

Properties of Covalently Bonded Layered-Silicate/Polystyrene Nanocomposites Synthesized via Atom Transfer Radical Polymerization

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ABSTRACT: Covalently bonded layered silicated/polystyrene nanocomposites were synthesized via atom transfer radical polymerization in the presence of initiator-modified layered silicate. The resulting nanocomposites had an intercalated and partially exfoliated structure, as confirmed by X-ray diffraction and transmission electron microscopy. The thermal properties of the nanocomposites improved substantially over those of neat polystyrene. In particular, a maximum increase of 35.5 °C in the degradation temperature was displayed by these nanocomposites. Additionally, the surface elastic modulus and hardness of these nanocomposites were more than double those of pure polystyrene. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 43: 534–542, 2005

Keywords: polystyrene; clay; atom transfer radical polymerization (ATRP); nanocomposites

INTRODUCTION

Hybrid organic–inorganic nanocomposites have attracted substantial interest because of their unique properties, which are otherwise difficult to obtain with their individual components.^{1,2} Ionically bonded layered-silicate/polymer nanocomposites produced from organically modified silicates are examples.^{3–18} In these nanocomposites, montmorillonite is typically used as the source of layered silicates. Through the replacement of the metal ions in intergalleries of stacked silicates in montmorillonite with alkyl or aromatic ammonium ions, intercalated or exfoliated layered-silicate/polymer nanocomposites are produced. These nanocomposites display substantially higher mechanical properties¹⁶ but modest increases in the degradation tem-

perature in comparison with pure polymers. On the other hand, if the nanocomposites are formed by covalent bonding between polymers and layered silicates, the interfacial strength between these dissimilar materials becomes stronger and further enhances their thermal stability and mechanical properties.^{18,19} There are several methods for preparing layered-silicate/polymer nanocomposites. The *in situ* polymerization of the monomer in the presence of a layered silicate is one of the most common ways of achieving a highly efficient dispersion of nanometer-sized layered silicate in a polymer.^{20–22} One particular method of *in situ* polymerization involves surface grafting via living/controlled radical polymerization.^{23–27} One kind of living/controlled radical polymerization is atom transfer radical polymerization (ATRP).^{28–36} To control the molecular weight and molecular weight distribution of the polymer chains, we chose the ATRP method to prepare layered-silicate/polymer nanocomposites because it produces a narrower molecular weight

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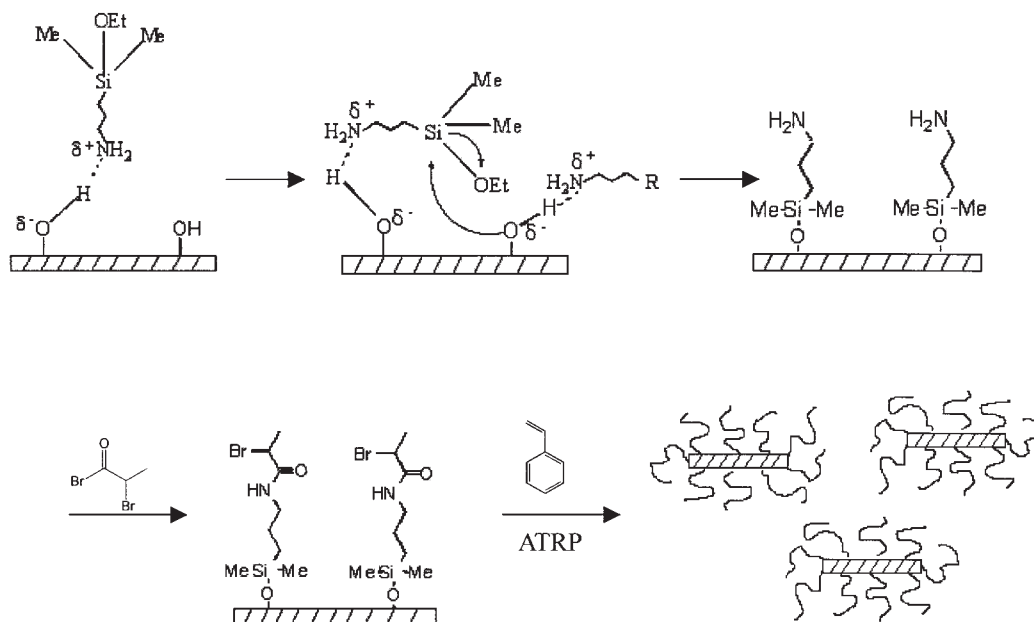


