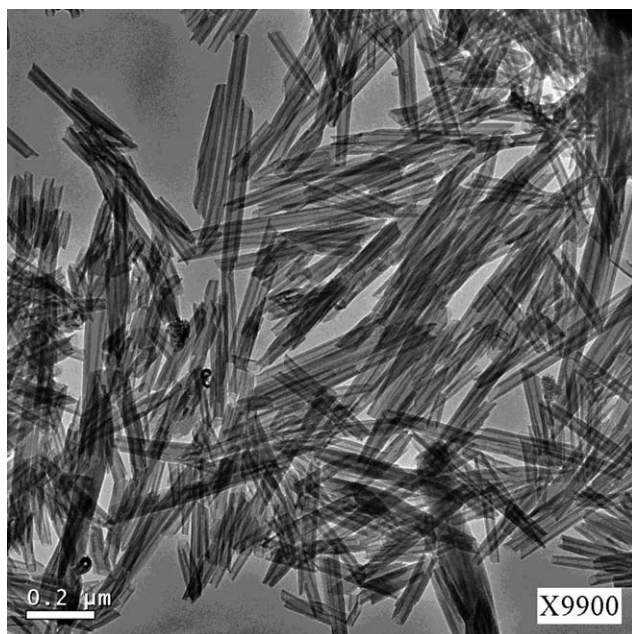


Figure 1 TEM image of HNTs.

chloride and multi-amidocyanogen was adopted to increase the amount of anchored double bonds. Therefore, the polymer chains containing both hydrophilic and hydrophobic segments were grafted onto HNTs. Although previous research about the properties of modified nanotubes was focused on the dispersion behavior in a single solvent,<sup>21</sup> the dispersion of the HNTs in biphasic liquids was studied according to the copolymer properties.

## EXPERIMENTAL

### Materials

HNTs having a radius of about 20–30 nm and a length of about 400–600 nm originated from Henan, China. The transmission electron microscopy (TEM) image is shown in Figure 1. St, BA, and AA (Sino-pharm Chemical Reagent Co., Ltd.) were chemically pure grade and were used after reduced-pressure distillation. Potassium persulfate (Tianjin Kermel Chemical Reagents Co., Ltd., China) was purified by recrystallization. *N*-(β-aminoethyl)-γ-aminopropyltrimethoxysilane (Z6020; Shandong Qufu Wanda Co., Ltd., China) and acryloyl chloride (Sigma–Aldrich, 97.0%) were used as received. The other reagents (Tianjin Kermel Chemical Reagents Co., Ltd., China), including chloroform (CHCl<sub>3</sub>) and toluene, were used directly without further purification.

### Treatment of the HNTs with Z6020

The HNTs (4.0 g), after they were baked at 400°C for 2 h in a muffle furnace, were dispersed under ultra-

sonication in toluene (40 mL) in a flask equipped with a condensation tube, and Z6020 (8.0 g, 32.3 mmol) was added. The suspension was refluxed at 100°C for 48 h, and then, the reaction mixture was centrifuged. The obtained particulates were washed with toluene (three times for each wash with 20 mL) followed by centrifugation. The product (3.4 g) was obtained after overnight drying *in vacuo* at 80°C and was named M-HNTs.

### Anchoring of the double bond

M-HNTs (3.0 g) were dispersed in CHCl<sub>3</sub> (25 mL), and then, acryloyl chloride (6.5 mL) was added dropwise under stirring. The suspension was stirred for 4 h at room temperature, and then, the reaction mixture was centrifuged. The obtained particulates were washed with CHCl<sub>3</sub> (three times for each wash with 20 mL) followed with centrifugation. The product (2.9 g) was obtained after drying overnight *in vacuo* at room temperature and was named V-HNTs.

### *In situ* emulsifier-free copolymerization

The *in situ* soap-free emulsion copolymerization of St, BA, and AA in the presence of HNTs is summarized by the following steps. V-HNTs (2.7 g) and AA (8.6 mL) were dispersed into 300 mL of deionized water. The polymerization temperature was set at 75°C with an oil bath. The initiator, potassium persulfate (0.54 g) was added, and a mixture of St (30 mL) and BA (60 mL) were added dropwise over 2 h under stirring at 400 rpm; then, the reaction was retained at this temperature for another 3 h. The product was filtered through a 0.2-μm Nylon membrane and dried at 80°C *in vacuo* for 24 h (Fig. 2).

