Preparation of Poly(styrene-*block*-acrylamide)/Organic Montmorillonite Nanocomposites via Reversible Addition–Fragmentation Chain Transfer

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ABSTRACT: Using dithioester as a chain-transfer agent and azobisisobutyronitrile as an initiator, we synthesized amphiphilic poly(styrene-*block*-acrylamide) [P(St-*b*-Am)] by the reversible addition–fragmentation chain transfer (RAFT) polymerization method. To improve the heat stability of the block polymers, amphiphilic P(St-*b*-Am)/organic montmorillonite (O-MMT) nanocomposites were successfully prepared by the addition of O-MMT during the preparation of the block polymer. The nanocomposites were tested by gel permeation chromatography, IR spectroscopy, X-ray diffraction, transmission electron microscopy, and thermogravimetry. As for polystyrene (PSt)/O-MMT, RAFT polymerization could control the molecular weight and the molecular weight distribution of PSt. PSt/O-MMT was used as a macro RAFT agent to conduct the polymerization of acrylamide, and P(St-*b*-Am)/O-MMT nanocomposites were prepared. Nanosize layers of montmorillonite were dispersed in the block polymer matrix, and exfoliative nanocomposites were formed. Therefore, the P(St-*b*-Am)/O-MMT nanocomposites had a better heat stability than before. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 387–391, 2008

Key words: reversible addition-fragmentation chain transfer (RAFT); block copolymers; nanocomposites

INTRODUCTION

Amphiphilic block polymers are a class of functional polymer materials. Because of their amphiphilic properties and the microphase separation of their structures, they have been widely used in many fields, such as oil drilling and production,[1,2] polymer surfactants,[3] and medical polymer materials.[4,5] Because there is quite a difference in polarity between oil-soluble monomers and water-soluble monomers, it is difficult to synthesize amphiphilic block polymers by conventional methods. Reversible addition–fragmentation chain transfer (RAFT) polymerization,[6–11] developed in recent years, is a new living free-radical polymerization method for the preparation of block polymers from monomers with great polarity differences. With dithioester as a chain-transfer agent, RAFT can be performed with a wide range of monomers and reaction conditions. The living polymerization processes can provide controlled molecular weight polymers with very narrow polydispersities.[12–15]

With nanotechnology on the rise, layered clay/polymer composites with nanometer dimensions have recently become a hot direction for new materials development. More and more attention has been paid to so-called nanocomposites. Among nanocomposites, polymer/montmorillonite (MMT) nanocomposites are a kind of composite in which nanosize layers of MMT are dispersed in the polymer matrix. The process is different from the simple mixing process between organic matter and inorganic matter, and it makes use of the surface effect and quantum-size effect of the nanosize MMT layers to make the MMT layers exfoliated or thoroughly homogenized into the polymer matrix. The rigidity, dimensional stability, and heat stability of MMT and the toughness, processability, and dielectric properties of polymers are well combined. Therefore, the properties of polymers have apparently been improved, including physical properties, heat stability, gas barrier properties, and electric conductive properties.[16,17]

In this article, we report the polymerization of amphiphilic poly(styrene-*block*-acrylamide) [P(St-*b*-Am)] by RAFT with 2-cyanoprop-2-yl 1-dithionaphthalate (DTE) as a chain-transfer agent and azobisisobutyronitrile (AIBN) as an initiator. To improve the heat stability of the block polymers, amphiphilic P(St-*b*-Am)/organic montmorillonite (O-MMT) nanocomposites were successfully prepared by the addition of O-MMT during the preparation of the block polymers.

EXPERIMENTAL

Materials and reagents

Styrene (St; Xilong Chemical Plant in Shantou in Guangdong, China) was distilled under reduced pressure and kept in a refrigerator under 4°C before use. Acrylamide (AM; Beijing Yili Fine Chemical Co., Ltd., China) was recrystallized from chloroform and dried *in vacuo*. Analytical-grade AIBN (Tianjin Fucheng Chemical Reagent Factory, China) and cetyltrimethyl ammonium chloride (CTAC; Tianjin Fucheng Chemical Reagent Factory) were all used as supplied. Sodium montmorillonite (Na-MMT) was made in Huai'an in Hebei (China). DTE was synthesized according to refs. 12 and 18.

