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Macromolecules
NOTE

A Novel Polymer Nanocomposite: Polystyrene-Layered Methylbenzamidephenylsilica

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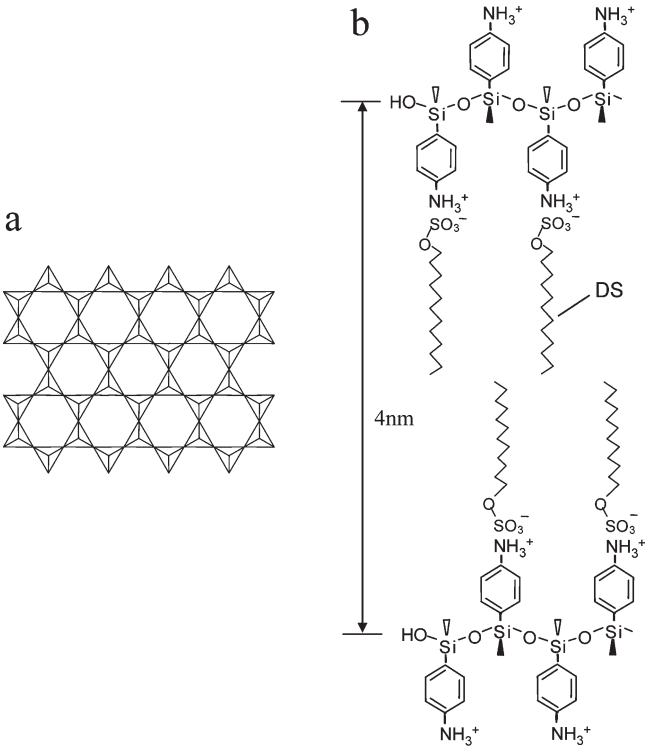
Introduction

Polymer-layered silicate nanocomposites have been widely investigated because it is promising to improve the properties of polymers by incorporating dispersed layered silicate materials into a polymer matrix.[1−16] However, the nanolayers are not easily and stably dispersed in most polymers due to their preferred face-to-face stacking in agglomerated tactoids, and this confines the further applications of polymer-layered silicate nanocomposites as practical polymer materials.

Previously, we developed novel two-dimensional organosilica (layered aminophenylsilica [APhTMS-DS]) with regular ammonium groups in the structure, using aminophenyltrimethoxysilane (trifunctional organosilanes) templated with anionic surfactant (sodium dodecyl sulfate, [SDS]) under acidic conditions.[17] The aminophenyltrimethoxysilane with three hydrolyzable points tends to form a two-dimensional structure when aminophenyltrimethoxysilane was hydrolyzed on the surface of DS micells. The two-dimensional lamellar organosilica structures were also reported to be obtained by direct concentration of *n*-alkyltrichlorosilanes,[18] organotrialkoxysilanes,[19] 3-aminopropyltrimethoxysilane,[20] and cyanoalkyltrialkoxysilane.[21] The inorganic part of layered APhTMS-DS was a Si−O hexagonal sheet, as illustrated in Scheme 1 in an idealized structure. The ammonium groups were considered that arranged on both sides of the layer sheet.[17] We also developed organic−inorganic hybrid layered organosilica with regular double bonds (layered acrylamidephenylsilica, [AAPhS]) by grafting acrylic acid in APhTMS-DS.[22] The polymerization process of acrylic acid in layered aminopropylsilica was also investigated.[23] The acrylic acid regularly fixed in layered aminopropylsilica was completely polymerized to form a novel organic−inorganic nanocomposite material called layered polyacrylamidepropylsilica (ATMS-PAA) with monolayers of polyacrylamide in a layer space of layered aminopropylsilica without initiator.

However, polymer materials with practical value cannot be formed using AAPhS because it is difficult to form high molecular weight polymer nanocomposite due to self-polymerization of double bonds in the layer structure of AAPhS. Here, we report on a novel polymer nanocomposite with practical value that is directly synthesized by atom transfer radical polymerization (ATRP) of styrene using organic−inorganic hybrid layered organosilica with regular chlorine groups as initiator. The silica layer is completely dispersed in polymer matrix because the polymerization directly occurs on both sides of each silica layer. This research exhibits the potential of novel polymer-layered silica nanocomposites with practical value, which can be directly formed by utilizing an organic−inorganic hybrid layered organosilica with a regular organic structure.

