Chem. Mater. **2003,** *15,* 2693−2695 2693

Preparation of Poly(styrene-*block*-butyl acrylate) Block Copolymer−Silicate Nanocomposites

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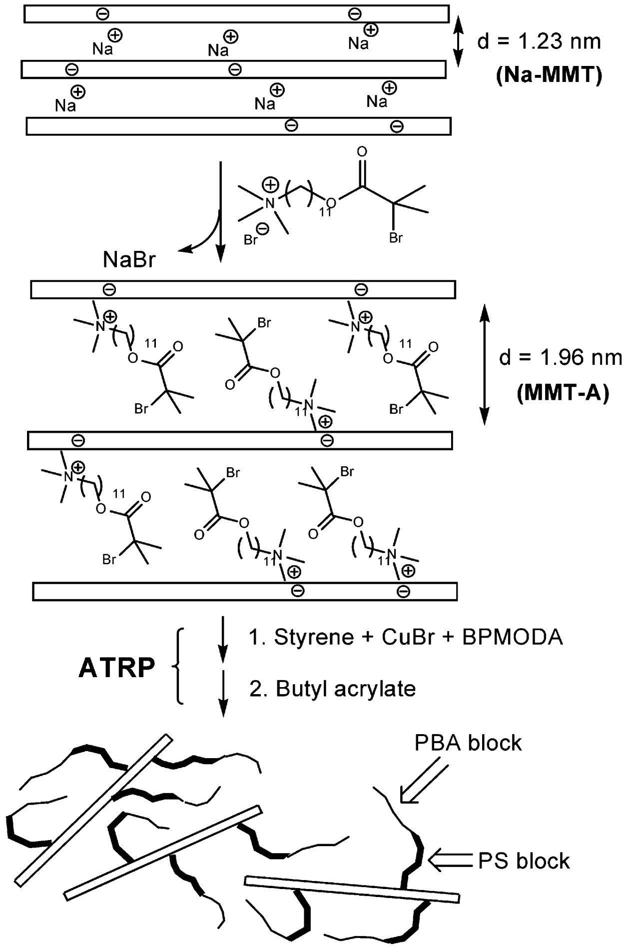
Received January 16, 2003
Revised Manuscript Received June 3, 2003

The publication of Toyota's pioneering work on polymer−silicate (or clay) nanocomposites a decade ago[1] has generated great interest in the materials science community.[2,3] By introducing a few weight percent of clay into the polymer matrix, these nanocomposites exhibit significant increases in many properties, such as mechanical properties,[4] thermal stability,[5] and flame retardance.[6] Of the methods used in the preparation of polymer−silicate nanocomposites,[7] in situ polymerization offers the ability to impart significant control over both the polymer architecture and the final structure of the composite. Various polymerization techniques have been used in the preparation of polymer−silicate nanocomposites in this manner.[8−13]

Recently, we reported[14] the first synthesis of polystyrene, poly(butyl acrylate), and poly(styrene-*block*-butyl acrylate) block copolymer−silicate nanocomposites by in situ ATRP, a polymerization method that exhibits living characteristics.[15] Furthermore, for the first time we demonstrated that block copolymer synthesis was also feasible. In this paper we report the synthesis and characterization of a poly(styrene-*block*-butyl acrylate) (PSBA) block copolymer−clay nanocomposite by in situ ATRP (Scheme 1). This type of block copolymer contains soft (BA) and hard (PS) blocks and has potential applications as elastomeric and adhesive materials.

Scheme 1



Although many polymer−silicate nanocomposites have been produced using various techniques, there are very few literature examples of block copolymer−silicate nanocomposites that have been made or studied.[16] The few examples are restricted to nanocomposites made via melt or solution intercalation only. It is also expected that nanocomposites made from in situ block copolymerization will give significantly different morphologies and material properties compared with their counter-

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10.1021/cm034013y CCC: $25.00

Table 1. Molecular Weight and Polydispersity Data of Block Copolymers

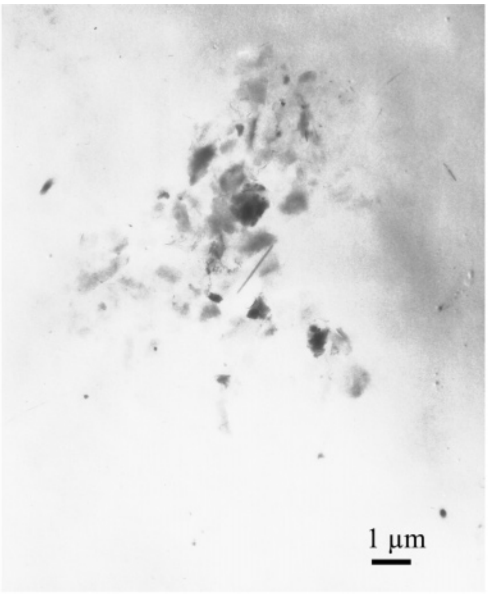
	PS macroinitiator		block copolymer	
sample	M_n	M_w/M_n	M_n	M_w/M_n
PSBA1	21280	1.32	56680	1.38
PSBA2	26160	1.31	39570	1.15

