

# Ordered Multilayer Nanocomposites Prepared by Electrostatic Layer-by-Layer Assembly between Aluminosilicate Nanoplatelets and Substituted Ionic Polyacetylenes

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Received April 12, 2002. Revised Manuscript Received June 17, 2002

Ordered multilayer nanocomposites have been prepared by electrostatic layer-by-layer assembly between exfoliated aluminosilicate nanoplatelets and substituted ionic polyacetylenes. Aluminosilicate saponite particles were exfoliated by means of extensive shaking and sonication of their water suspension. Atomic force microscopy and transmission electron microscopy data suggest that the exfoliated platelets have the shape of ultrathin disks with an average width of  $170 \pm 30$  nm. Conjugated ionic polyacetylene poly(*N*-octadecyl-2-ethynylpyridinium bromide) (PEPy-C18) was synthesized by spontaneous polymerization of 2-ethynylpyridine quaternized with 1-bromooctadecane. Linear build-up of multilayer nanocomposites between the exfoliated saponite particles and substituted ionic polyacetylenes was monitored by UV–vis absorption spectroscopy. AFM surface topography of the resulting films indicates that the saponite platelets cover the entire surface of the underlying layers. TEM cross-sectional images of such films show that the saponite platelets are aligned parallel to the film surface to form ordered layers. Polarized UV–vis absorption spectroscopy suggests that the polyacetylene chains are oriented parallel to the surface of the saponite layers.

## Introduction

Electrostatic layer-by-layer deposition using polyelectrolyte templates has evolved as one of the simplest and most cost-effective methods for thin film preparation of charged materials on solid supports.<sup>1–6</sup> The principle of electrostatic multilayer assembly is based on the spontaneous adsorption of oppositely charged polyelectrolytes from their dilute solutions and is specially suitable for the production of high-quality films with a defined composition in the nanometer range. It has been also successfully applied to the preparation of multilayer films of polyelectrolytes with other materials such as

proteins,<sup>7</sup> graphite oxides,<sup>8</sup> gold colloids,<sup>9</sup> dyes,<sup>10</sup> and nanoparticles.<sup>11</sup> Compared to the distinct ordering in Langmuir–Blodgett films, however, the layer-by-layer assembly technique is often limited by extensive interpenetration between neighboring polyelectrolyte layers, leading to disruption of internal ordering in the films.<sup>1,12,13</sup>

Smectite-type aluminosilicates such as montmorillonite and saponite are characterized by their lamellar structure and can be broken down into 1-nm-thick layers through exfoliation. The resulting aluminosilicate platelets with a strong negative charge on the surface have been used to prepare multilayer nanocomposites via layer-by-layer assembly with several polycations.<sup>14–24</sup>

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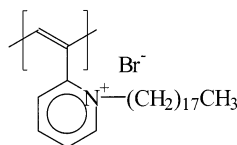
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**Figure 1.** The chemical structure of poly(*N*-octadecyl-2-ethynylpyridinium bromide) (PEPy-C18).

The high surface area of the platelets may help to eliminate interpenetration of polyelectrolytes between neighboring layers and also minimize packing defects from underlying layers. This can lead to ultrathin nanocomposite films with an internal structural order.

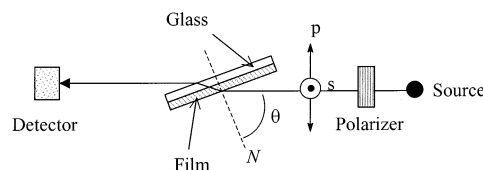
In a recent paper, Zhou and Blumstein had reported on the synthesis and characterization of conjugated ionic poly(*N*-octadecyl-2-ethynylpyridinium bromide) (Figure 1) with a long alkyl chain attached to the quaternized nitrogen with a tendency to orient at the interface.<sup>25</sup> It was prepared by quaternization of the pyridine ring of 2-ethynylpyridine with octadecyl bromide.