Scheme 1. Schematic Illustrations of the Layered Aminophenylsilica: (a) Top View of Si−O Hexagonal Sheet; (b) Vertical Cross-Section View of APhTMS-DS



Experimental Section

All the reagents were purchased from Aldrich Chemical Co. APhTMS-DS was synthesized by the slow titration of HCl into a mixture of *p*-aminophenyltrimethoxysilane (APhTMS, 2.78 mmol) and SDS (2.92 mmol) in aqueous solution, and the suspension was stirred at room temperature for 2 weeks (pH 2.0−3.0). APhTMS-DS was obtained as a light pink precipitate. The CMBAPhS was synthesized by mixing 0.2 g of APhTMS-DS and 0.5 g of 4-(chloromethyl)benzoyl chloride in 30 mL of THF solution, and the suspension was stirred at 50 °C for 24 h. The precipitate was filtered and washed with THF and ethanol and then dried in a vacuum.

The CMBAPhS as initiator was then used in the ATRP of styrene to form polystyrene-layered methylbenzamidephenylsilica (PS-CMBAPhS) nanocomposite. The air-dried layered CMBAPhS (0.05 g), CuBr (0.3 mmol), and 4,4-dinonyl-2,2-dipyridyl

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(0.6 mmol, Aldrich, 97%) were mixed with 20 mL of styrene, and the mixture suspension was then stirred at 130 °C for 3 h after being degassed three times by freeze−pump−thaw cycles under a nitrogen atmosphere.[24−26] The polymer-like yellow precipitate was obtained after the curdled mixture suspension was thoroughly washed with THF and dried in air.

Data on the molecular weight of polystyrene were obtained by etching the silica layer in PS-CMBAPhS. PS-CMBAPhS was first dispersed in THF, and 5 wt % aqueous HF solution was added and stirred for 6 h at room temperature in a PTFE griffin beaker. Polystyrene, which was free from silica layer, was then extracted with toluene and analyzed using an Agilent 1100 gel permeation chromatography (GPC) system. The amount CMBAPhS in PS-CMBAPhS was calculated based on the amount of Si. The amount of Si in CMBAPhS or PS-CMBAPhS was measured as fellows: CMBAPhS or PS-CMBAPhS was heated at 600 °C for 24 h, and the sample was then dissolved with 0.2 M NaOH aqueous solution at room temperature. The amount of Si was then determined by inductively coupled plasma (ICP) emission spectroscopy (Thermo ICAP 6300). Chemical analyses were performed by elementary organic microanalysis for C, N, and S in a VerioEL III element analyzer. The amount of Cl in CMBAPhS was determined using the oxygen flask combustion method. The ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were recorded on a Bruker MSL-500WB spectrometer at 75.47 MHz for ^{13}C. Chemical shifts for ^{13}C NMR were referenced to tetramethylsilane (TMS) at 0 ppm. FTIR spectra were obtained using an Avatar 370 spectrophotometer from Nicolet. Sample preparation involved dispersing and gently grinding the powder in KBr. X-ray diffraction (XRD) data on the powder samples were recorded with an X-ray diffractometer (Rigaku, D/max 2550) using Cu Kα radiation (0.1541 nm) under the conditions of 40 kV and 30 mA. The transmission electron microscopy (TEM) image was recorded by a JEM-4000EX with an acceleration voltage of 120 kV. TEM samples were prepared by evaporating a dilute THF suspension of PS-CMBAPhS onto carbon-coated copper grids. The scanning electron microscope (SEM) micrographs were recorded with a JEOL JSM-6700F SEM with an accelerating voltage of 3 kV. The SEM micrographs were obtained from the samples coated with a conductive layer of sputtered gold.

