

# Nitroxide-Mediated Polymerization of Styrene Initiated from the Surface of Montmorillonite Clay Platelets

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**ABSTRACT:** Polymer-grafted montmorillonite (MMT) hybrid composites which possess a hard backbone of MMT and a soft shell of brush-like polystyrene (PSt) were prepared via “grafting from” strategy based on nitroxide-mediated radical polymerization (NMRP) using 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) as mediator. Three steps were used to graft PSt chains to the surface of MMT: anchoring of methacrylateethyl trimethyl ammonium chloride (DMC) onto the surface of MMT by ion exchange reaction first. And then, the surface alkoxyamine initiator was produced in a one-step process by reacting simultane-

ously TEMPO, BPO, and DMC in the presence of MMT. Next, PSt chains with controlled molecular weights and polydispersities were grown from the alkoxyamine functionalized MMT surface. The prepared PSt-g-MMT hybrid particles have been extensively characterized by FTIR, XPS, XRD, TGA, TEM, respectively. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1198–1203, 2010

**Key words:** nitroxide-mediated polymerization; surface-initiated polymerization; TEMPO; montmorillonite; composites

## INTRODUCTION

In these years, the polymer/clay nanocomposites have attracted intensive academic activities and extensive industrial attentions due to their exhibiting unique chemical and physical properties, such as mechanical properties, thermal stability and flame retardance, gas barrier properties, biodegradation and abrasion resistance.<sup>1–5</sup> However, as the silicate layers which compose primary clay particles are held together by electrostatic forces into stacky agglomerates, efforts must be done to separate the original clay stacks into individual layers and disperse them into polymers.<sup>6</sup> To this purpose, many explorations have been done in the recent literature to modify solid surfaces with polymers, including physisorption, covalent attachment (such as silane coupling agents),<sup>7</sup> and electrostatic adsorption (such as replacing the interlayer metal cations by organic

quaternized ammonium salts).<sup>8</sup> Physisorption is relatively easy, but suffers from solvolytic and thermal instabilities due to the absence of stable covalent bonds with the surface.<sup>9</sup> Therefore, there are two approaches to graft polymer chains to surface: (1) the “grafting to” method,<sup>10,11</sup> where the end-functionalized polymers react with an appropriate surface; (2) the “grafting from” method,<sup>12,13</sup> where polymer chains are grown from initiator-terminated self-assembled monolayer.

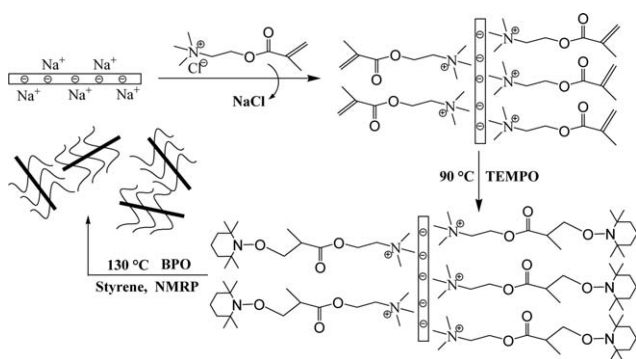
Actually, the controlled living polymerization technique (CLRP) such as nitroxide-mediated radical polymerization (NMRP) in conjunction with surface-initiated polymerization<sup>6,14–19</sup> is among the most useful synthetic routes to precisely design and functionalize the surfaces of various solid materials by well-defined polymers. However, because of the preparation of functional alkoxyamine is complicated multistep processes,<sup>20</sup> there are a few explorations about synthesis of polymer/MMT hybrid composites by NMRP in recent years. It excited us to find a simple way to attach the polymer onto the MMT surface.

Considering the above factors, herein, we describe an effective strategy to prepared polymer-grafted MMT hybrid composites which possess a hard backbone of MMT and a soft shell of brush-like PSt via surface-initiated NMRP using TEMPO as mediator. Scheme 1 presents the overall synthesis route.