In this work we have prepared multilayer nanocomposites by electrostatic layer-by-layer assembly of exfoliated saponite particles and substituted ionic polyacetylenes. We have studied the structural order of the resulting multilayer films by AFM and TEM techniques. In addition, the orientation of polyacetylene chains on the surface of saponite layers in the multilayer nanocomposite films were studied by polarized UV-vis absorption spectroscopy. Such studies are of interest, because it appears that the resulting layered nanostructures may combine properties of both the organic and inorganic components, which could lead to nanofilms with high conductivity anisotropy and selective gas barrier properties.<sup>26–29</sup>

## Experimental Section

**Materials.** Saponite was provided by Source Clay Minerals Repository, University of Missouri. 2-Ethynylpyridine was purchased from GFS Chemicals and vacuum distilled before use. 1-Bromooctadecane, cellulose acetate, and poly(sodium 4-styrenesulfonate) were purchased from Aldrich and used as received. All other solvents and chemicals are analytical grade and used as received.

**Preparation of Exfoliated Saponite Platelets.** Saponite particles were dispersed in deionized water at a concentration of 0.2 wt %. The dispersion was shaken for 1 day, sonicated



**Figure 2.** Schematic illustration of the setup for polarized absorption spectroscopy (top view). Incidence angle  $\theta$  is about  $80^\circ$ .  $N$  is normal to the film surface.

for 4–6 h, and then shaken again for an additional 12–24 h. After the larger unexfoliated particles (or aggregates) were separated by centrifuge, the resulting clear supernatant was used for the multilayer build-up. The concentration of exfoliated platelets in the water suspension was determined by measuring the residual solid content. Exfoliated saponite particles were suspended in water at a concentration of 0.14 wt %. They were deposited on a carbon-covered copper grid and their shape and size were observed by transmission electron microscopy.

**Synthesis of Poly(*N*-octadecyl-2-ethynylpyridinium bromide) (PEPy-C18).** Poly(*N*-octadecyl-2-ethynylpyridinium bromide) (PEPy-C18) with a long alkyl chain attached to the quaternized nitrogen in the pyridine ring was prepared by spontaneous polymerization of 2-ethynylpyridine quaternized with 1-bromooctadecane as described.<sup>25</sup> The structure of PEPy-C18 is depicted in Figure 1.

**Multilayer Nanocomposite Films via Layer-by-Layer Deposition.** All glass substrates were dipped in Chem-solv solution (aqueous alkaline alcohol) under sonication.<sup>23</sup> The substrates were then rinsed several times with deionized water. The procedure was used to hydrophilize the substrate and charge it negatively for subsequent polycation adsorption. Multilayer nanocomposite films were obtained by a layer-by-layer deposition method. Substituted ionic polyacetylenes were dissolved in methanol (typically 0.1 wt %) and were used for build-up of polycation layers. The aqueous suspension of exfoliated saponite particles was used for the polyanion build-up. The overall process of layer-by-layer deposition consisted of a cyclic repetition of the following steps: (1) dipping the substrate into the polyacetylene solution for 1 min, (2) rinsing with methanol and drying under a stream of dry nitrogen, (3) dipping into an aqueous dispersion of the exfoliated saponite platelets for 1 min, and (4) final rinsing with deionized water and drying under dry nitrogen. The build-up of multilayered films was monitored by UV-vis absorption spectroscopy.

Ultrathin free-standing nanocomposite films were also obtained by layer-by-layer assembly as described in the literature.<sup>30</sup> Exfoliated saponite particles and PEPy-C18 were alternately deposited on glass coated with cellulose acetate, and the cellulose acetate substrate was then dissolved in acetone in order to peel the nanocomposite films off the glass. To obtain TEM images of cross sections of the films, the free-standing film embedded in epoxy resin was microtomed into ultrathin slices and then deposited on a carbon-covered 200-mesh copper grids.