Results and Discussion

First, layered aminophenylsilica APhTMS-DS was treated with 4-(chloromethyl)benzoyl chloride to form a layered material with regular chlorine groups (layered chloromethylbenzamide-phenylsilica; CMBAPhS) as shown in Scheme 2a. A new vibration peak at 1654 cm^{-1} appeared in the IR spectrum of the reaction precipitates (CMBAPhS) between APhTMS-DS and 4-(chloromethyl)benzoyl chloride compared with layered APhTMS-DS (Figure 1). The peak was assigned to carbonyl in the amide formed between the ammonium groups of layered APhTMS−DS and acyl chloride groups of 4-(chloromethyl)-benzoyl chloride, as illustrated in Scheme 2a. The stronger peaks at 2851, 2920, and 2953 cm^{-1} assigned to symmetric C−H stretching vibrations of dodecyl sulfate DS (Figure 1a) were not observed in CMBAPhS (Figure 1b). It can be considered that the DS anions in layered APhTMS-DS disappeared, and the chloromethyl benzoyl groups were successfully grafted in layered aminophenylsilica, as the ammonium groups in layered APh-TMS-DS reacted with the acyl chloride groups of 4-(chloro-methyl)benzoyl chloride to form amide. The ^{13}C CP/MAS NMR spectra were also used to confirm further the formation of CMBAPhS. The resonance peaks at 125 and 135 ppm observed in the ^{13}C CP/MAS NMR spectrum of APhTMS-DS (Figure 2a) were attributed to the superposition of the resonances of carbon species in the aromatic rings of aminophenylsilica, as the aromatic rings are fixed in the framework of silica as a layer plate.

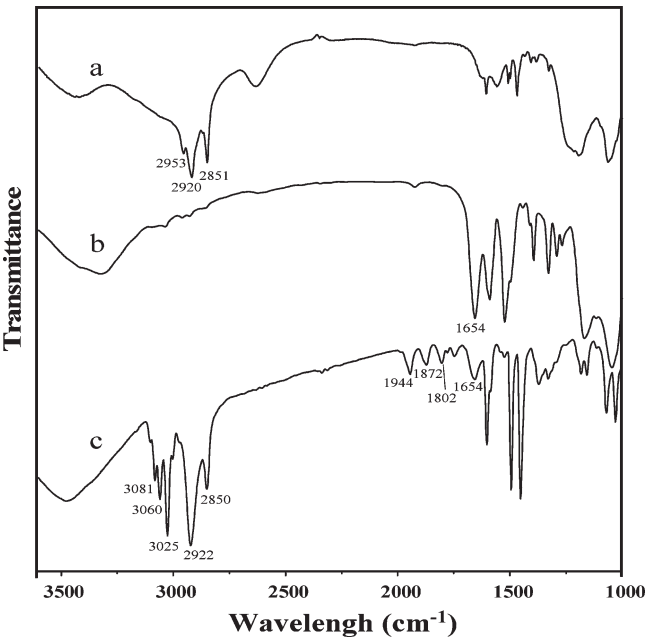
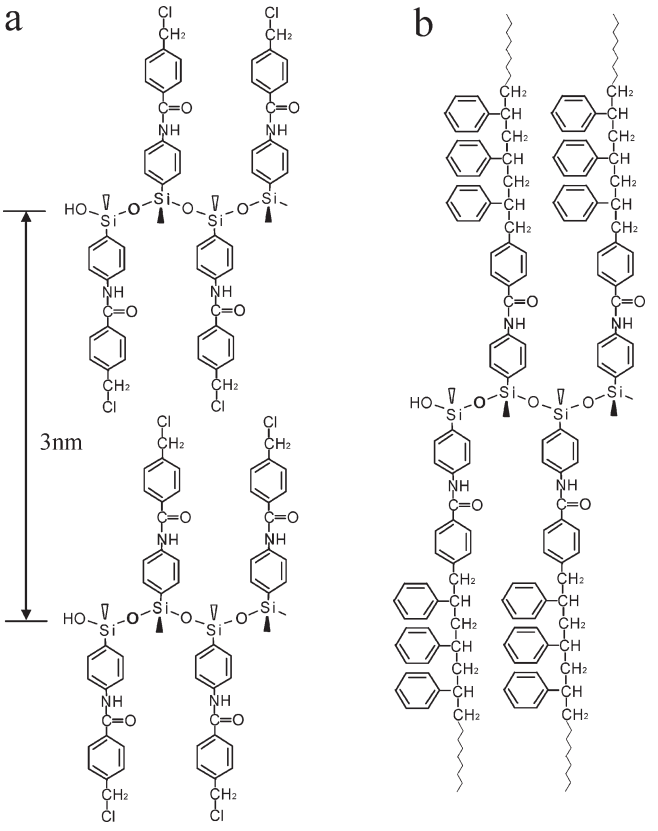


Figure 1. IR spectra of (a) APhTMS-DS, (b) CMBAPhS, and (c) PS-CMBAPhS.