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**Scheme 1** The grafting polymerization of styrene from the alkoxyamine modified MMT surface.

## EXPERIMENTAL

### Materials

Styrene (St) (AR, Shanghai Chemical Reagent Plant, Shanghai, China) were washed with 5% NaOH and ion-free water, stirred over CaH<sub>2</sub> overnight, and distilled before use. Stable free radical 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) were purchased from Aldrich and used without further purification. Sodium montmorillonite (MMT) with an exchange capacity of 80 meq./100 g was provided by Gansu Linze Company (Gansu, China). Benzoyl peroxide (BPO) was purified by recrystallization with chloroform/methanol. Tetrahydrofuran (THF) was refluxed over sodium and distilled twice before use. 2-methacryloyloxyethyl trimethyl ammonium chloride (DMC) (Yantai Spark Chemicals Co., Yantai, China) and all other reagents were used without further purification.

### Instruments and measurements

FT-IR spectroscopy patterns were performed on a Dig lab FTS 3000 instrument. Thermogravimetric analysis (TGA) was performed in nitrogen at a heating rate of 10°C/min on a Perkin Elmer instrument TG/DTA 6300. The microstructure of these hybrid nanocomposites was imaged using Hitachi H-600 equipment, TEM samples of nanoparticles were prepared by casting one drop of a dilute colloid solution onto a carbon-coated copper grid. X-ray photoelectron spectra (XPS) were performed on a PHI-5702 instrument using MgK $\alpha$  radiation with pass energy of 29.35 eV. Gel permeation chromatography (GPC) analysis of the samples was performed at a flow rate of 1.0 mL/min and 40°C in THF by using Waters GPCV2000 equipment. Wide angle X-ray diffraction (WXR) with a Rigaku D/max-2400 diffractometer (CuK $\alpha$  radiation = 0.15 nm, generator voltage = 40 kV, current = 60 mA) was used to calculate *d*-spacing of MMT and PSt-g-MMT. Ultrasound dispersed was using NXS control ultrasonic

wave washing machine (working frequency: 80 KHz; consuming power: 600 W).

### Preparation of the PSt/MMT composites through nitroxide-mediated radical polymerization

#### Preparation of the DMC modified MMT platelets

Into a 250 mL dried round-bottom flask, 3 g MMT was ultrasound dispersed in 60 mL deionized water/ethanol mixture [50/50 (v/v)] for 30 min, 3.0 g DMC was dissolved in 20 mL deionized water/ethanol mixture [50/50 (v/v)] and added dropwise to the MMT suspension. The mixtures were stirred at 50°C for 24 h. They were next centrifuged, and the product was dried in vacuum at 30°C for 24 h.

#### Anchoring of the alkoxyamine initiator onto the DMC modified MMT surface

The alkoxyamine initiator was formed *in situ* by introducing 0.36 g of TEMPO (2.31 mmol) and 0.27 g BPO (1.11 mmol) into 80 mL of toluene containing 1.5 g of the DMC modified MMT platelets. The suspension was degassed by five freeze-pump-thaw cycles, and the mixture was heated to 90°C for 24 h to yield the alkoxyamine modified MMT. They were next centrifuged, and the product was dried in vacuum at 30°C for 24 h.

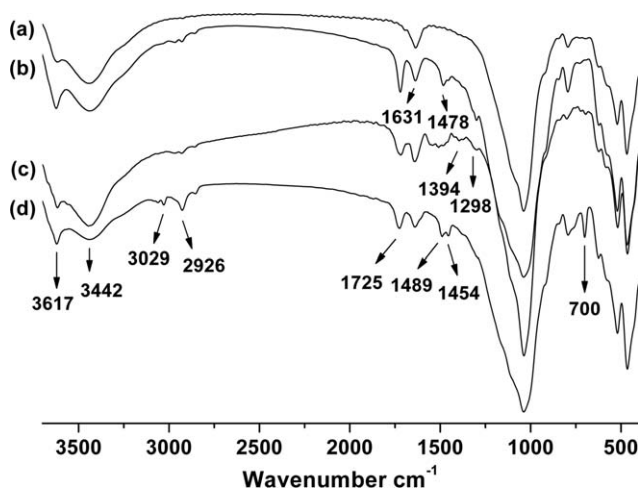
### Preparation of the PSt/MMT composites via nitroxide-mediated polymerization