**Characterization and Measurement.** UV-vis absorption spectra were taken by means of a Perkin-Elmer Lambda 9 spectrophotometer. Polarized absorption spectra were recorded by shining polarized light with the electric field vector parallel (*p*-polarization) or perpendicular (*s*-polarization) to the plane of incidence at an incidence angle  $\theta = 80^\circ$  (Figure 2). Bright-field TEM images were obtained on samples prepared on carbon-covered 200-mesh copper grids, using a Philips EM400T (operating at 120 kV) equipped with Noran instrument energy-dispersive X-ray spectrometer (EDXS). Surface topography of the nanocomposite films was investigated by an atomic force microscope (Park Scientific, CA) operated in the contact mode using a standard silicon nitride cantilever (force constant 0.10 N/m, resonance frequency 38 kHz) in ambient air. The scan rate is 0.5–1.0 Hz and the set point is 25 nN. The samples for

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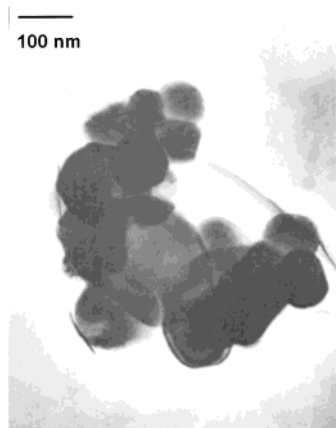
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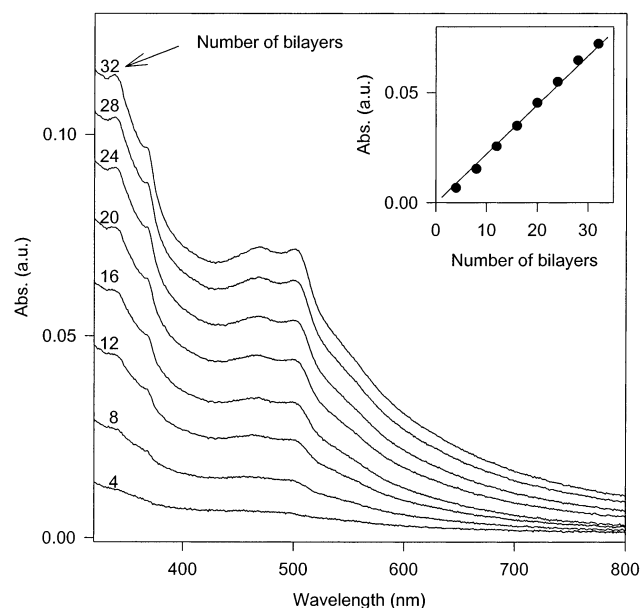
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**Figure 3.** TEM image of the exfoliated saponite particles deposited on a carbon-covered copper grid.



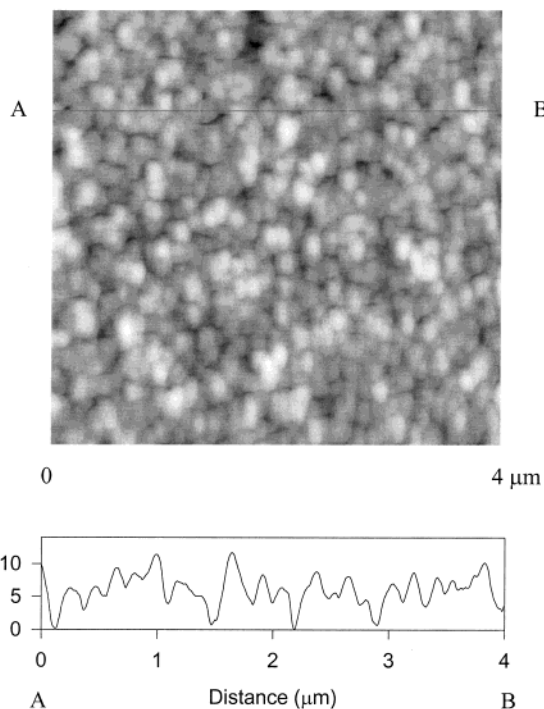
**Figure 4.** UV-vis absorption spectra of multilayered nanocomposite films of exfoliated saponite nanoplatelets and PEPy-C18 as a function of the number of deposition cycles.

AFM were prepared on silicon substrates by electrostatic layer-by-layer deposition method.