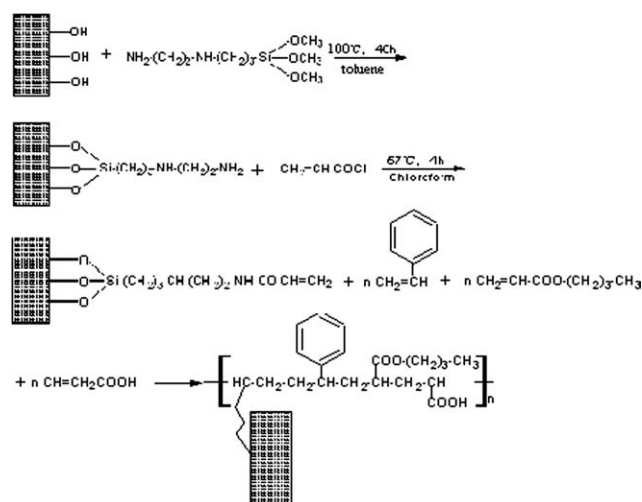
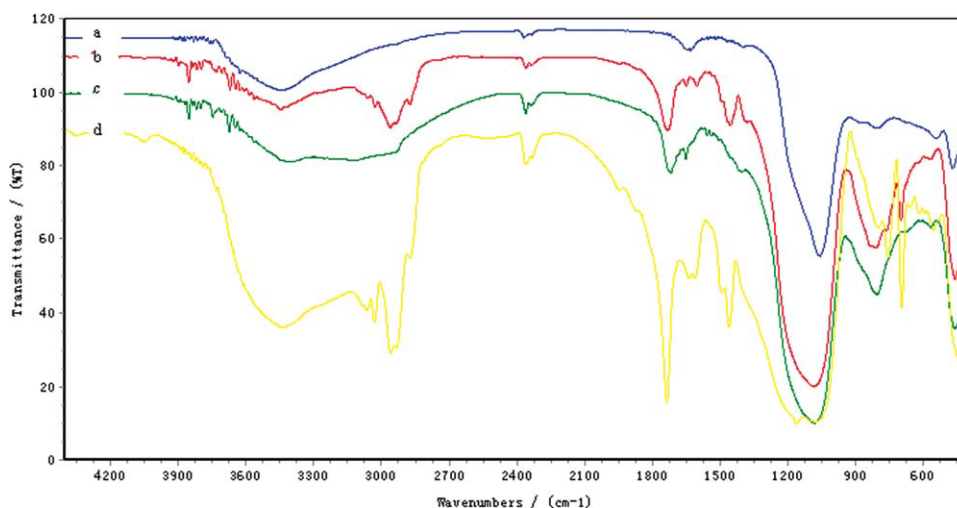


Figure 2 Scheme of the modification steps.



**Figure 3** FTIR spectra of (a) HNTs, (b) M-HNTs, (c) V-HNTs, and (d) G-HNTs. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Removal of the free polymers

During *in situ* polymerization, the production of free polymers is unavoidable. To study the structure and properties of the HNTs grafted with poly(styrene-butyl acrylate-acrylic acid) (P-SBA), which were labeled G-HNTs, the G-HNTs were separated from the free polymers and purified with the following method. The polymerization product was wrapped with filter paper and extracted with boiled  $\text{CH}_3\text{Cl}$  in a Soxhlet extractor for 24 h. The residue was dried at  $80^\circ\text{C}$  for 12 h.