Figure 1. Synthetic procedure for Br-magadiite/polystyrene nanocomposites from initiator-modified magadiite via ATRP.

distribution than conventional free-radical polymerization. In this investigation, covalently bonded layered-silicate/polystyrene nanocomposites were synthesized via ATRP in the presence of initiator-modified layered silicates.

In our study, hydrothermally synthesized Na-magadiite ($\text{Na}_2\text{Si}_{14}\text{O}_{29} \cdot n\text{H}_2\text{O}$) was chosen as the

source of layered silicates.³⁷ Upon acidification, Na-magadiite is converted into H-magadiite,^{38,39} and the dangling surface OH groups on the surface of H-magadiite are able to form covalent bonds with surfactants containing amine groups.^{40–42} The modification of H-magadiite with surfactants (3-aminopropyl-dimethylethox-

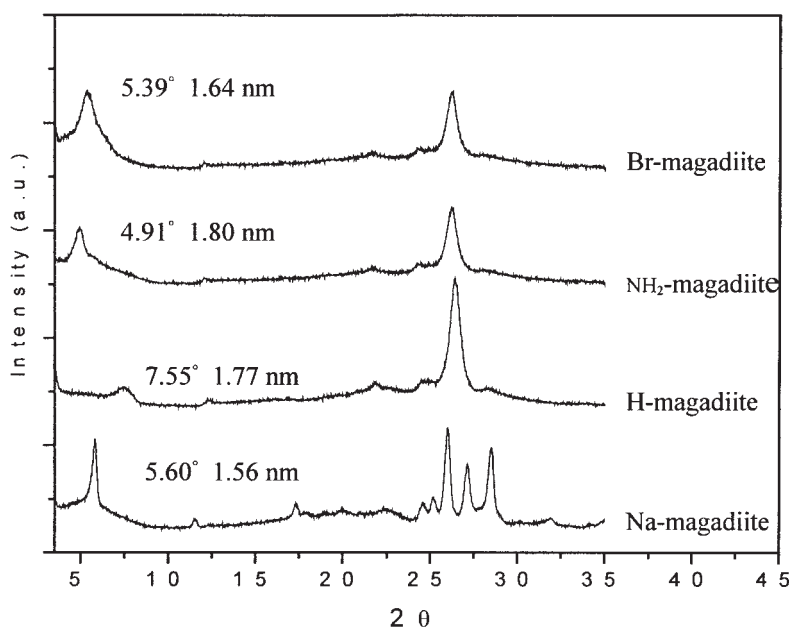


Figure 2. X-ray diffraction curves of Na-magadiite, H-magadiite, NH₂-magadiite, and Br-magadiite.

ysilane) requires polar organic solvents such as *N*-methylformamide (DMF), dimethyl sulfoxide, and *N,N*-dimethylacetamide. Then, 2-bromopropionyl bromide, an initiator of ATRP, is added to the mixture to react with the NH_2 groups of the surfactant. For the polymer chain to graft from the intergallery of the layered silicate, the diffusion of the monomer and catalyst into the intergallery of the layered silicate is very important. A schematic drawing of the preparation of magadiite/polystyrene nanocomposites by ATRP is presented in Figure 1.