### Results and Discussion

Figure 3 gives a TEM image of exfoliated platelets and of platelets partially aggregated during the process of sample preparation. Multilayers of exfoliated saponite nanoparticles and conjugated ionic polyacetylene PEPy-C18 were deposited onto glass substrates alternately from a dilute saponite suspension and a polymer solution. UV-vis absorption spectroscopy was used to monitor the consecutive build-up of the oppositely charged species. The absorption pattern due to polycation layers of PEPy-C18 is characterized by two absorption peaks at 471 and 502 nm (Figure 4). The inset shows that the intensity of the absorption increases linearly as a function of deposition cycles. This indicates that the sequential assembly between the saponite particles and polyacetylenes is linear with the deposition cycles. It is also reproducible.

AFM surface topography shows a uniform deposition of saponite nanoplatelets. Figure 5 gives an AFM image



**Figure 5.** AFM image of the exfoliated saponite nanoplatelets deposited on the layer of PEPy-C18. The cross-sectional image was taken along the line A-B.

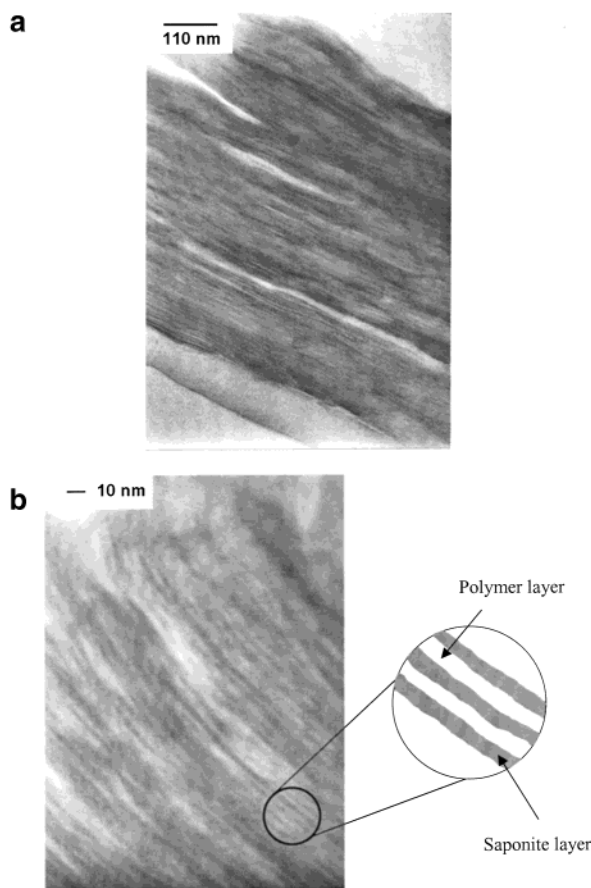
of saponite particles deposited by electrostatic assembly on a positively charged layer of PEPy-C18. It indicates that the saponite platelets cover the entire surface of the underlying polymer layer. The cross-sectional AFM image suggests that the individual saponite platelets are lying "flat" on the surface. From AFM observation it follows that these exfoliated platelets have a shape of disks with an average width of  $170 \pm 30$  nm. The average height (thickness) of the individual saponite particles is estimated to be approximately 3–6 nm (cross-sectional AFM image). It is also noted that these particles have a relatively regular shape, which is essential for preparing well-organized structures.

The above results are in good agreement with TEM observations, which can provide more details concerning the morphology of the nanocomplexes.