Modification of MMT with CTAC

According to the cation-exchange capacity of Na-MMT, the corresponding concentration of CTAC solution was prepared in a beaker. The solution was added dropwise to the Na-MMT base mud. The mixed solution was vigorously stirred for 2–4 h at 80°C and then stood overnight. The white precipitate was filtered, washed with deionized water until no chloride ion could be detected by an aqueous AgNO$_3$ solution (0.01 mol/L), and then dried in a vacuum oven. The clay was placed in petroleum ether and stirred for 1 h; it was then filtered and washed with petroleum ether several times. The procedure resulted in the formation of a powdery O-MMT that could be easily dispersed in the monomer.[19] Finally, O-MMT was dried in a vacuum oven overnight.

Preparation of the polystyrene (PSt)/O-MMT macro chain-transfer agent

PSt/O-MMT macro chain-transfer agent was synthesized by RAFT. A mixture of St, DTE, O-MMT, and AIBN was added to a 250-mL, three-necked flask equipped with a stirrer and thermometer. The St/DTE/AIBN molar ratio was 300 : 3 : 1, and the weight of O-MMT was 3% of St. The system was sealed after bubbling with N$_2$ for 20 min to eliminate O$_2$. The mixture was stirred until it became homogeneous. The polymerization was performed in an oil bath at 110°C. After reacting for a predetermined time, the system was cooled in an ice-water bath. Then, the seal was opened, and the mixture was precipitated in methanol. The mixture was filtered and dried *in vacuo*. Thus, the PSt/O-MMT macro chain-transfer agent was prepared.

Preparation of the P(St-*b*-Am)/O-MMT nanocomposites

A mixture of a predetermined concentration of Am, PSt/O-MMT, and AIBN was added to a three-necked flask equipped with a stirrer and thermometer. The Am : PSt/O-MMT (St) : AIBN molar ratio was 400 : 100 : 1. The mixture was dispersed in 1,4-dioxane. The system was sealed after bubbling with N$_2$ for 20 min to eliminate O$_2$. The polymerization was performed in a water bath at 70°C. After reacting for predetermined time, the system was cooled in an ice-water bath. Then, the seal was opened, and the mixture was precipitated in methanol and then filtered. The precipitate was extracted with toluene to eliminate homopolystyrene. Thus, the P(St-*b*-Am)/O-MMT nanocomposites were successfully prepared after drying *in vacuo*.

Measurements

Monomer conversions were measured gravimetrically. A Waters (USA) 150C gel permeation chromatograph (GPC) was used to measure the number-average molecular weight (M_n) and the molecular weight distribution [polydispersity index (PDI)] values of the polymers. PSt standards were used, and tetrahydrofuran was used as an eluent with a flow rate of 1.0 mL/min. X-ray diffraction (XRD) spectra were collected on a SIMENS (Karlsruhe, Germany) D5005D diffractometer equipped with an intrinsic germanium detector system with Cu Kα radiation (λ = 1.54 Å). Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet (USA) FTIR NEXUS-470 IR spectrometer. Transmission electron microscopy (TEM) was carried out on a TECNAI (Eindhoven, Netherlands) F20 electron microscope. Thermogravimetric analysis (TGA) was performed on a TA5000-DSC2910 (USA) thermogravimetric analyzer under a flowing nitrogen atmosphere at a scan rate of 10°C/min from 50 to 800°C.

