



Hydrophobic barrier: Molecular self-assembly of amphiphilic polyacetylenes within aluminosilicate nanoplatelets

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Abstract

In this paper, we describe nano-assembly of amphiphilic polyelectrolytes within aluminosilicate nanoplates by layer-by-layer deposition and demonstrate how the resulting films are capable of functioning as hydrophobic barrier. The polyelectrolytes with a rigid backbone and long alkyl substitutes organized within the inorganic nanosheets, to form a double layer of interdigitated alkyl substitutes. The resulting 100 nm-thick hydrophobic barriers efficiently blocked transport of moisture and hence enhanced the water vapor barrier properties of a relatively thick substrate (Nafion membrane, ca. 50 μm) up to 22 times.

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Keywords: Layer-by-layer assembly; Amphiphilic polyelectrolytes; Hydrophobic barrier; Water vapor diffusion resistance

1. Introduction

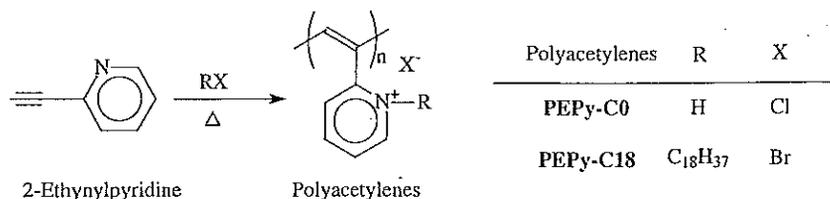
The barrier properties of packaging films are often crucial for particular applications. For example, the packaging for food or electronic devices must be impermeable to moisture and oxygen. Hence there is a strong need for barrier coatings that can be prepared by a cost-effective method and provide exceptional barrier properties.

Layer-by-layer assembly via electrostatic interaction is a cost-effective and versatile method for the fabrication of functional thin films [1–4] and hence is very promising for the barrier coatings [5]. The principle of electrostatic multilayer assembly is based on the spontaneous adsorption of oppositely charged polyelectrolytes from their dilute solutions and is especially suitable for the production of the 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 [6], gold colloids [7], dyes [8] and nanoparticles [9]. However, the intrinsic hydrophilicity of polyelectrolytes hindered their applications in the moisture barrier coating. One of the approaches to overcome such problem is to increase hydrophobicity by using an amphiphilic polyelectrolyte.

In a recent paper, Zhou and Blumstein had reported on the synthesis and characterization of amphiphilic polyelectrolyte poly(*N*-octadecyl-2-ethynylpyridinium bromide) with a long alkyl chain attached to the quarternized nitrogen (Scheme 1) [10,11]. It was prepared in a spontaneous manner by quarternization of the pyridine ring of 2-ethynylpyridine with octadecylbromide.

Aluminosilicates such as montmorillonite and saponite are characterized by their lamellar structure and can be broken down to 1 nm-thick nanosheet through exfoliation. The resulting aluminosilicates platelets with a strong negative charge on the surface have been used to prepare multilayer nanocomposites via layer-by-layer assembly with several polycations. The high surface area of platelets may help to eliminate interpenetration



Scheme 1. Preparation of amphiphilic polyacetylenes.

of polyelectrolytes between neighboring layers and also minimize packing defects from underlying layers. Hence such quasi two-dimensional nanoplatelets allow the formation of ordered ultrathin hybrid films with dimensional integrity and are considered promising particularly for the barrier applications [12–17].

In this work, we prepared nano-assembly of amphiphilic polyelectrolytes within aluminosilicate nanoplates by layer-by-layer deposition and demonstrated how the resulting films were capable of functioning as hydrophobic barrier. The polyelectrolytes with a rigid backbone and long alkyl substitutes organized within the inorganic nanosheets, to form a double layer of interdigitated alkyl substitutes. The resulting 100 nm-thick hydrophobic barriers efficiently blocked transport of moisture and hence enhanced the water vapor barrier properties of a relatively thick substrate (Nafion substrate, ca. 50 μm) up to 22 times.

2. Experimental

2.1. Materials

Saponite (cation exchange capacity: 0.80 mequiv/g) was supplied by Source Clay Minerals Repository, University of Missouri. 2-Ethynylpyridine was purchased from GFS Chemicals and vacuum distilled before use. 1-Bromooctadecane and Nafion perfluorinated membrane (Nafion 112, 50 μm thick) were purchased from Aldrich. All other solvents and chemicals are analytical grade and used as received.