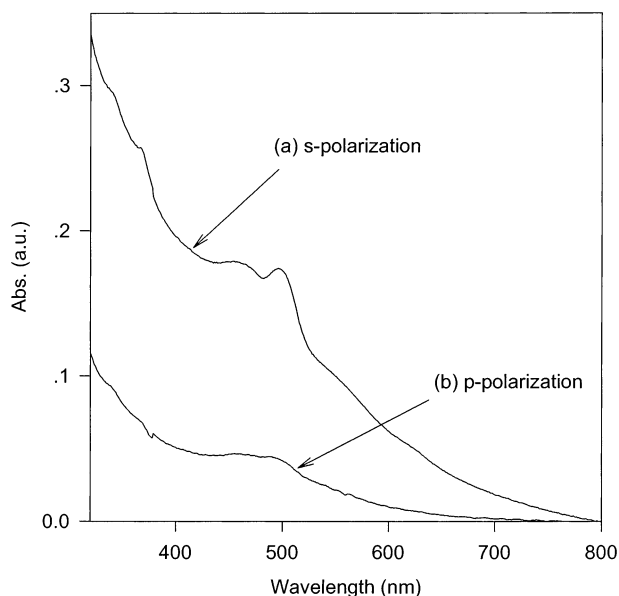
It can be seen from cross-sectional images of the free-standing film of layer-by-layer assembled nanocomposites that AFM images are real and not a possible artifact of a defective AFM tip. Figure 6 shows that alternating black and white narrow bands span along the whole cross-section of the film. The dark lines (parallel to the film surface) are due to layers of saponite platelets, while the bright ones being due to polyacetylene layers. Ultrathin aluminosilicate platelets with their large aspect ratio appear to be oriented parallel to the film surface. Both kinds of alternating layers are of a uniform thickness of 2–3 nm. Such aligned and ordered saponite layers confining polymer molecules would minimize their interpenetration, as is qualitatively shown by TEM observation.

Polarized absorption spectroscopy was also used to assess the orientation of PEPy-C18 polymer molecules on ordered saponite layers. Figure 7 shows the polarized absorption spectra of PEPy-C18/saponite 32-bilayer films. The relatively large difference in optical absorp-



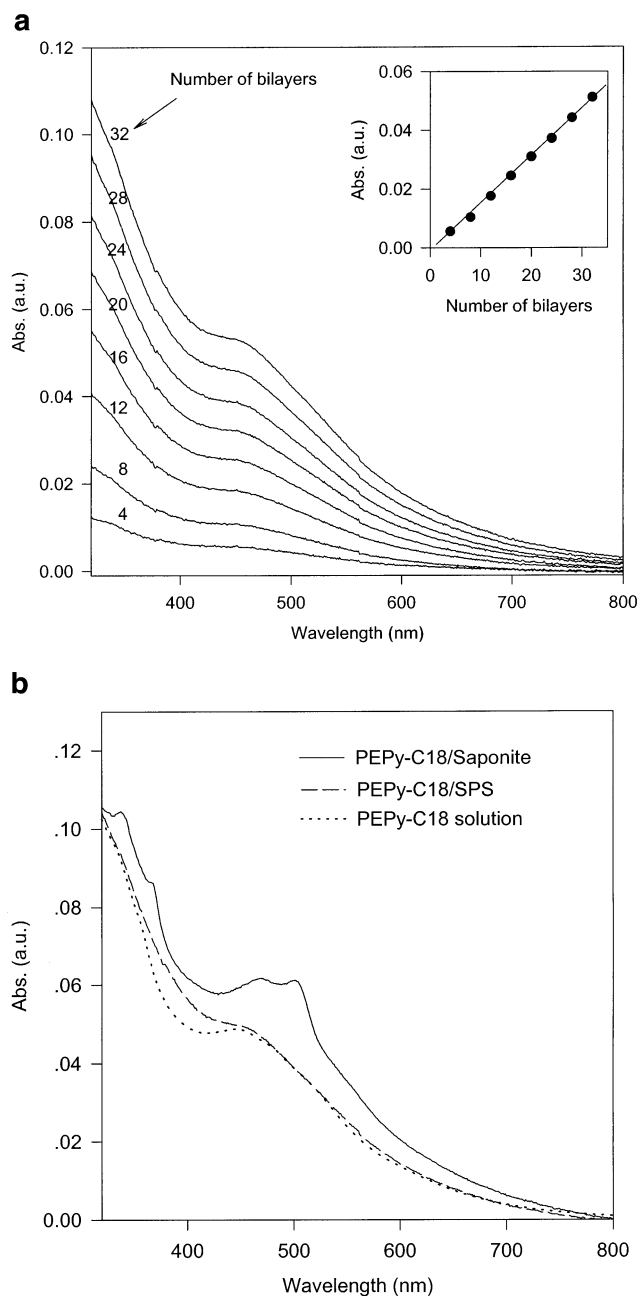


**Figure 6.** Bright-field transmission electron micrographs of the cross sections of free-standing nanocomposite films of saponite nanoplatelets and PEPy-C18 (65-bilayer film): (a) low magnification and (b) high magnification. In the process of embedding the free-standing films in epoxy resin for TEM study, the thin films were folded together. The black arrows indicate the gap between the folded neighboring films in part a.