RESULTS AND DISCUSSION

GPC measurement

During the preparation of the PSt/O-MMT macro chain-transfer agent, samples were taken and analyzed at various time intervals. For the GPC measurements, polymers were detached from O-MMT through refluxing for about 3 h in a tetrahydrofuran/LiBr solution (5 wt %) and were then centrifuged and filtered.[20] The plots of the molecular weight and PDI values of PSt extracted from the PSt/O-MMT samples versus monomer conversion are shown in Figure 1. M_n values of PSt increased linearly with monomer conversion, whereas the polydispersity remained at a relative low value (PDI < 1.25). The results indicate that the RAFT polymerization was successful in controlling the molecular weight and the molecular weight distribution for the
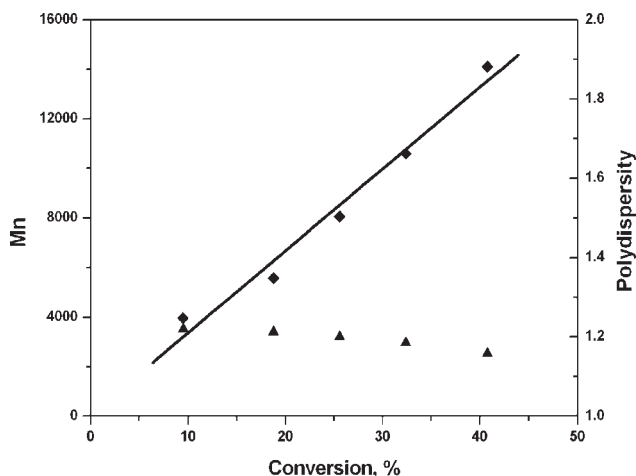
Figure 1 (◆) Relative molecular weight (M_n) and (▲) PDI of PSt extracted from PSt/O-MMT samples versus monomer conversion.

PSt/O-MMT macro chain-transfer agent. The addition of O-MMT had no influence on the effective control of the molecular weight and the molecular weight distribution of PSt by RAFT.

On the basis of the RAFT polymerization mechanism, PSt/O-MMT was used as a macro RAFT agent to conduct the polymerization of AM to form the block polymer. The GPC spectra of PSt and P(St-*b*-Am) after the removal O-MMT are shown in Figure 2. There was an obvious peak shift from PSt to P(St-*b*-Am). The peak of PSt disappeared thoroughly in the spectrum of P(St-*b*-Am), which demonstrated that PSt converted to P(St-*b*-Am) copolymer. In addition, the polydispersity of P(St-*b*-Am) was a little larger than that of PSt (from 1.185 to 1.480). This might have been caused by the small-portion homopolymerization of AM initiated by AIBN and the dead polymer (without the dithioester fragment) that existed in the PSt/O-MMT macro chain-transfer agent.[21]
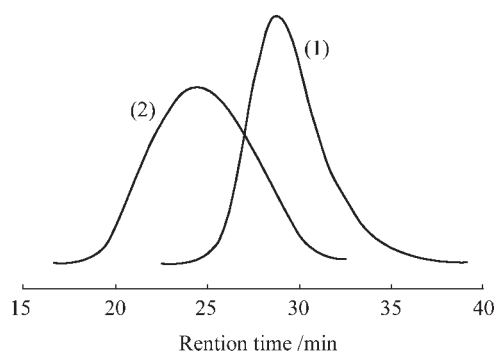

Figure 2 GPC curves of (1) PSt (M_n = 10,600 and PDI = 1.185) and (2) P(St-*b*-Am) (M_n = 22,840 and PDI = 1.480) after the removal of O-MMT.
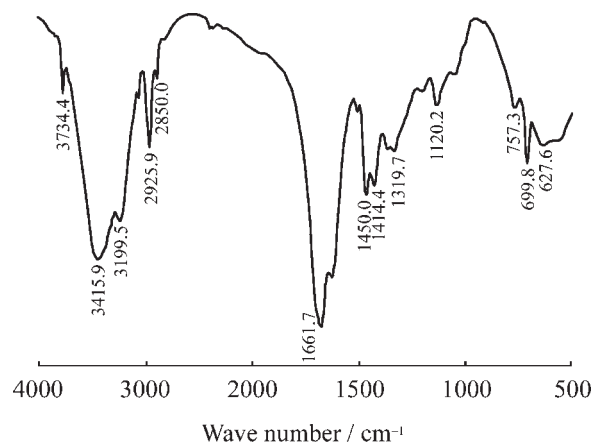

Figure 3 FTIR spectrum of the P(St-*b*-Am)/O-MMT nanocomposite.