Scheme 2. Schematic Illustrations of (a) CMBAPhS and (b) PS-CMBAPhS



The resonance peaks at 5−70 ppm observed in the ^{13}C CP/MAS NMR spectrum of APhTMS-DS (Figure 2a) were attributed to the methyl and methylenes of DS that existed in the layer space of APhTMS-DS. A resonance peak at 167 ppm (Figure 2b) appeared in the ^{13}C CP/MAS NMR spectrum of CMBAPhS; the peak was assigned to carbonyl in amide −*C*(═O)−NH− formed between the amino groups of APhTMS-DS and acyl chloride groups of 4-(chloromethyl)benzoyl chloride, as illustrated in

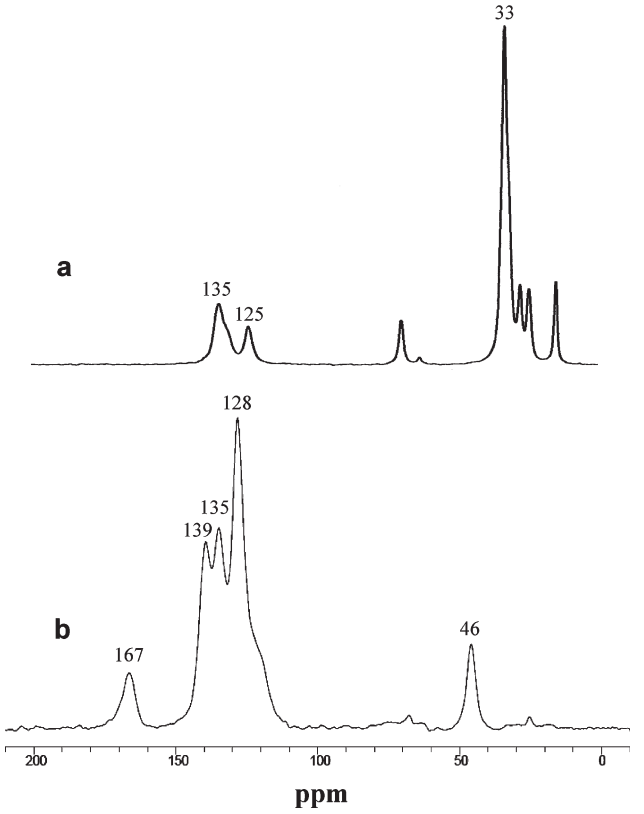


Figure 2. ^{13}C CP/MAS NMR spectra of (a) APhTMS-DS and (b) CMBAPhS.

Scheme 2a. The resonance peaks at 128, 135, and 138 ppm were attributed to the superposition of resonances of carbon species in the aromatic rings of CMBAPhS. The resonance peak at 46 was assigned to the carbon species of methylene in CMBAPhS (Scheme 2a). The sharp resonance peaks assigned to the methyl and methylenes of DS in APhTMS-DS were not observed in the ^{13}C CP/MAS NMR spectrum of CMBAPhS. The result of IR and ^{13}C CP/MAS NMR spectra of CMBAPhS indicated that DS completely disappeared due to the ammonium groups in layered APhTMS-DS that completely reacted with the acyl chloride groups of 4-(chloromethyl)benzoyl chloride to form amide and that the chlorine groups were successfully grafted in layered aminopropylsilica to form a two-dimensional layered materials of chloromethybenzoylamidephenylsilica with regular chlorine groups.

The X-ray diffraction peak of CMBAPhS assigned to the 001 reflection shifted from $2\theta = 2.2°$ in APhTMS-DS to $2\theta = 2.8°$in CMBAPhS, corresponding to the interlayer distance shifted from 4.1 nm in APhTMS-DS to 3.1 nm in CMBAPhS, as shown in Figure 3. The change in the interlayer distance was consistent with the change in the molecular length from APhTMS-DS to CMBAPhS, as shown in Schemes 1 and 2. The 002 diffraction peak of CMBAPhS was observed at $2\theta = 5.7°$ (1.5 nm). The results of the XRD indicated that the two-dimensional layer structure had been retained in CMBAPhS after the grafting reaction and that the chlorine groups were regularly arranged in the layer structure of CMBAPhS. A similar TEM micrograph with APhTMS-DS was confirmed in CMBAPhS as shown in Figure 4, and a stacked-layer-like structure was observed at the edge of the sample. The TEM micrograph further indicated that CPAPhS retained the layer structure after the graft reaction. The elemental analytical results of CMBAPhS are shown in Table 1. No sulfur atom was observed in CMBAPhS. This further indicates that DS in the two-dimensional molecular space of