### Characterization

Fourier transforms infrared (FTIR) spectra were recorded on a Bio-Rad 3500 GX spectrophotometer in the  $400\text{--}4000\text{-cm}^{-1}$  range. We obtained the KBr pellets by crushing the solids (1.0 mg) around spectroscopic-grade KBr (100.0 mg). All of the spectra were collected with a resolution of  $4\text{ cm}^{-1}$  and with the accumulation of 64 scans. A specific surface area analyzer (Quantachrome NOVA4200e) was used to probe the surface area change. TEM images were acquired with a Tecnai G220 TEM instrument operating at 100 kV. Thermogravimetric analysis (TGA) was performed on a DTG-60 (Shimadzu Corp., Japan) at a heating rate of  $20^\circ\text{C}/\text{min}$  from room temperature to  $700^\circ\text{C}$  under a nitrogen flow ( $40\text{ mL}/\text{min}$ ).

## RESULTS AND DISCUSSION

### FTIR spectroscopy

To understand the procedure of grafted polymerization, the HNTs, M-HNTs, V-HNTs, and G-HNTs were characterized with FTIR spectroscopy, and the spectra are shown in Figure 3. The broad peak at

about  $3437\text{ cm}^{-1}$  in Figure 3(a), which was attributed to hydroxyl group ( $-\text{OH}$ ) stretching, indicated the ability of reactions with other groups, such as trimethoxysilane. Compared with those shown in Figure 3(a), the absorption peaks at  $2960$  and  $1734\text{--}1455\text{ cm}^{-1}$  in Figure 3(b), corresponding to amino group ( $-\text{NH}_2$ ) stretching, indicated that Z6020 reacted with the hydroxyl groups on the HNTs, and amino groups were attached to the HNTs. As shown in Figure 3(c), the absorption peaks at  $2940$  and  $1653\text{ cm}^{-1}$ , corresponding to the absorptions of  $\text{C}=\text{C}$  and  $=\text{CO}$  stretching indicated that double bonds were successfully anchored onto the HNTs through an amidation reaction. Compared with those in Figure 3(c), several new peaks appear in Figure 3(d). The peaks at  $3064\text{ cm}^{-1}$ , due to the benzene ring;  $1612\text{ cm}^{-1}$ , due to the  $\text{C}-\text{H}$  on phenyl, which showed the existence of St; and  $1736$  and  $1163\text{ cm}^{-1}$ , due to the  $\text{C}=\text{O}$  of BA and  $\text{C}-\text{O}$  of AA, respectively, which show the existence of BA and AA; indicated that the P-SBA chains were grafted onto the HNTs.

### TEM

TEM was used to characterize the structural changes of the HNTs before and after modification. Figure 4 shows the images of the HNTs, M-HNTs, V-HNTs, and G-HNTs. After modification with Z6020 and anchoring with double bonds, the walls of the M-HNTs [Fig. 4(b)] and V-HNTs [Fig. 4(c)] became thicker, and the inner diameters were smaller than those of the HNTs [Fig. 4(a)]. This indicated that the inner and outer walls of the HNTs were modified at the same time and meant that the following graft polymerization occurred in and out of the nanotubes. The TEM image of the G-HNTs proved this. Figure 4(d) shows that the outer walls of the HNTs were