EXPERIMENTAL

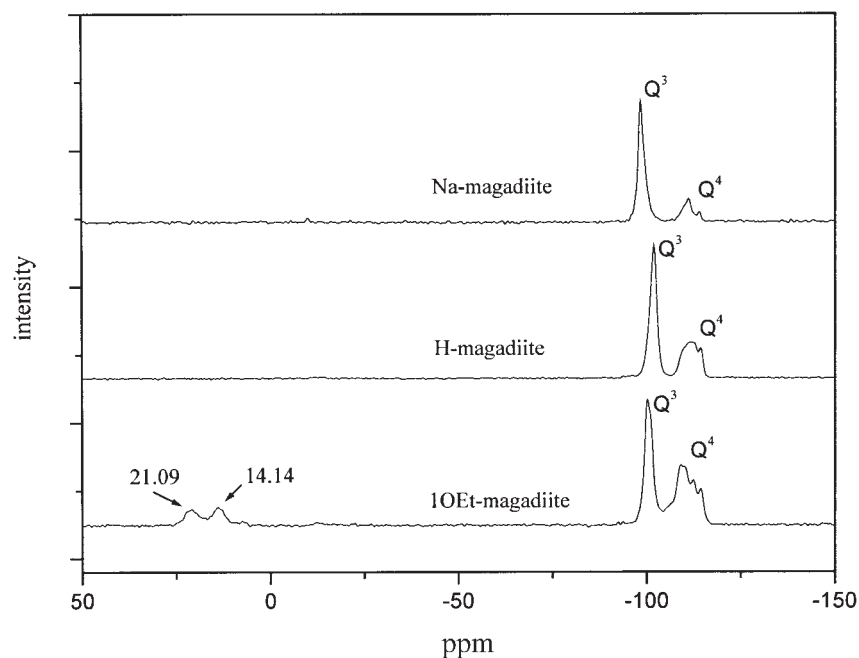
Materials

A sodium silicate solution was purchased from Showa (Japan). NaOH, HCl, acetone, MeOH,

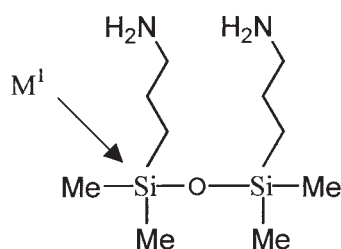
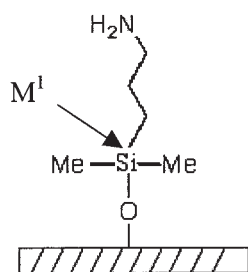
DL-ethyl-2-bromopropionate, and DMF were obtained from Aldrich. 3-Aminopropyl-dimethylethoxysilane, 2-bromopropionyl bromide, styrene, CuBr, and 2,2'-dipyridine were purchased from TCI (Tokyo, Japan).

Synthesis of Na-Magadiite and H-Magadiite

Na-magadiite was synthesized via a hydrothermal method in our laboratory. A suspension of amorphous silica, sodium hydroxide, and water in a molar ratio of 1.8:1:150 was reacted at 150 °C for 48 h in a sealed Teflon-lined reactor. The product was washed with a dilute NaOH aqueous solution and then dried in air. H-magadiite was obtained by an ion-exchange reaction of 5 g of magadiite and 3 g of a 37.5 wt % HCl aqueous solution in 1 L of deionized water after 5 days of stirring at room temperature.



(a)



(b)

Figure 3. ^{29}Si NMR spectra of Na-magadiite, H-magadiite, and NH_2 -magadiite.

Modification of H-Magadiite with Coupling and an Initiator

A total of 4.0 g of the H-magadiite was suspended in 100 mL of anhydrous DMF under a nitrogen purge at 25 °C for 12 h. Then, 8.5 mL of 3-aminopropyl-dimethylethoxysilane was added to the suspension and stirred for 3 days. After the treatment, the suspension was stirred under a nitrogen purge at 70 °C for 3 days and then was filtered and washed with DMF and acetone. The precipitated solid (NH₂-magadiite) was dried *in vacuo* at 100 °C for 24 h.

Br-magadiite (initiator magadiite) was synthesized from NH₂-magadiite and 2-bromopropionyl bromide in DMF. A total of 3.0 g of NH₂-magadiite was placed in a three-necked flask containing 30 mL of DMF under a nitrogen purge at 25 °C and was stirred for 3 h. When the NH₂-magadiite was well suspended in DMF, 1.85 mL of 2-bromopropionyl bromide was added drop by drop to the solution at 0 °C and was stirred for 12 h. After the treatment, the mixture was filtered and washed with DMF and acetone. The precipitated solid (Br-magadiite) was dried *in vacuo* at 100 °C for 24 h.