2.2. Synthesis of poly(*N*-octadecyl-2-ethynylpyridinium bromide) (PEPy-C18)

Poly(*N*-octadecyl-2-ethynylpyridinium bromide) with a long alkyl chain attached to the quaternized nitrogen in the pyridine ring were prepared by spontaneous polymerization of 2-ethynylpyridine quaternized with 1-bromooctadecane as described in the previous work [10,11]. The structure of PEPy-C18 is depicted in Scheme 1.

2.3. Synthesis of poly(ethynylpyridinium chloride) (PEPy-C0) [18]

Concentrated hydrochloric acid (0.71 g, 0.02 mol) was added dropwise to freshly distilled 2-ethynylpyridine (2.06 g, 0.02 mol). (*Caution: An exothermic reaction ensued.*) The reaction mixture acquired a dark color immediately accompanied by a rapid increase in viscosity. The polymer separated out as a black solid mass. It was washed with diethylether and dried

in vacuum at 40 °C. The dry polymer, poly(ethynylpyridinium chloride) (PEPy-C0) was obtained as a lustrous black powder and its structure is depicted in Scheme 1. The molecular weight of PEPy-C0 was determined by vapor pressure osmometer in chloroform and the value was 1300. The structure of PEPy-C0 is shown in Scheme 1.

2.4. Preparation of exfoliated aluminosilicate nanoplatelets [19]

Saponite particles were dispersed in deionized water at a concentration of 0.2 wt%. The dispersion was shaken for 1 day, sonicated for 4–6 h and then shaken again for 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 their water suspension was determined by measuring the residual solid content. Exfoliated saponite particles were suspended in water at a concentration of 0.14 wt%.

2.5. Multilayer films by layer-by-layer deposition

Multilayer nanocomposite films were obtained by a layer-by-layer deposition method. Amphiphilic polyelectrolytes 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 (glass or Nafion membrane) into the amphiphilic polyelectrolytes solution for 3 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 3 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.

2.6. Characterization and measurement

UV–vis absorption spectra were taken by means of a Perkin-Elmer Lambda 9 spectrophotometer.

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 a Noran instrument energy-dispersive X-ray spectrometer (EDXS).

Surface topography of the nanocomposite films was investigated by an atomic force microscopy (Park Scientific, CA) operated in the contact mode using a standard silicon nitride can-

tilever (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.

XRD measurements were run on a Philips 3 kW X-ray generator and vertical diffractometer utilizing Cu K α radiation. The diffractometer is in the Bragg Breantano type affiliated with a spinner attachment, scintillation detector and graphite monochromator. Samples were scanned at 1° min⁻¹ with counting rates of 500–1000 counts per second.

Thickness of the multilayers was measured by ellipsometer (Rudolph Research AutoEL III) with a 632.8 nm He–Ne laser as a light source. Thickness data were average values obtained from 10 different points on a given sample. The 30-bilayer films of C18 polymer/saponite on the glass substrate was measured 156.1 nm thick. This corresponds to 5.20 nm/bilayer. Hence 10-bilayer C18/saponite film deposited on each side of Nafion substrate was estimated to be ~50 nm thick. This value was in good agreement with the thickness estimated from the cross-sectional TEM image (see Ref. [19]) for the multilayer film.

The water vapor diffusion resistance of the multilayer films deposited on the Nafion membrane was measured by dynamic moisture permeation cell (DMPC). The flow rate was 2 mL/min and the relative humidity was 95% at 30 °C. Detailed experimental set-up and procedures were described in the literature [20].

3. Results and discussion

We prepared an amphiphilic polyelectrolyte, [poly(*N*-octadecyl-2-ethynylpyridinium bromide), PEPy-C18], by spontaneous polymerization of 2-ethynylpyridine in the presence of octadecyl bromide as shown in Scheme 1. Saponite particles were exfoliated into the 1 nm-thick nanosheets by extensive shaking and sonication. Then we deposited alternately the PEPy-C18 polymer and saponite nanosheets on Nafion substrate by layer-by-layer assembly. Linear increase of the absorbance with the number of deposition cycles, which was monitored by UV–vis absorption spectroscopy, indicates a regular and uniform build-up of the multilayer assemblies [19].

The water vapor diffusion resistance of the multilayer assembly was measured by DMPC. Nanocomposite coating with as few as 10 bilayers showed significant improvement (22 times higher) in diffusion resistance than the pristine Nafion substrate (Fig. 1b). Such substantial enhancement of barrier properties is quite exceptional when compared to the Nafion substrate deposited with 10 bilayers of PEPy-C18 and sulfonated polystyrene (SPS). The multilayer coating of PEPy-C18 and SPS achieved only 60% increase of water vapor diffusion resistance (Fig. 1c).