Into a 25 mL dried round-bottom flask containing 0.1 g of the quaternary ammonium alkoxyamine modified MMT, styrene (6 mL, 0.052 mol) and xylene (3 mL, 0.025 mol), TEMPO (0.012 g, 0.077 mmol) and BPO (0.018 g, 0.074 mmol) were added. The mixture was degassed by five freeze-pump-thaw cycles, and stirred under argon at 130°C for several hours. After the polymerization, the composites and the solution were separated by centrifugation; the polymer solution was diluted with THF and precipitated with methanol. The composites were Soxhlet extracted with THF for 12 h, and the physical adsorption polymer can be removed from the surface of MMT. The product was dried in vacuum at 50°C for 24 h.

The polymer grafting (%) was determined by TGA and was calculated by eq. (1)<sup>21</sup>

$$\text{polymer grafting (\%)} = \frac{\text{organic composition (g)}}{\text{Bare MMT (g)}} \times 100 \quad (1)$$

Where the amount of organic composition (g) was calculated from the TGA weight loss from 150°C to 650°C corresponding to the decomposition of PSt.



**Figure 1** FTIR spectra of (a) MMT, (b) DMC modified MMT, (c) alkoxyamine modified MMT, and (d) PSt-g-MMT.

Bare MMT (g) is the weight retention by TGA corresponding to the bare MMT.

## RESULTS AND DISCUSSION

### Analysis of FTIR

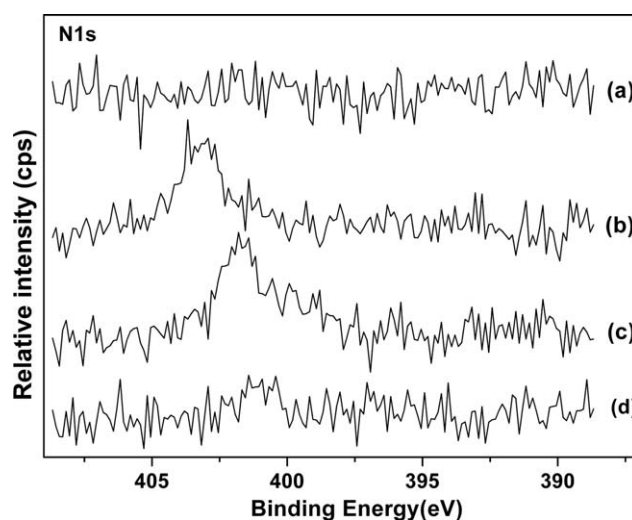
Evidence of exchange of the sodium ions by the DMC salts, alkoxyamine modified MMT, and PSt brushes grafted from MMT (PSt-g-MMT) were provided by FTIR and XPS analysis. Figure 1 shows the FTIR analysis of (a) MMT, (b) DMC modified MMT, (c) alkoxyamine modified MMT, and (d) PSt-g-MMT. Compared with MMT, the FTIR spectra of DMC modified MMT [Fig. 1(b)] shows the characteristic vibration of the carbonyl ( $\nu\text{C}=\text{O}$   $1725\text{ cm}^{-1}$ ) and the aliphatic ( $\delta\text{C}-\text{H}$ ,  $1478\text{ cm}^{-1}$ ), also, a vibration at  $1631\text{ cm}^{-1}$  was observed and attributed to the characteristic stretching vibration of the double bond. The FTIR spectra of alkoxyamine modified MMT [Fig. 1(c)] shows the characteristic peak such as the aliphatic ( $\nu\text{C}-\text{H}$ ,  $2926$ ;  $\delta\text{C}-\text{H}$ ,  $1489$  and  $1454\text{ cm}^{-1}$ ), the nitroxide ( $\nu\text{N}-\text{O}$ ,  $1394\text{ cm}^{-1}$ ), and the cyanide ( $\nu\text{C}-\text{N}$ ,  $1298\text{ cm}^{-1}$ ) groups of the alkoxyamine compound clearly attest for the presence of TEMPO on the MMT surface. The FTIR spectrum of PSt-g-MMT [Fig. 1(d)] shows the characteristic peak such as aromatic ( $\nu\text{C}-\text{H}$ ,  $3029\text{ cm}^{-1}$ ) and styrenic ( $700\text{ cm}^{-1}$ ). Moreover, the FTIR spectrum exhibits a wide O-H stretching vibration peak at  $3442$  and  $3617\text{ cm}^{-1}$  due to physical adsorption water and hydrogen-bonded silanol groups, respectively. These results indicate that PSt are grafted onto the surface of MMT particles.