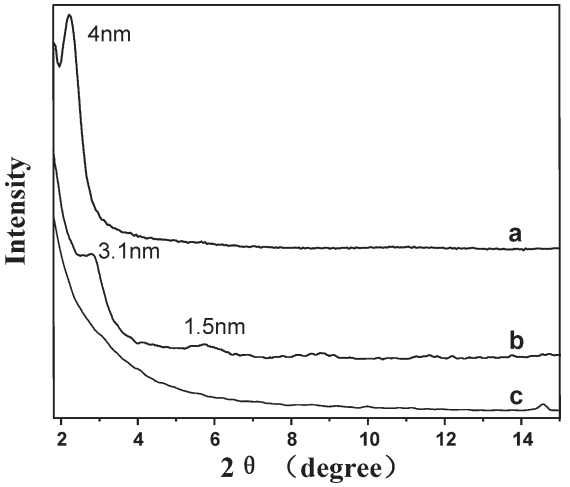


Figure 3. Powder XRD patterns of (a) APhTMS-DS, (b) CMBAPhS, and (c) PS-CMBAPhS.

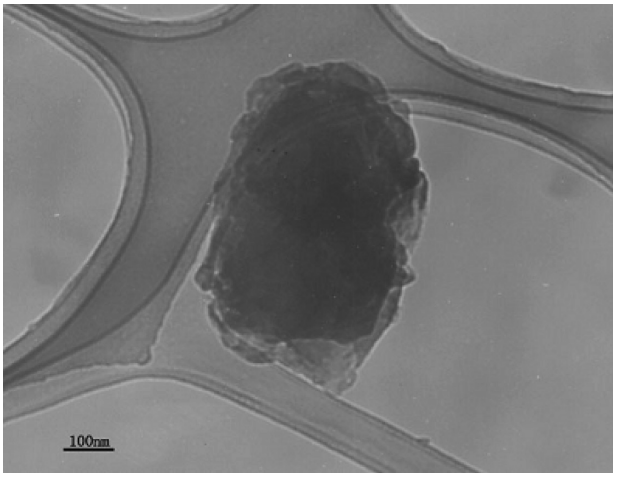


Figure 4. TEM micrograph of CMBAPhS.

APhTMS-DS was completely replaced by the chloromethylbenzamide groups in CMBAPhS. The elemental analytical results indicated that nearly 100% of the amino groups in layered APhTMS-DS reacted with 4-(chloromethyl)benzoyl chloride to form CMBAPhS, and the chlorine groups was confirmed in the CMBAPhS. The ^{13}C CP/MAS NMR spectrum, TEM micrograph, XRD pattern, and elemental analytical results indicated that the two-dimensional structure was retained in the CMBAPhS as a grafting compound of APhTMS-DS.

The CMBAPhS as initiator was then used in the ATRP of styrene to form PS-CMBAPhS nanocomposite, and a polymer-like yellow precipitate was obtained. The stretching vibration peaks of C−H in the benzene ring of polystyrene at 3081, 3060, and 3025 cm^{-1} appeared in the IR spectrum of polymerization precipitates; the peaks at 1944, 1872, and 1802 cm^{-1} were also assigned to the bending vibrations peaks of them (Figure 1c). The peaks at 2922 and 2850 cm^{-1} were assigned to the stretching vibration peaks of methylenes in polystyrene (Figure 1c). The vibration peak at 1654 cm^{-1}, which was assigned to carbonyl of amide, was also observed in polymerization precipitates. The IR spectrum of polymerization precipitates indicates that the ATRP reaction of styrene successfully occurred in the presence of CMBAPhS, and the polymerization precipitate called PS-CMBAPhS was obtained, as shown in Scheme 2b. No XRD peak was observed in PS-CMBAPhS (Figure 3c). The disappearance of the XRD peak in PS-CMBAPhS indicates that the

Table 1. Elemental Analytical Results of CMBAPhS

sample	C (wt %)	N (wt %)	Cl (wt %)	S (wt %)	Si (wt %)	attempted formula
CMBAPhS	48.93	4.44	9.43	0	8.09	$SiO_{1.5}C_6H_4NHCOC_6H_4CH_2Cl\cdot 2.7H_2O$