Preparation of the Magadiite/Polystyrene Nanocomposites

Polystyrene was synthesized from the surface of the magadiite via ATRP. Different concentrations

of Br-magadiite in acetone were prepared by 0.25, 0.15, or 0.05 g of Br-magadiite and 2 mL of degassed acetone being placed in three-necked flasks under a nitrogen purge at 25 °C. Each solution was stirred for 3 h, and then the styrene monomer was added to each three-necked flask. The first one-necked flasks contained CuBr (0.115 g) and bipyridine (0.25 g), the second contained CuBr (0.069 g) and bipyridine (0.15 g), and the third contained CuBr (0.032 g) and bipyridine (0.05 g). Degassed acetone (1 mL) was added to each flask, and the solution was stirred for 0.5 h under a nitrogen purge at 25 °C. When each solution had completely dissolved, it was transferred to the magadiite/acetone dispersion via a syringe and stirred in a 55 °C oil bath for 6 h under nitrogen. Pure polystyrene was synthesized with DL-ethyl-2-bromopropionate as an initiator via a normal ATRP procedure. After the completion of the polymerization reaction, the mixture was diluted with acetone, and the nanocomposite was precipitated in methanol. The solid material was washed and precipitated with acetone/methanol three times and dried in a vacuum oven at 80 °C for 24 h.

Characterization

An X-ray diffraction study was carried out with a MAC Science MXP 18 X-ray diffractometer

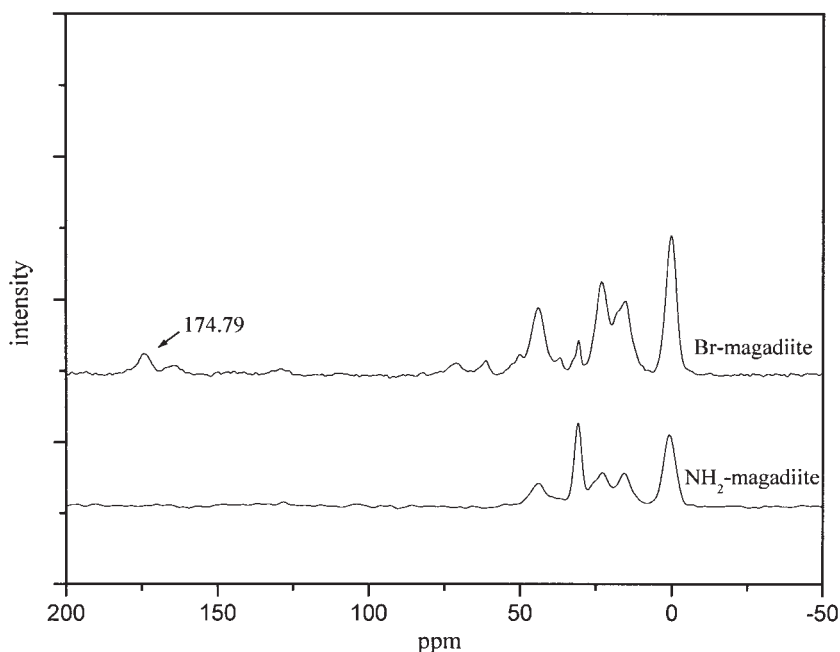


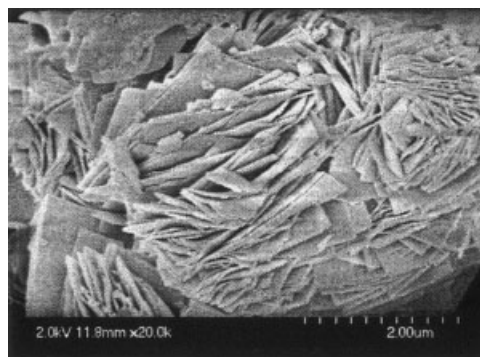
Figure 4. ¹³C NMR spectra of NH₂-magadiite and Br-magadiite.