### Analysis of XPS

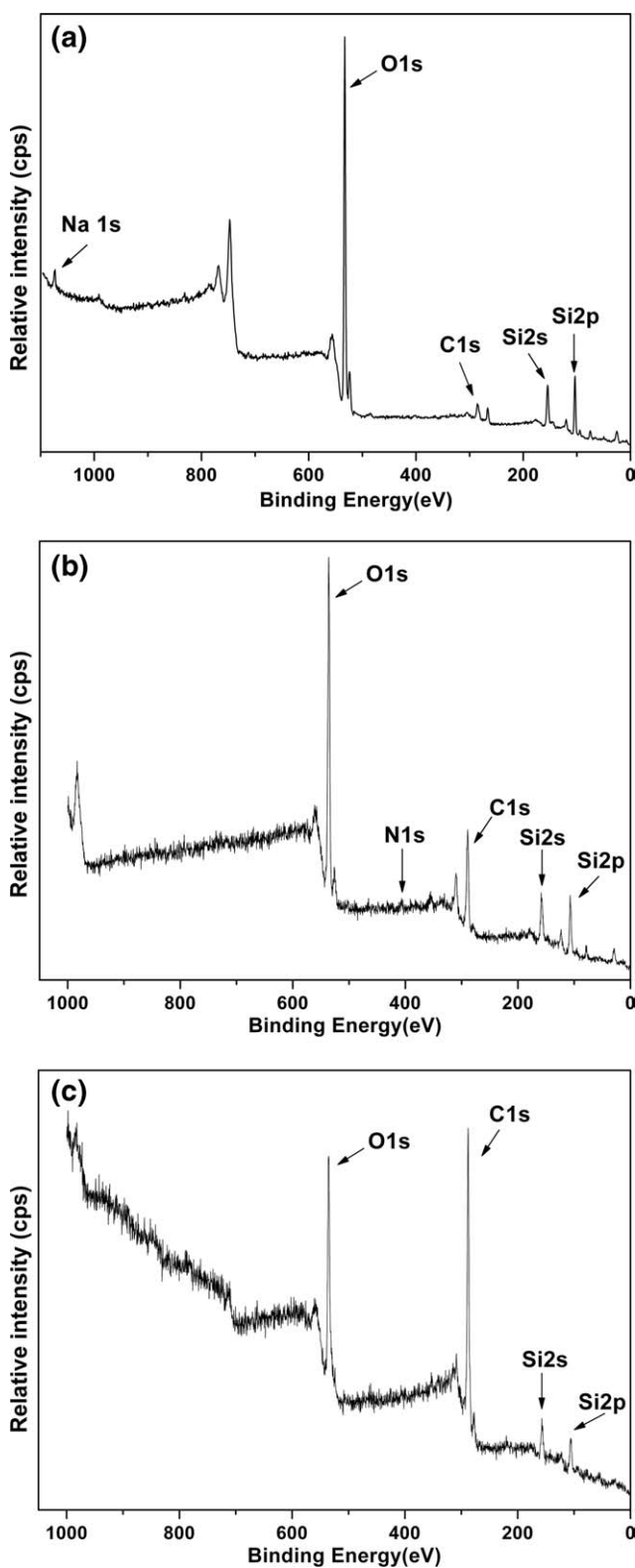
To further investigate the composition of the polymer on the MMT surface, XPS measurement was