In order to estimate the effect of aluminosilicate itself on the barrier properties, we have also prepared an ionic polyacetylene with no alkyl chains (PEPy-C0, Scheme 1). Then we deposited 10 bilayers of PEPy-C0 and saponite on the Nafion substrate. The 10-bilayer coating enhanced the water vapor diffusion resistance only three times with respect to the pristine Nafion (Fig. 1d). This strongly suggests that saponite itself cannot account for the 22-fold increase in diffusion resistance of the multilayer coating of PEPy-C18 and saponite. Hence the

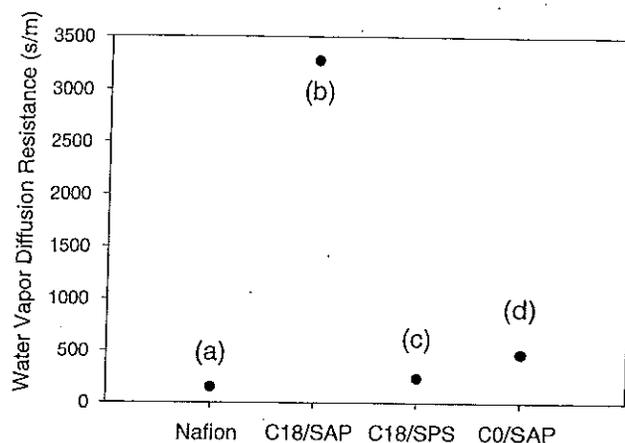


Fig. 1. Water vapor diffusion resistance of (a) pristine Nafion substrate, (b) 10-bilayer film of PEPy-C18 and saponite, (c) 10-bilayer film of PEPy-C18 and sulfonated polystyrene (SPS) and (d) 10-bilayer film of PEPy-C0 and saponite on the Nafion substrate.

PEPy-C18 polymer in conjunction with saponite nanosheets is responsible for the high barrier properties of this multilayered film.

In the previous work [19], AFM and TEM images showed that in the multilayer films of PEPy-C18 and saponite, the inorganic nanosheets displayed a tendency to lie flat on the substrate covering its entire surface. In addition, absorption spectroscopy indicated that the backbone of the polyacetylenes was also oriented parallel to the surface of the film. However, such oriented assembly of the polyacetylenes was not observed in the multilayer films of PEPy-C18 polymer and SPS. Hence such oriented assembly might be responsible for the substantially high barrier properties of the PEPy-C18/saponite multilayer films.

In order to investigate assembly of the amphiphilic polyacetylene within the saponite layers, X-ray diffraction patterns were obtained from the multilayer films of the polyelectrolyte and saponite nanosheets deposited on Si wafer. The thickness of the PEPy-C0 polymer layer between saponite layers was estimated to be 0.6–0.7 nm from the XRD peak in Fig. 2a. Previous report suggested that such polyacetylenes intercalated between aluminosilicate layers adopt a trans-transoidal conformation with the pyridine rings of the side groups tilted with respect to the surface [21]. For such a case, the interlayer spacing was between 0.6 and 0.7 nm, corresponding to the transversal van der Waals dimension of the pyridine ring. Hence XRD data indicates that a single layer of PEPy-C0 polymer was deposited between the saponite layers.

The thickness of the PEPy-C18 polymer layer was estimated from the XRD data to be about 2.4–3.0 nm, which was much larger than PEPy-C0. Such large value can only be explained by a profound conformational change of the inserted PEPy-C18 polymer with respect to the conformation of the PEPy-C0 polymer. Then we can think that hydrophobic interactions of long alkyl chains of the PEPy-C18 polymer may lead to energetically more favorable side chain rearrangement.

Fig. 3 gives a possible model of a double layer of tilted interdigitated side chains of the PEPy-C18 polymer within the saponite layers. Such interdigitated assembly was also observed

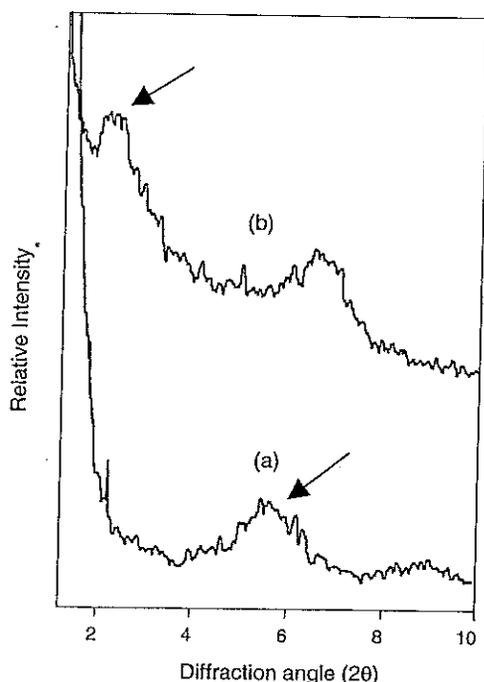


Fig. 2. X-ray diffraction patterns of silicon wafer deposited with 40-bilayer films of (a) PEPy-C0/saponite and (b) PEPy-C18/saponite. The arrows pointed to the XRD peaks due to the interlayer spacing.