(30 kV, 20 mA) with a copper target at a scanning rate of 4°/min. ^{13}C and ^{29}Si solid-state cross-polarization/magic-angle-spinning NMR spectra were recorded on a DSX400 NMR spectrometer. Scanning electron microscopy (SEM) micrographs of the samples were obtained with a thermal field emission scanning electron microscope (JSM-6500F) at an accelerating voltage of 20 kV. The stack sizes of 1 wt % layered silicates in water were obtained with a Honeywell ultrafine particle size analyzer.

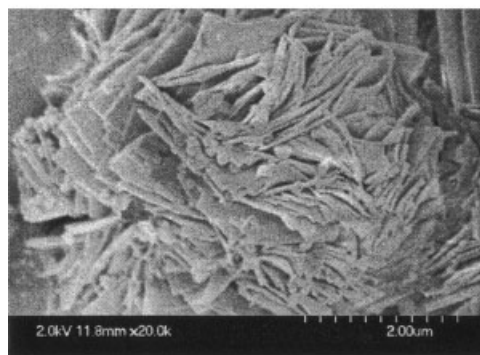
The samples for the transmission electron microscopy (TEM) study were prepared by the placement of the magadiite/polystyrene films in epoxy capsules and the subsequent curing of the epoxy at 70 °C for 48 h in a vacuum oven. Then, the cured epoxy samples were microtomed with a Leica Ultracut Uct into approximately 90-nm-thick slices. Subsequently, a layer of carbon approximately 3 nm thick was deposited onto these slices and placed on 400-mesh copper nets for TEM observation. The TEM instrument was a JEOL-2000 FX with an acceleration voltage of 200 kV. Thermogravimetric and thermal transition analyses of the magadiite/polystyrene nanocomposite films were carried out with a DuPont TGA 2950 and a DuPont DSC 2910 at a heating rate of 10°/min with a nitrogen purge. The molecular weight and polydispersity of the synthesized polystyrene were measured by gel permeation chromatography after the layered silicates were etched with an HF/H₂O solution (1/100 v/v) and washed a few times with water to produce free polymer chains. In the nanoindentation experiments, the samples were prepared by the spin coating of a Br-magadiite/polystyrene solution onto a silicon substrate, and the thickness of the films was approximately 7 μm. A Berkovich indenter (Hysitron, Inc.), mounted with a three-sided, triangular-based, pyramidal diamond (TI-039), was used in the nanoindentation experiments. The cross section of the base of the Berkovich indenter was 6 μm × 6 μm and provided a maximum load of 1000 μN. The loading and unloading times were 20 s, and there was a waiting time of 5 s during the nanoindentation experiments.

RESULTS AND DISCUSSION

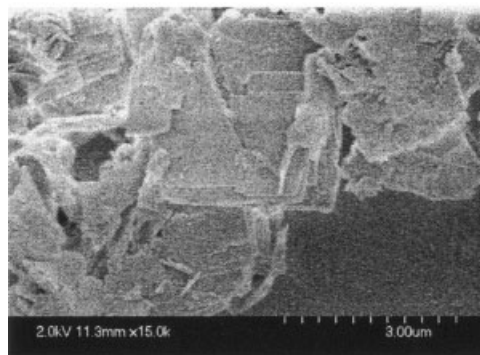
The X-ray diffraction curves of four different forms of magadiite are presented in Figure 2. The X-ray diffraction curves of Na-magadiite and H-



Na-magadiite



H-magadiite



NH₂-magadiite

Figure 5. SEM micrographs of Na-magadiite, H-magadiite, and NH₂-magadiite.

magadiite show *d*-spacings of 1.56 and 1.17 nm in the layered silicates, respectively, and are consistent with previous reports.^{43,44} For NH₂-magadi-

ite, the peak at $2\theta = 4.91^\circ$ (d -spacing = 1.80 nm) resulted from the diffraction of (001) crystal surfaces of the layered silicates and indicates that

the interlayers of the silicate were intercalated by 3-aminopropyl-dimethylethoxysilane molecules. A peak at $2\theta = 5.39^\circ$ (d -spacing = 1.64 nm) can be