used. Figure 2 shows N1s spectra for the MMT (a), DMC modified MMT (b), alkoxyamine modified MMT (c), and PSt-g-MMT (d). Compared with MMT, from Figure 2(b), for the DMC modified MMT, the presence of the N1s signals at the BEs of about  $403.7\text{ eV}$  was attributed to the  $\text{N}-(\text{CH}_3)_3^+$  species. After the alkoxyamine modified in Figure 2(c), the N1s signal intensity was weakly enhanced. The N1s peak at the BEs of about  $401.8\text{ eV}$  and  $401.3\text{ eV}$  was attributed to the  $\text{N}-(\text{CH}_3)_3^+$  and TEMPO species, respectively. As for PSt-g-MMT in Figure 2(d), the N1s signal intensity was nearly disappeared, indicating MMT particles are basically encapsulated with PSt.

The wide scan XPS spectra for MMT (a), alkoxyamine modified MMT (b), and PSt-g-MMT (c) are shown in Figure 3. From Figure 3(a), for the MMT, the presence of the C1s signals is probably associated with the adsorption of carbon dioxide ( $\text{CO}_2$ ) or the presence of a trace amount of carbonaceous contaminants on the surface of MMT,<sup>22</sup> and the signal is weak. After alkoxyamine modification, the C1s signal ( $287.7\text{ eV}$ ) intensity was enhanced largely. As for PSt-g-MMT in Figure 3(c), the strongest signal is appeared; it corresponds to the aliphatic hydrocarbon ( $\text{C}-\text{C}/\text{C}-\text{H}$ , at a binding energy of  $287.8\text{ eV}$ ). These signals indicate the presence of PSt on the surface. Meanwhile, compared with MMT, from Figure 3(b), for the DMC modified MMT, the presence of the Na1s signals at the BEs of about  $1076.2\text{ eV}$  was disappeared after ion exchange reaction, indicating the MMT has been successfully modified by DMC. We can see the signals of Si2s ( $153.6\text{ eV}$ ) and Si2p ( $102.7\text{ eV}$ ) in Figure 3(c) are much weaker than in Figure 3(b), indicating MMT particles are basically



**Figure 2** XPS analysis of N1s spectra for the MMT (a), DMC modified MMT (b), alkoxyamine modified MMT (c), and PSt-g-MMT (d).



**Figure 3** The wide scan XPS spectra for MMT (a), alkoxyamine modified MMT (b), and PSt-g-MMT (c).

encapsulated with PSt. Judging by combination of FTIR and XPS results, we can conclude that a functionalized surface generated by the method outlined in Scheme 1.