parts made from melt or solution intercalation since in situ polymerization from an initiator attached to silicate layers is expected to be more akin to polymer brushes at a surface (e.g., Scheme 1).

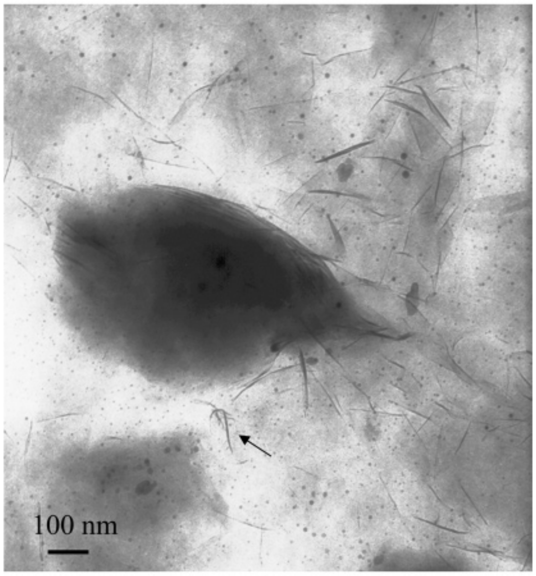
11′-(*N*,*N*,*N*-Trimethylammonium bromide)-undecyl-2-bromo-2-methyl propionate[14] was intercalated into the individual layers of the Na^+−montmorillonite clay (MMT; Southern Clay Products) by stirring MMT and the initiator in acetone. The intercalation was evident from the increase in interlayer spacing from $d_{001} = 1.23$ nm for the unmodified clay to $d_{001} = 1.96$ nm for the intercalated clay (**MMT-A**), as measured by XRD.[17] The TGA result revealed that 21.4 wt % of **MMT-A** is the alkylammonium initiator.[17] ATRP of styrene initiated by **MMT-A** was carried out at 110 °C in a N_2 atmosphere. Cu(I)Br complexed by the ligand *N*,*N*-bis(2-pyridiylmethyl)octadecylamine (BPMODA)[18] was used as the transition metal catalyst. After the polymerization of the PS block, the unreacted monomer was removed by applying a vacuum. ATRP was restarted at 70 °C after PS was dissolved in the BA monomer (Scheme 1).

Molecular weights were measured by gel permeation chromatography (GPC) after the polymer chains were cleaved from the silicate layers by refluxing in THF/methanol solution (80/20, v/v) of LiBr. The molecular weight and polydispersity data of two PSBA block copolymers and their corresponding PS blocks are listed in Table 1. The d_{001} diffraction peak on XRD spectra of the PSBA2/clay nanocomposite disappeared,[17] potentially indicating that much of the layered structure in the clay particles was destroyed by in situ block copolymerization. However, a caveat is that the low clay content and low 2θ values limit XRD analysis in terms of providing definitive proof or quantitative measurement of exfoliation.[19]

TEM images of the PSBA2/clay nanocomposite are shown in Figure 1. Figure 1a shows a large view at a low magnification, permitting the observation of the dispersion of the clay in the polymer matrix. It can be seen that although most of the clay is dispersed in the polymer matrix, some clay-rich areas with a diameter of a few hundreds of nanometers can be observed. This means that the polymerization conditions were not sufficient to destroy all of the layered structure and did not achieve a completely homogeneous dispersion of individual silicate platelets. At high magnification, the TEM image (Figure 1b) reveals both very thin isolated clay layers (indicated by an arrow) and parallel clay layers on the edge of the clay particles, indicating that a mixture of exfoliated and intercalated structures have been produced in the nanocomposite.



(a)



(b)

Figure 1. TEM images of PSBA2/clay nanocomposites at low (a) and high (b) magnification.