**Figure 7.** Polarized absorption spectra of PEPy-C18/saponite 32-bilayer films obtained by irradiating (a) s-polarized light and (b) p-polarized light (incidence angle  $\theta = 80^\circ$ ).

tion with the direction of polarization of the incident light reveals the molecular orientation of polymer



**Figure 8.** (a) UV-vis absorption spectrum of multilayered films of sulfonated polystyrene (SPS) and PEPy-C18 as a function of the number of deposition cycles. (b) UV-vis absorption spectra of PEPy-C18/SPS 32-bilayer film, PEPy-C18/Saponite 32-bilayer film, and PEPy-C18 solution in methanol.

chains. The absorption peaks at 471 and 502 nm are much more intense when observed in s-polarized light than in p-polarized light. This suggests that the polymer chains are oriented parallel to the plane of film.<sup>31,32</sup>

Figure 8 compares the linear UV-vis absorption spectra of multilayer films of PEPy-C18 and poly(sodium 4-styrenesulfonate) (SPS). In Figure 8b the spectra of 32-bilayer films of PEPy-C18 on saponite and SPS are compared. The spectrum of a solution of PEPy-C18 in methanol is also given. While the PEPy-C18

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solution or PEPy-C18/SPS films have an absorption peak at 450 nm, the PEPy-C18/saponite nanocomposite films have red-shifted peaks at 471 and 502 nm. Such bathochromic shift of the absorption maximum of conjugated polymers could be mainly due to an increase in the effective conjugation length or due to an increased  $\pi$ - $\pi$  contact ( $\pi$ -stacking) between the double bonds of neighboring conjugated polymer chains as a result of chain orientation.<sup>33,34</sup> The average molecular weight of the PEPy-C18 is approximately 3500, corresponding to eight monomer units (vapor pressure osmometry). This value is in agreement with the average conjugation length estimated from the UV-vis absorption maximum in methanol solution.<sup>25,35</sup> There is no reason for the polymer to increase its degree of polymerization on adsorption on the saponite layers. Since orientation of PEPy-C18 polymer molecules on the flat surface of ordered saponite layers may increase the number of  $\pi$ -stackings between the neighboring conjugated polymer chains, the appearance of the bathochromic shift points toward increased  $\pi$ - $\pi$  interaction. This may result in the red shift of the absorption maximum in the PEPy-C18/saponite films.

In case of the PEPy-C18/SPS films, polyacetylene molecules seem not to be oriented on the surface of the

SPS layers, because the SPS polymer chains are coiled. The absorption spectrum of the PEPy-C18/SPS films is virtually the same as the absorption spectrum of PEPy-C18 solution. This indicates that the conformation of PEPy-C18 polymer molecules on the surface of the SPS layers is random.

## Conclusion

Stratified nanocomposite films with structural order have been prepared by electrostatic layer-by-layer assembly of exfoliated saponite nanoplatelets and conjugated ionic polyacetylenes. Ultrathin disks of saponite nanoplatelets due to their high aspect ratio were highly aligned parallel to the film surface. Such aligned and ordered saponite layers confine polymer molecules and minimize their interpenetration, leading to internal ordering in the film. Upon adsorption on the saponite layers the conjugated polymer molecules orient parallel to the plane of the film with enhanced  $\pi$ - $\pi$  contacts between the neighboring conjugated polymer chains.

**Acknowledgment.** We acknowledge the financial support of US Army Natick Contracting Division (#DAAD16-01-C-0011). Thanks are expressed to Prof. D. Sandman for useful discussions.

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