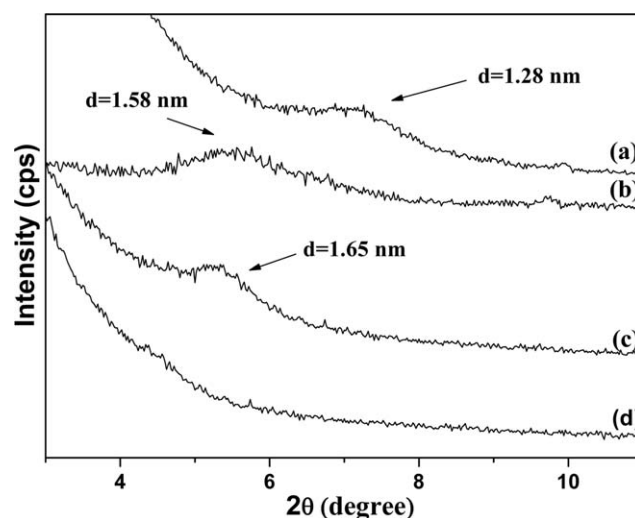
### Analysis by XRD

Generally speaking, there are two terms used to describe the prepared polymer/clay composite: intercalated and exfoliated composite. In the intercalated structures case, the polymer chains occupy the interlayer spaces between stacking silicate platelets. In the exfoliated structures case, the discrete clay layers are dispersed in the polymer matrix.

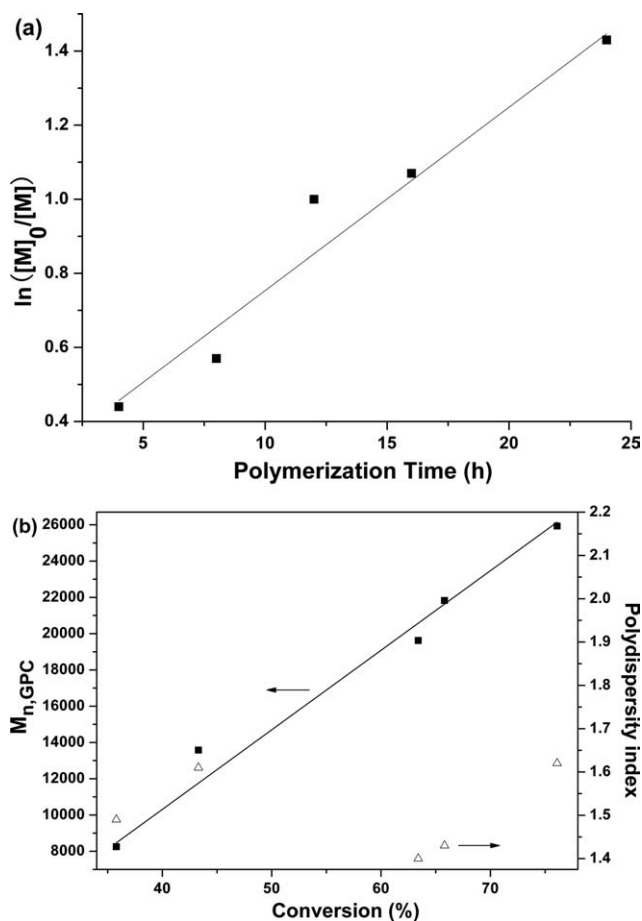
In this work, the structure and apparent interlayer spacing ( $d$ -spacing) of the MMT and PSt-g-MMT have been detected. Figure 4 shows the XRD pattern for MMT (a), DMC modified MMT (b), alkoxyamine modified MMT (c), and PSt-g-MMT (d). As reported earlier, when  $d001$  peak shift to a lower angle, the interlayer of the MMT will be widened.<sup>23</sup> The interlayer spacing can be calculated according to the Bragg equation ( $2d\sin\theta = n\lambda$ ). It can be found that the crystalline peak of the MMT is at  $2\theta = 6.88$  ( $d001 = 1.28$  nm), when the modification with DMC [Fig. 4(b)] and alkoxyamine [Fig. 4(c)] takes place, there is a shift of the diffraction peak toward lower angles, it is at  $2\theta = 5.56$  ( $d001 = 1.58$  nm) and  $5.36$  ( $d001 = 1.65$  nm). As for PSt-g-MMT in Figure 4(d), it can be found that the crystalline peak of the MMT has disappeared. Therefore, we can conclude that the  $N-(CH_3)_3^+$  species are intercalated into the MMT gallery by ion exchange reaction, and these indicate that the molecular chains of polymer have exfoliated the clay gallery and the PSt-g-MMT composites have an exfoliated nanostructure.