in the Langmuir–Blodgett films of PEPy-C18 polymer in our previous report [10,22]. The report has estimated by ellipsometry that height of the double layer was about 3 nm, which was well compatible with the above X-ray data. This model also supports the previous result by polarized absorption spectroscopy that the polyacetylene backbone chains are oriented parallel to the surface of the saponite layers [19].

In fact, the PEPy-C18 polymer possesses a strong tendency for micellisation due to its amphiphilic nature. Fig. 4 shows that the PEPy-C18 polymer aggregates with a relatively uniform domain size are covering the entire surface of mica substrate. The average height of the aggregates is about 2–3 nm which compares well with the XRD data in Fig. 2.

Several literatures have reported deposition of a double layer of amphiphilic molecules on a certain solid substrate when the micelles of the amphiphilic molecules in the solution were adsorbed on the substrate [23]. For example, Messerschmidt et al. reported that the spherical micelles of amphiphilic molecules in the solution was rearranged to a planar double layer with the

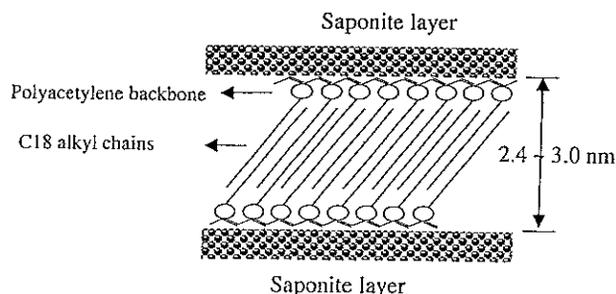


Fig. 3. Plausible model of the molecular assembly of amphiphilic polyacetylene PEPy-C18 between the saponite nanosheets.

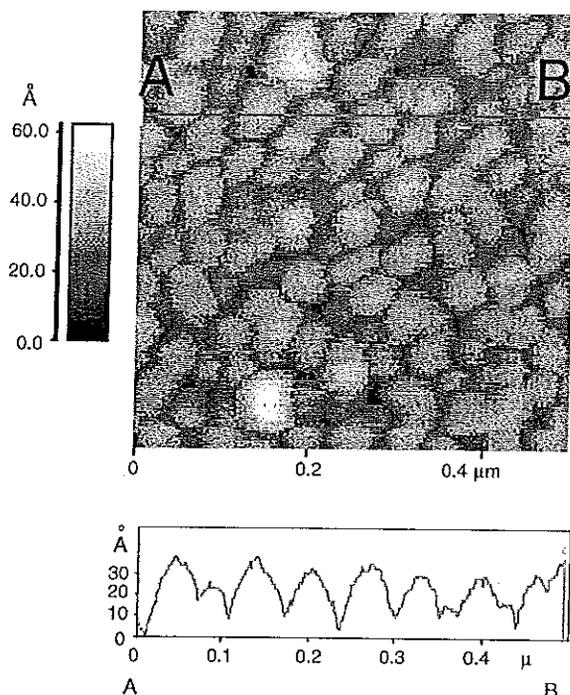


Fig. 4. AFM image of PEPy-C18 polymers deposited on the mica substrate from the methanol solution. The samples for AFM were prepared by dipping the mica substrate into the methanol solution of the PEPy-C18 polymer for 10 s, followed by washing and drying.

alkyl chains interdigitated upon adsorption on the mica substrate [23a].

In a similar way, a double layer of PEPy-C18 polymers with the alkyl chains interdigitated may deposit upon adsorption of the PEPy-C18 polymer micelles on the surface of saponite layers. The hydrophobic interdigitated assembly of the PEPy-C18 polymer within the saponite layers may well be responsible for the unusually high barrier properties against water vapor.

4. Conclusion

In conclusion, the quasi two-dimensional aluminosilicate nanosheets offered a smooth, rigid substrate for molecular assembly of amphiphilic polyacetylenes with the alkyl chains interdigitated. The resulting hydrophobic barrier efficiently blocked transport of the water molecules and hence showed substantially high barrier properties.

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