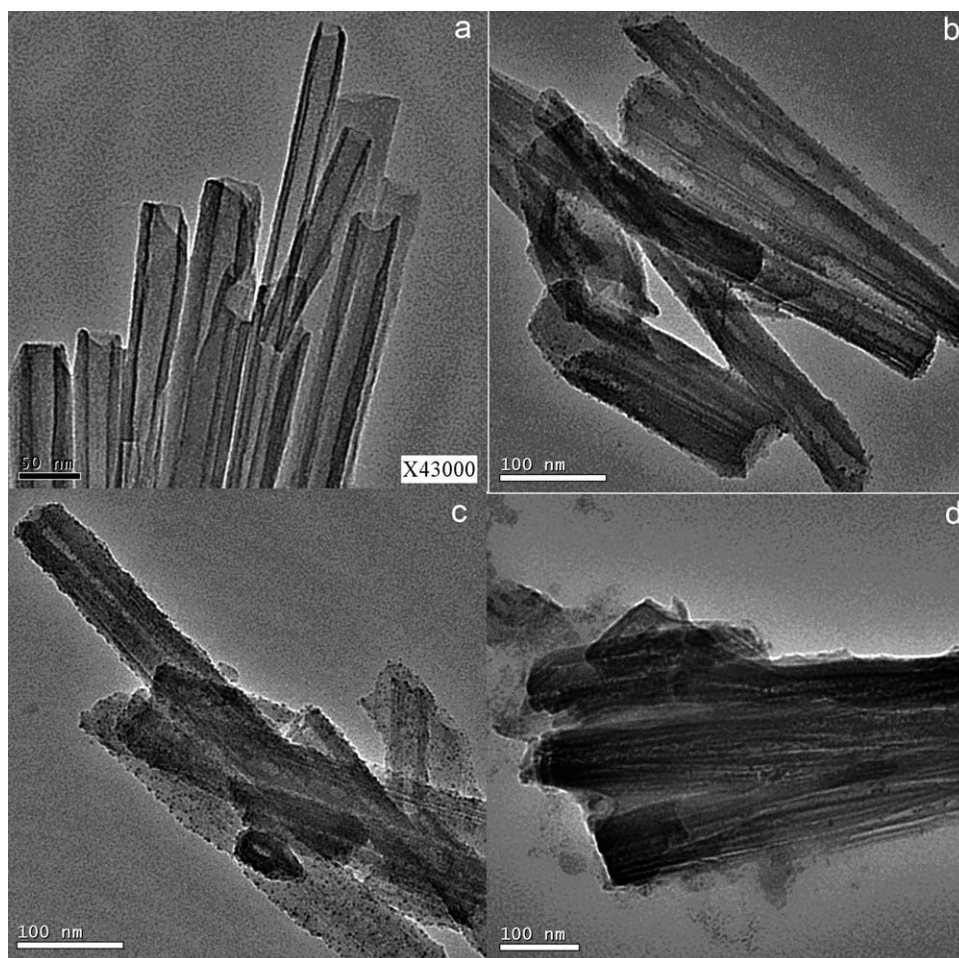


Figure 4 TEM images of (a) HNTs, (b) M-HNTs, (c) V-HNTs, and (d) G-HNTs.

coated with a polymer layer and that the inner space of the HNTs was filled by grafted polymers.

**Specific surface area**

From the previous TEM characterization, we know that the grafted P-SBA chains had a tremendous effect on the structure of the HNTs. Therefore, the surface area, one important parameter of nanosized materials, was measured on a Quantachrome NOVA4200e, and the results are listed in Table I. The data showed that, as the modification steps went on, the surface area of the HNTs decreased. This indicated that bigger functional groups brought the surface area down more effectively and that the

inner space of the HNTs was filled completely by P-SBA chains. Of course, the decrement of the HNT mass due to organic components was also considered to decrease the surface area.

TABLE I  
Surface Areas of the HNTs, M-HNTs, V-HNTs, and G-HNTs

	Sample			
	HNTs	M-HNTs	V-HNTs	G-HNTs
Surface area (m <sup>2</sup> /g)	62.23	46.11	20.75	0.17