### Analysis by GPC

Fan et al.<sup>24</sup> have found that there is a certain proportion relation between the molecular weight of the surface grafted polymer and the polymer forming in

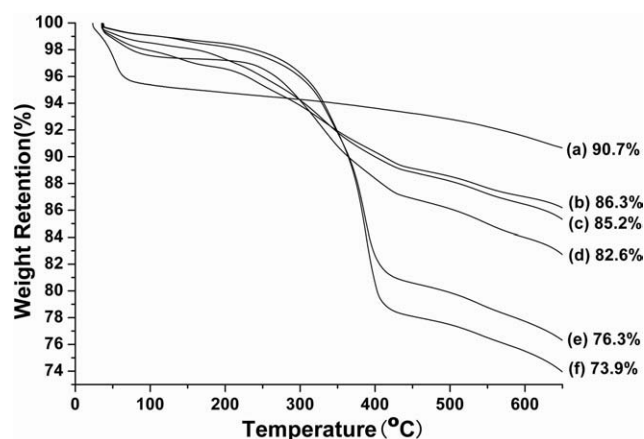


**Figure 4** WAXRD results of (a) MMT, (b) DMC modified MMT, (c) alkoxyamine modified MMT, and (d) PSt-g-MMT-16 h.



**Figure 5** First order kinetic plot (a) and molecular weight versus conversion plot (b) for the NMRP of PSt formed in solution. Experimental conditions:  $[BPO]/[TEMPO]/[St] = 1 : 1 : 675$ ,  $T = 130^\circ\text{C}$ .

solution. So we use the polymer formed by free initiator in solution to illuminate the surface-grafted polymerization process.  $\ln([M]_0/[M])$  versus reaction time plot is shown in Figure 5(a), a linear relationship indicated that the polymerization was a first-order reaction with respect to the PSt concentration. Molecular weight versus conversion plot is shown in Figure 5(b), the  $M_n$  of PSt increases linearly with the increase of conversion, and the molecular weight



**Figure 6** Thermogravimetric analysis (TGA) of (a) MMT, (b) DMC modified MMT, (c) alkoxyamine modified MMT, (d) PSt-g-MMT-4 h, (e) PSt-g-MMT-16 h, and (f) PSt-g-MMT-24 h, TGA was performed in nitrogen at a heating rate of  $10^\circ\text{C}/\text{min}$ .

distributions are less than 1.62 indicating the presence of the DMC modified MMT has some negative effect on the polymerization. The above results revealed that the graft polymerization of PSt from MMT surface via NMRP is a “living”/controlled polymerization. Table I summarizes the results of all polymerization under various experimental times.

### Analysis by TGA

The thermogravimetric analysis (TGA) for MMT and PSt-g-MMT composites is shown in Figure 6. The weight loss below  $200^\circ\text{C}$  is attributed to the physisorbed water and residual organic solvent was 5.3% for MMT particles. The weight loss is from 4.4% to 5.5% when the MMT was modified by DMC and alkoxyamine, respectively. As for PSt-g-MMT composites, the beginning decomposition at  $260^\circ\text{C}$ , which corresponds to the decomposed temperature of PSt covalently attached to MMT particles, the weight loss is from 8.1% to 16.8% when the polymerization reaction time from 4 h to 24 h and polymer grafting is from 8.9% to 18.5%. These results

**TABLE I**  
Experimental Conditions and Results for the NMRP of PSt in Solution

Experiment	Reaction time (h)	Conversion (%) <sup>a</sup>	$M_n$ GPC $\times 10^{-3}$	$M_w \times 10^{-3}$	PDI <sup>b</sup>	Grafting (%) <sup>c</sup>
1	4	35.8	8.3	12.3	1.49	8.9
2	8	43.3	13.6	21.9	1.61	10.7
3	12	63.4	19.6	27.6	1.40	12.2
4	16	65.8	21.8	31.2	1.43	15.9
5	24	76.1	25.9	42.0	1.62	18.5

Conditions:  $[BPO]/[TEMPO]/[St] = 1 : 1 : 675$ ; xylene as the solvent;  $T = 130^\circ\text{C}$ .