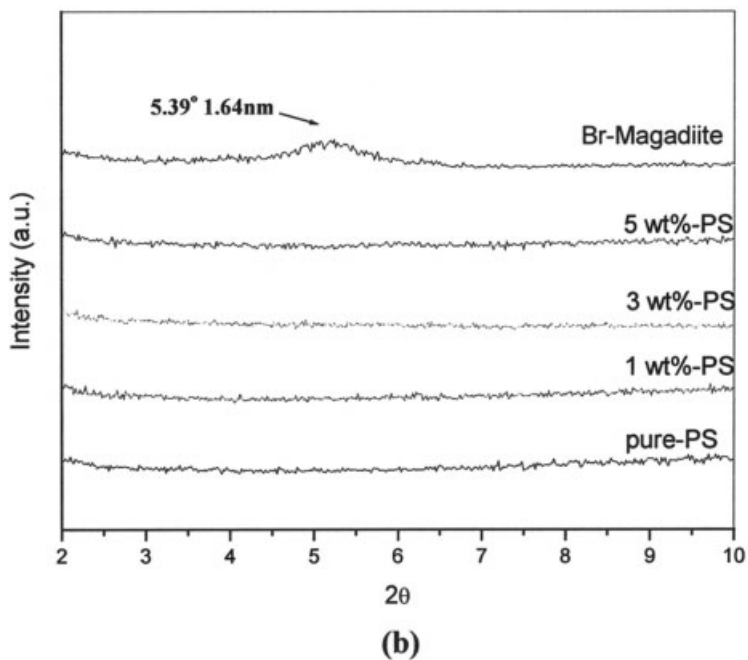
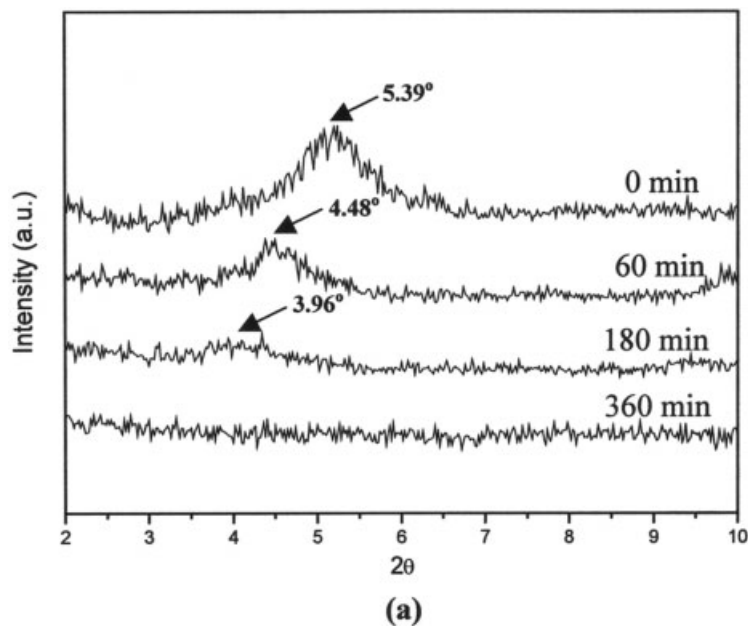


Figure 6. (a) X-ray diffraction curves of 5 wt % Br-magadiite/polystyrene taken at different times during polymerization and (b) X-ray diffraction curves of 1, 3, and 5 wt % Br-magadiite/polystyrene.

Table 1. Molecular Weight Control in the Synthesis of 5.0 wt % Br-Magadiite/Polystyrene Nanocomposites at Different Polymerization Times

Time (min)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
60	29.6	22.1	1.34
180	41.0	31.8	1.29
360	83.5	62.8	1.33

observed for Br-magadiite. The d -spacing of Br-magadiite was smaller than that of NH_2 -magadiite because of the loss of hydrogen bonds between the amine and OH groups of layered silicates when 2-bromopropionyl bromide reacted with NH_2 -magadiite.