Figure 2 is a TEM picture of PSBA2/clay nanocomposite stained by hydrazine and osmium tetraoxide.[20] The dark dots in the picture represent PBA phases in the exfoliated clay layers. The diameter of the PBA phases is in the range from 2 to 5 nm, which is smaller than the size of the microphase of the pure (unattached) block copolymer (≈40 nm). It is well-known that diblock copolymer chains are driven to organize into regularly structured microdomains.[21] However, in the PSBA/clay nanocomposites the block copolymer chains are immobilized on the surface of clay platelets (similar to polymer brushes[22]), thus limiting the assembly of the polymer chains. Therefore, the sizes of the polymer

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[17] See Supporting Information.

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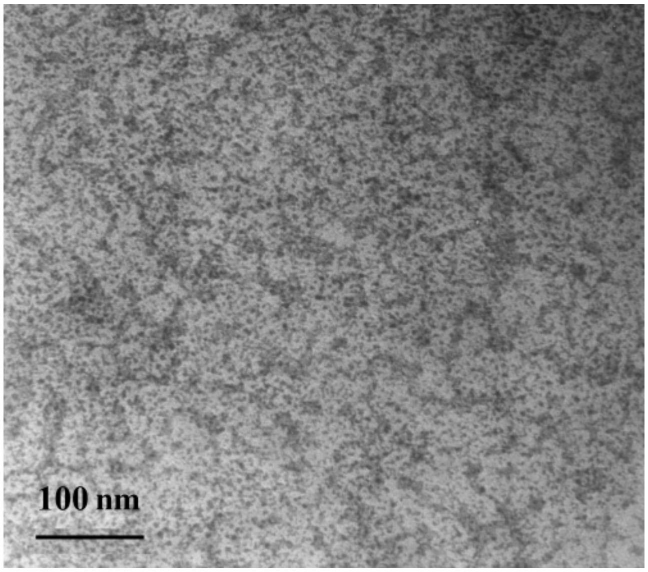

Figure 2. TEM image of PSBA2/clay nanocomposites stained by hydrazine and osmium tetraoxide.

domains organized in this way are expected to be much smaller than that of the phases created by untethered block copolymer chains.

Figure 3 shows differential scanning calorimetry (DSC) traces of pure PSBA2 block copolymer and PSBA2/clay nanocomposite.[23] For the free block copolymer (i.e., having been detached from the clay), two glass transitions can be detected at about −40 and 93 °C corresponding to the transitions of the PBA and PS segments, respectively. For the nanocomposite, the PBA block exhibits a glass transition at −40 °C and in the region of 93 °C there is a shallow hump. Giannelis et al. reported that intercalated PS−organosilicates do not show the characteristic bulk glass transition for PS.[24] In the PSBA/clay nanocomposites studied here, XRD and TEM results indicate that exfoliated structures dominate. In this case, the PS blocks are linked to the clay plates, limiting the movement of the PS segments and thus increasing the glass transition temperature of the PS. The small hump at 93 °C may be due to minor amounts of untethered PS generated from thermal initiation of styrene. Compared with the confined PS segments, the movements of PBA segments are relatively free so they show a characteristic glass transition.

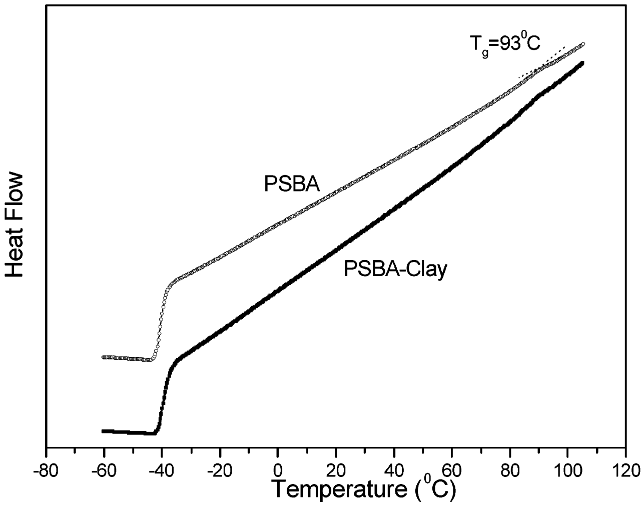

Figure 3. DSC traces of PSBA2 block copolymer and PSBA2/clay nanocomposite.

In summary, PSBA−silicate nanocomposites were synthesized and mixtures of exfoliated and intercalated structures were observed. The PBA segments form microdomains with an average size of 2−5 nm.

Acknowledgment. We thank the Center for Advanced Materials Processing at Clarkson University, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. We also thank Brendan Farrell for technical assistance.

Supporting Information Available: XRD spectra and TGA thermograms of the unmodified and initiator-modified MMT, along with the XRD spectra of a polymer−silicate nanocomposite (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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