<sup>a</sup> Conversion values determined using gravimetric analysis.

<sup>b</sup> PDI: molecular weight distribution is calculated from  $M_w/M_n$ .

<sup>c</sup> Polymer grafting (%) is calculated from eq. (1).

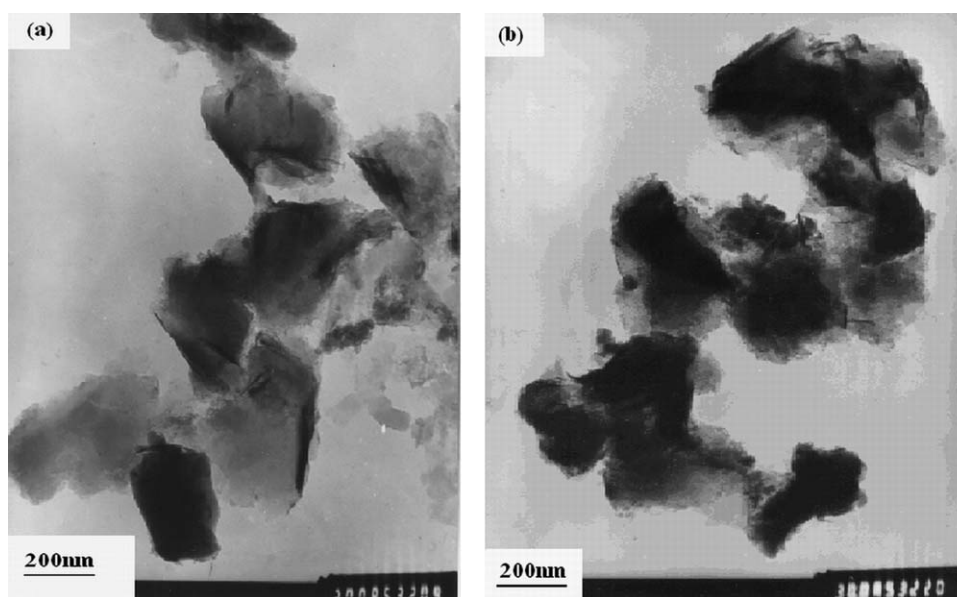


Figure 7 TEM images of (a) MMT and (b) PSt-g-MMT hybrid composites cast from dilute ethanol suspensions.

show that the amount of the grafted PSt increased with reaction times and indicate that PSt have grafted onto the surface of MMT.

#### Analysis by TEM

The morphologies of MMT particles and PSt-g-MMT hybrid composites were investigated using TEM (Fig. 7). We can see from Figure 7(a) that MMT platelets are well dispersed and have a schistic like morphology. However, in hybrid composites, as shown in Figure 7(b), MMT platelets are completely encapsulated with PSt, the size of PSt-g-MMT particles is obviously larger than MMT particles, It can be concluded that PSt can successfully encapsulate grafted MMT once MMT particles are modified by the DMC.

#### CONCLUSIONS

A simple and convenient "grafting from" strategy involves the three steps reaction to prepare of PSt/MMT hybrid composites by NMRP is reported. This new route allows an easy control of molecular weight, molecular weight distributions, and architecture of grafted polymers onto clay surfaces. The number of grafted chains per platelets is found to be an important parameter. It depends on the grafting of DMC onto MMT surfaces. So the grafting of polymer can be adjusted in a wide range by simply controlling the introduction and the conversion of the alkoxyamine onto the MMT surface. This work is still needed to optimize all these parameters and obtain composites with well properties.

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