Figures 3 and 4 show the chemical structure evidence for the covalent bonding of 3-aminopropyl-dimethylethoxysilane onto the layered silicates in H-magadiite and of 2-bromopropionyl bromide with NH_2 -magadiite, respectively, by solid-state ^{13}C and ^{29}Si NMR spectra. In Figure 3(a), the peaks at -100 and -112 ppm (Q^3 and Q^4) are due to the chemical structures of $\text{Si}(\text{OSi})_3\text{OH}$ and $\text{Si}(\text{OSi})_4$, respectively, in the layered silicates of magadiite. The ^{29}Si peaks at 21.09 ppm in Figure 3(a) were caused by the covalent attachment of 3-aminopropyl-dimethylethoxysilane to the surface of the layered silicates, whereas the peak at 14.14 ppm is due to the self-reaction of 3-aminopropyl-dimethylethoxysilane to form a dimer $[\text{R}_3\text{SiOSi}]$. The M^1 structure is shown in Figure 3(b). The ^{29}Si NMR spectra provide direct evidence of covalent bonding between 3-aminopropyl-dimethylethoxysilane and layered silicates in magadiite. Figure 4 displays a peak at 174.79 ppm that can be attributed to the $\text{C}=\text{O}$ group of the 2-bromopropionyl bromide. The peak of 2-bromopropionyl bromide shifted from 166.07 to 174.79 ppm because the chemical environment changed, and this implies that 2-bromopropionyl bromide reacted with NH_2 -magadiite.

SEM micrographs of the different forms of magadiite are shown in Figure 5. Na-magadiite and H-magadiite formed spherical nodules resembling rosettes. The rosette was exfoliated into a smaller structure after silylation by 3-aminopropyl-dimethylethoxysilane. The stack sizes of Na-magadiite, H-magadiite, and NH_2 -magadiite were between 1.0 and 1.5 μm .

Figure 6(a) shows the evolution of the d -spacing of layered silicates by X-ray diffraction during

the ATRP of polystyrene. The d_{001} peaks of layered silicate at 5.39° for Br-magadiite at the inception of polymerization became 4.48 and 3.96° after 60 and 180 min, respectively. After 360 min of polymerization, the peak disappeared, and this indicated an intercalated and partially exfoliated structure. Hence, the d_{001} peaks of layered silicate shifted to smaller angles and became weaker as the polymerization time increased. Additionally, the evolution of the molecular weight of PS-magadiite is given in Table 1. The dispersity values remained reasonable during the polymerization. Figure 6(b) shows X-ray diffraction patterns of various compositions of Br-magadiite/polystyrene. There is no peak between $2\theta = 2^\circ$ and $2\theta = 10^\circ$ for polystyrene containing 1.0, 3.0, or 5.0 wt % Br-magadiite, and this indicates that the d -spacing between the silicates was greater than 3 nm in these cases; thus, the silicates were intercalated and partially exfoliated. The dispersion model of silicates can be found in the TEM examination of a cross section of magadiite/polystyrene, as shown in Figure 7. In the TEM micrograph, the dispersion model of polystyrene containing 5 wt % Br-magadiite can be observed, and it reveals an intercalated and partially exfoliated structure.

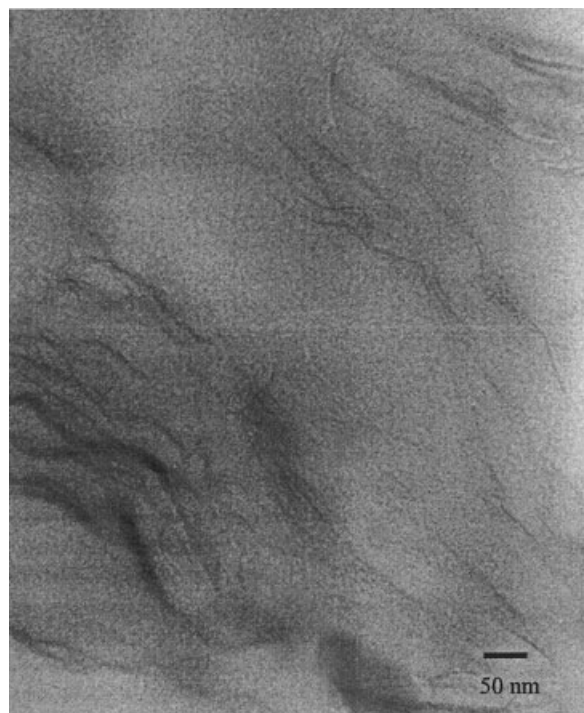
**Figure 7.** TEM micrograph of 5 wt % Br-magadiite/polystyrene.