FTIR analysis

The IR spectrum of the P(St-*b*-Am)/O-MMT nanocomposite is shown in Figure 3. As shown in Figure 3, the peak located at 3734.4 cm^{-1} was the stretch vibration absorption peak of —OH in O-MMT, and the peak located at 3415.9 cm^{-1} was the stretch vibration absorption peak of C—H in the naphthalene ring. Figure 3 shows the characteristic peaks of the St fragment, including the absorption peak of the benzene ring at 1450.0 cm^{-1} and the characteristic peak of monosubstituted benzene at 699.8 cm^{-1}. In addition, the peaks located at 3199.5 and 1661.7 cm^{-1} were the characteristic absorption peaks of the carboxamide bond. All of these peaks demonstrated that St and Am fragments coexisted in the P(St-*b*-Am)/O-MMT nanocomposites. Because the product was fully extracted with toluene, the P(St-*b*-Am)/O-MMT nanocomposites did not contain homopolystyrene. Associated with the GPC measurement, the PSt polymers linked to the PAm fragments and converted to the block polymers.

XRD characterization

Na-MMT could not be homogeneously dispersed in St because of its hydrophilic properties, and it was difficult for Na-MMT and St to directly perform the intercalative polymerization. After modification with CTAC, the interlayer distance of O-MMT increased. Covered with the organic cations on the surface of the layers, MMT's characteristics were from hydrophilic to hydrophobic. Thus, the St monomer molecules could move into the interlayers of O-MMT and carry out *in situ* polymerization under the initiator. The XRD patterns of the different materials are shown in Figure 4.

During the polymerization of PSt/O-MMT, St monomers inserted themselves into the interlayers of O-MMT and polymerized within the interlayers
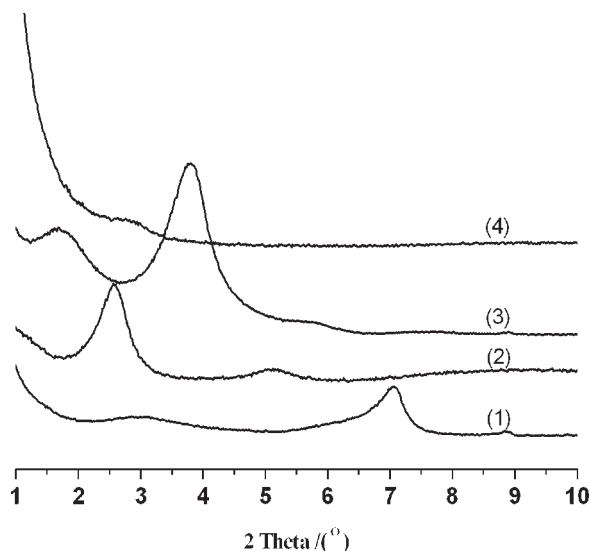
Figure 4 XRD patterns of Na-MMT, O-MMT, PSt/O-MMT, and P(St-*b*-Am)/O-MMT: (1) Na-MMT, $d_{001} = 1.25$ nm; (2) O-MMT, $d_{001} = 2.33$ nm; (3) PSt/O-MMT, $d_{001} = 3.45$ nm; and (4) P(St-*b*-Am)/O-MMT.

under the initiator. As a result, the interlayer distance of O-MMT further increased. Through the addition of AM of the predicted concentration and the use of PSt/O-MMT as the macro chain-transfer agent, the P(St-*b*-Am)/O-MMT nanocomposite was
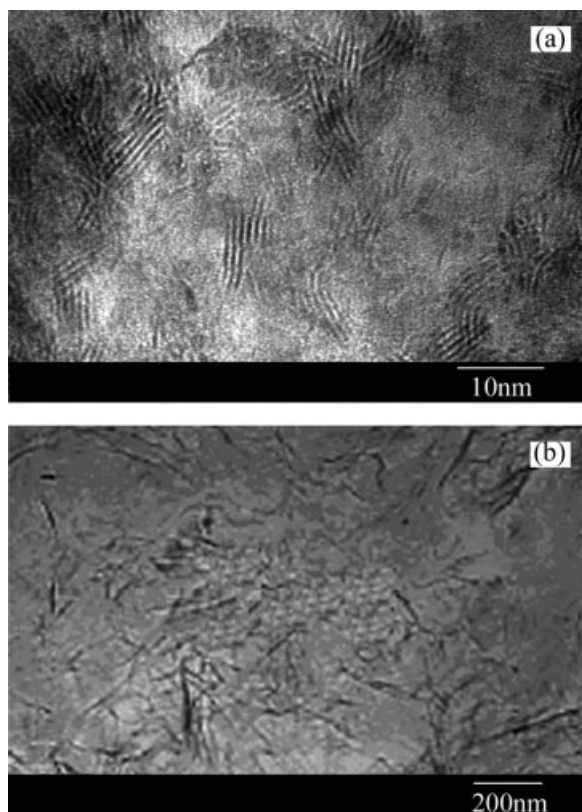
prepared. By XRD, no obvious diffraction peak was detected in P(St-*b*-Am)/O-MMT. The result indicates that the layers of MMT were completely exfoliated and the nanocomposites were formed.[22]