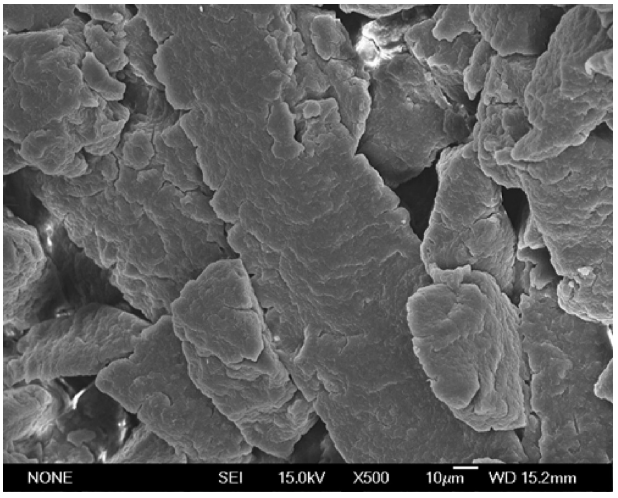


Figure 5. SEM micrograph of PS-CMBAPhS.

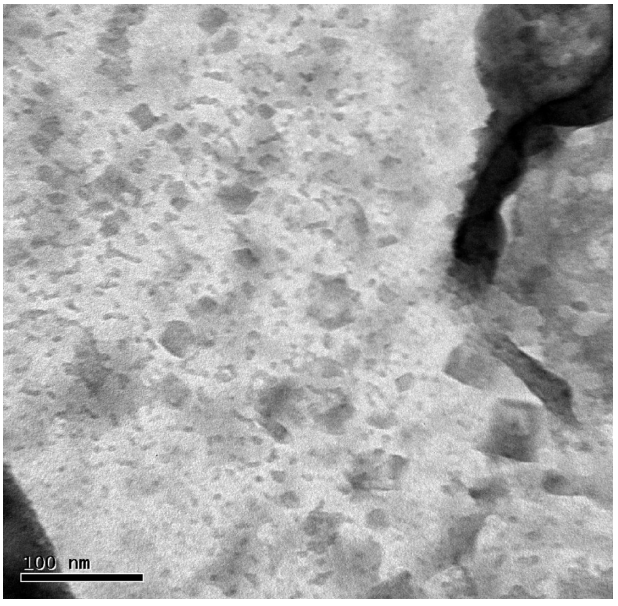


Figure 6. TEM micrograph of PS-CMBAPhS.

layered CMBAPhS was completely dispersed in polystyrene, and a novel polymer nanocomposite PS-CMBAPhS was obtained, as shown in Scheme 2b. The molecular weight of polystyrene in PS-CMBAPhS, M_n, was about 8.3×10^4 with lower polydispersities (M_w/M_n) 1.9, and the typical amount of CMBAPhS in PS-CMBAPhS was about 3.14 wt % in the conditions of this study, although the molecular weights and distributions of aspect ratios could be controlled in different polymerization conditions. A typical polymer material could be observed in the SEM micrograph of PS-CMBAPhS (Figure 5). The TEM micrograph of polymer nanocomposite PS-CMBAPhS is shown in Figure 6. The light areas in TEM micrograph of PS-CMBAPhS were polystyrene. The lamellar dark areas and linelike dark areas were hybrid silica sheets of CMBAPhS parallel and vertical to TEM sample surfaces, respectively. It could be confirmed that the hybrid silica sheets of CMBAPhS were well dispersed in polystyrene (Supporting Information). The results of IR spectra, GPC, SEM, and TEM indicate that a novel polymer material was obtained through the ATRP of styrene initiated by the organic−inorganic hybrid silica layer with regular chlorine groups and that a silica layer with regular organic structure completely dispersed in polymer.

Conclusions

A PS-CMBAPhS nanocomposite was successfully developed by utilizing the ATRP of styrene initiated by the organic−inorganic hybrid silica layer with regular chlorine groups. The silica layer was completely dispersed in polystyrene because polymerization reaction directly occurred on both sides of each silica layer. This research exhibited a potential to develop a series of novel polymer nanocomposites with a completely dispersed silica layer by utilizing polymerization reaction on the surface of organic−inorganic hybrid silica layer with regular organic structure. The molecular weights and aspect ratios of hybrid silica layer could be controlled in different polymerization conditions. Thus, the improvement of polymer properties, included mechanical properties, could be expected.

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Supporting Information Available: Other TEM micrograph of PS-CMBAPhS. This material is available free of charge via the Internet at http://pubs.acs.org.

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