Table 2. Thermal Properties, Molecular Weight, and Polydispersities of Br-Magadiite/Polystyrene Nanocomposites

Magadiite in Polystyrene (wt %)	T_d (°C) ^a	T_g (°C)	$M_n \times 10^{-3}$	M_w/M_n
0	384.6	91.1	68.8	1.23
1	412.7	100.3	65.1	1.28
3	417.5	102.8	63.2	1.32
5	420.1	104.2	62.8	1.33

^a Degradation temperature at a 5 wt % loss.

The thermal properties of Br-magadiite/polystyrene nanocomposites of different compositions are given in Table 1. The thermal degradation temperatures of the nanocomposites rose as the amount of Br-magadiite increased; a maximum increase of 35.5 °C was obtained for polystyrene containing 5 wt % Br-magadiite, in comparison with pure polystyrene. The increase in the thermal degradation temperature resulted from the fact that the covalently bonded nanosized layered silicates were able to sustain high temperatures and could retard heat diffusion into polystyrene. The glass-transition temperatures (T_g 's) of Br-magadiite/polystyrene also increased slightly with the amount of Br-magadiite that was incorporated. This phenomenon could be explained by the fact that the layered silicates that were covalently attached to polystyrene chains retarded the chain motion of polystyrene. The molecular weights and polydispersities of the Br-magadiite/polystyrene nanocomposites are also listed in Table 2. The polydispersity indices were between 1.2 and 1.3, and so the results were in good agreement with the proposed mechanism for ATRP.

Table 3 shows the surface nanomechanical properties of the nanocomposites. The surface hardness and reduced elastic modulus increased, whereas the maximum displacement

decreased slightly with increasing amounts of Br-magadiite. In particular, for 5 wt % Br-magadiite/polystyrene, the reduced elastic modulus was about three times as large as that of pure polystyrene (21.5 vs 6.7 GPa), and this indicated that the presence of Br-magadiite led to enhanced surface elasticity. The surface hardness of the nanocomposite also increased with the concentration amount of Br-magadiite. When the concentration amount of Br-magadiite in polystyrene reached 5 wt %, the hardness of the nanocomposite was about 2.3 times that of pure polystyrene (0.30 vs 0.13 GPa). The enhancement of the surface hardness and reduced elastic modulus of Br-magadiite resulted from the strength of the layered silicate and its special layered structure; the hardness helped to enhance the hardness of polystyrene, and the layered structure allowed the silicate to disperse parallel to the surface of the thin film when spin-coated samples were used. Because the layered silicate structure was oriented parallel to the surface of the thin film and the direction of the indentation load was vertical to the surface in the nanoindentation experiments, the silicates provided resistance to the indenting load. Therefore, the reduced elastic modulus and the surface hardness increased

Table 3. Surface Nanomechanical Properties of Br-Magadiite/Polystyrene Nanocomposites by Nanoindentation Measurements

Magadiite in Polystyrene (wt %)	Reduced Elastic Modulus (GPa)	Surface Hardness (GPa)	Maximum Displacement (nm)
0	6.7 ± 0.1	0.13 ± 0.02	410.18 ± 0.01
1.0	15.2 ± 0.1	0.15 ± 0.01	335.51 ± 0.02
3.0	18.5 ± 0.1	0.22 ± 0.01	317.10 ± 0.01
5.0	21.5 ± 0.1	0.30 ± 0.02	268.97 ± 0.02

with the addition of Br-magadiite to polystyrene.

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