TEM characterization

TEM images of the PSt/O-MMT and P(St-*b*-Am)/O-MMT nanocomposites are shown in Figure 5. The dark stripes in Figure 5 are the cross sections of the MMT layers.

The TEM images of PSt/O-MMT and P(St-*b*-Am)/O-MMT confirmed the good dispersion of the MMT layers in the polymer matrix. Compared with O-MMT, the distance of MMT layers in PSt/O-MMT further increased, and PSt/O-MMT belonged to the intercalative nanocomposite. Although the MMT layers were completely exfoliated in P(St-*b*-Am)/O-MMT and the nanosize layers of MMT were dispersed in the block polymer matrix, P(St-*b*-Am)/O-MMT belonged to the exfoliative nanocomposite. In the preparation process of the P(St-*b*-Am)/O-MMT nanocomposites via RAFT, the monomers performed the *in situ* polymerization between the layers of O-MMT. The O-MMT layers were homogenized into the polymer matrix, and the mixture components could not be separated from each other because of the surface effect and quantum-size effect of the nanosize MMT layers. So, the nanocomposites were completely different from the mixture obtained by the simple mixing of P(St-*b*-Am) and O-MMT.

TGA

Although O-MMT was not added and the other conditions were same as that of P(St-*b*-Am)/O-MMT during the polymerization, P(St-*b*-Am), an amphiphilic block polymer, was also synthesized by RAFT. Subsequently, the thermal properties of P(St-*b*-Am)
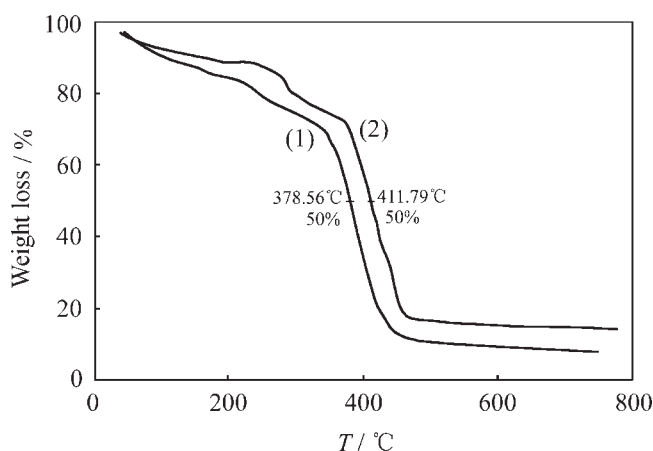

Figure 5 TEM images of (a) PSt/O-MMT and (b) P(St-*b*-Am)/O-MMT.

Figure 6 TGA curves of (1) P(St-*b*-Am) and (2) P(St-*b*-Am)/O-MMT.

and P(St-*b*-Am) were examined through TGA (Fig. 6). The temperatures at which P(St-*b*-Am) and P(St-*b*-Am)/O-MMT lost 50% of their weight were 378.56 and 411.79°C, respectively. The results indicate that the P(St-*b*-Am)/O-MMT nanocomposites had better thermal stability than the corresponding P(St-*b*-Am) (with no O-MMT present).

CONCLUSIONS

RAFT polymerization in the presence of O-MMT was shown to be a successful method for preparing silicate nanocomposites. As for PSt/O-MMT, RAFT polymerization could control the molecular weight and the molecular weight distribution of PSt. The obtained PSt/O-MMT was successfully used as a macro RAFT agent to conduct the polymerization of AM, and P(St-*b*-Am)/O-MMT nanocomposites were prepared. Nanosize layers of MMT were dispersed in the block polymer matrix, and the exfoliative nanocomposites were formed. Therefore, the P(St-*b*-Am)/O-MMT nanocomposites had a better heat stability than before.

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