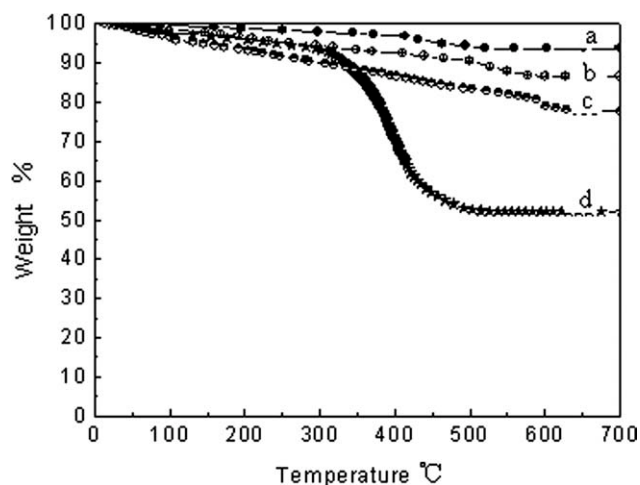


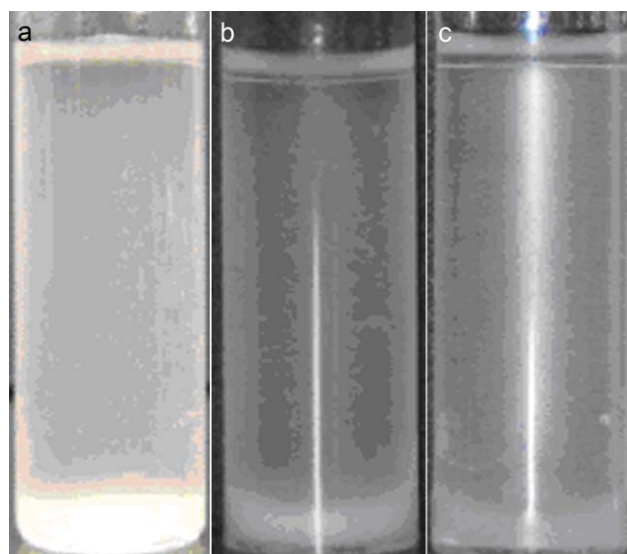
Figure 5 TGA curves of (a) HNTs, (b) M-HNTs, (c) V-HNTs, and (d) G-HNTs.

## TGA

The amount of grafted P-SBA was quantified by TGA. To explain the effect of organic components on the specific surface area, the HNTs, M-HNTs, and V-HNTs were also analyzed. Their TGA curves are shown in Figure 5. Because of the absorbed and combined water, 6.15 wt % of the HNTs was lost at 700°C. With this value taken as a reference, the increment of organic components of the M-HNTs, V-HNTs, and G-HNTs were calculated, and the results are listed in Table II. By assuming that all of the Z6020 moieties, except the Si element, were lost, we estimated the grafting density of the Z6020 functionality groups to be 0.1 molecule/nm<sup>2</sup>, and this value was smaller than that of the silica nanoparticles.<sup>22</sup> The TGA result of the G-HNTs indicates that only 25.21% of P-SBA could cover the outer walls and fill the inner space of the HNTs.

## Dispersion behavior of the G-HNTs in the biphasic system

Biphasic systems, such as emulsions, are widely used in the chemical and pharmaceutical industries. Cyclohexane is a typical nonpolar solvent and is insoluble in water. In this study, a cyclohexane/water (6/100) mixture was adopted to study the dispersion behavior of the G-HNTs. The HNTs, P-SBA, or G-HNTs (0.1 g) were added to 10 mL of cyclohexane/water biphasic system, and the system was sonicated for 10 min to form a homogeneous dispersion. Pictures were taken after 24 h to observe the dispersion behavior (Fig. 6). As shown in Figure 6(b,c), both the HNTs and P-SBA deposited on the bottom, and cyclohexane floated on the water. This indicated that both the HNTs and P-SBA failed to stabilize the cyclohexane/water biphasic system. Although the G-HNTs dispersed stably without phase separation, this indicated that the G-HNTs acted as the emulsifier of the biphasic system. The emulsifying effectiveness of the G-HNTs was attributed to the hydrophobic segments of the grafted P-SBA that made these G-HNTs unusually surface active at the oil/water



**Figure 6** Dispersion of (a) G-HNTs, (b) HNTs, and (c) P-SBA in cyclohexane/water (6/100). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

interface. This reason was similar to that reported by Tilton.<sup>23</sup>

## CONCLUSIONS

HNTs were successfully grafted with P-SBA via an *in situ* emulsifier-free emulsion polymerization. Through double bonds anchored onto the HNTs, 25.21% of P-SBA was grafted. P-SBA chains not only grafted onto the outer walls but also filled into the inner space of the HNTs, causing a tremendous decrease in the HNT surface area. The G-HNTs dispersed stably in the cyclohexane/water biphasic system and acted as an emulsifier to stabilize the biphasic system. Therefore, G-HNTs are promising for use in stabilizing emulsions.

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**TABLE II**  
Weight Losses and Increments of the Organic Components

	Sample			
	HNTs	M-HNTs	V-HNTs	G-HNTs
Weight loss at 700°C (%)	6.15	13.77	22.77	47.98
Increment of the organic components (%)	0	7.62	9	25.21

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