



Molecularly ordered structure and permeability properties of amphiphilic polyacetylene-multilayer nanocomposites

Bon-Cheol Ku^{a,1}, Dong Wook Kim^c, Diane Steeves^d, Ramaswamy Nagarajan^a, Alexandre Blumstein^a, Jayant Kumar^{b,*}, Philip W. Gibson^d, Jo An Ratto^d, Lynne A. Samuelson^d

^a Center for Advanced Materials, Polymer Science/Plastics Engineering Program, Department of Chemistry, University of Massachusetts Lowell, MA 01854, USA

^b Center for Advanced Materials, Polymer Science/Plastics Engineering Program, Department of Physics, University of Massachusetts Lowell, MA 01854, USA

^c Advanced Materials Division, Korea Research Institute of Chemical Technology, 100 Jangdong, Daejeon 305-600, Republic of Korea

^d US Army Natick Soldier Research, Development and Engineering Center, Natick, MA 01760, USA

ARTICLE INFO

Article history:

Received 19 December 2007

Received in revised form 15 June 2008

Accepted 6 August 2008

Available online 20 August 2008

Keywords:

Multilayer nanocomposites

Barrier membranes

Layer-by-layer assembly

Ionic polyacetylenes

ABSTRACT

Nanocomposite films consisting of amphiphilic ionic polyacetylenes (P2EPy-R) and layered aluminosilicates (saponite) have been prepared through electrostatic layer-by-layer assembly. The water vapor barrier properties of the nanocomposite films coated on NafionTM film have been studied. The Nafion film coated with poly(*N*-octadecyl-2-ethynylpyridinium bromide) (P2EPy-C18) and aluminosilicates showed 22 times higher diffusion resistance to water vapor and 95% reduction in water vapor permeability when compared with the pristine Nafion control film. The X-ray diffraction data, UV–vis absorption spectroscopy, transmission electron microscopy (TEM), and atomic force microscopy (AFM) suggest a strong tendency of micellization of P2EPy-C18 polymer and ordered structure on the surface of aluminosilicate nanosheets compared to short alkyl side chains, C12, C6, and C0. The micellized and ordered structure of P2EPy-C18 between aluminosilicate could explain the improved hydrophobic barrier properties of P2EPy-C18/aluminosilicate nanocomposites.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Since the seminal work of polymer intercalation into montmorillonite [1] polymer-layered aluminosilicate nanocomposites (PLSNs) have recently attracted much attention in many applications [2,3]. Such nanocomposites can provide significant improvements in various properties of polymers such as mechanical [4,5], thermal [1,6,7], barrier [8–12], and flame retardancy [7,13–15]. The applications of such materials extend to the automotive, electrical, biomedical and packaging industries [16]. The remarkable properties of PLSNs are due not only to their chemical structure but to the particular properties of the lattice expanding of layered clays allowing for relatively easy formation of nanocomposite materials and films.

Among many fabrication methods for PLSNs, electrostatic layer-by-layer (ELBL) assembly [17] is a simple, versatile and cost-effective procedure to obtain ultrathin functional nanocomposite films with high performance for many applications. The dipping process using positively charged polyelectrolytes and negatively charged

aluminosilicate nanoparticles can be repeated and varied to build ordered multilayered systems with several components leading to a variety of nanocomposite film structures which can be used for separation of gases and vapors and other barrier applications [18,19].

Recently, Kim et al. reported the ordering of substituted ionic polyacetylene, poly(*N*-octadecyl-2-ethynylpyridinium bromide) on saponite nanoparticles [20] and their permeability characteristics of methanol [21] and water vapor [12]. Compared to pristine Nafion film, the Nafion substrate coated with nanocomposites of poly(*N*-octadecyl-2-ethynylpyridinium bromide) (P2EPy-C18) and exfoliated aluminosilicate nanoplatelets (P2EPy-C18/saponite) displayed a 50% decrease in methanol permeability and a 95% reduction in water vapor permeability. The high barrier properties may be explained by interdigitated assembly of the long alkyl side chains of P2EPy-C18 and their ordering on the aluminosilicate nanoplatelets [12]. However, the effect of alkyl side chain length of substituted ionic polyacetylenes on ordering as well as permeability still remains unclear.

In this work, we prepared layer-by-layer assembled nanocomposite films of aluminosilicates (saponite) and amphiphilic polyacetylenes (P2EPy-R/Saponite) with different alkyl side chains and demonstrated how the side chain length affects the ordering and permeability. Only the polyacetylene (P2EPy-C18) with the long alkyl side chain showed the strong tendency to form

* Corresponding author.

E-mail address: Jayant_Kumar@uml.edu (J. Kumar).

¹ Present address: Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA.

interdigitated structures between the aluminosilicates, which resulted in significant enhancement in water vapor barrier properties.

2. Experimental

2.1. 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-Bromohexane, 1-bromododecane and 1-bromooctadecane were purchased from Aldrich and used as received. The thickness of Nafion® film (112) produced by DuPont was 50 μm . All other solvents and chemicals were analytical grade and used as received.

2.2. Preparation of exfoliated saponite nanoparticles [20]

Saponite particles were dispersed in deionized water at a concentration of 0.2 wt.%. The dispersion was shaken for 1 day, and sonicated for 4–6 h. After the large unexfoliated particles (or aggregates) were separated by centrifugation, the resulting clear supernatant was used for the multilayer build-up.

2.3. Synthesis of poly(2-ethynylpyridinium chloride) (P2EPy-C0), poly(N-hexyl-2-ethynyl pyridinium bromide) (P2EPy-C6), poly(N-dodecyl-2-ethynylpyridinium bromide) (P2EPy-C12) and poly(N-octadodecyl-2-ethynylpyridinium bromide) (P2EPy-C18)

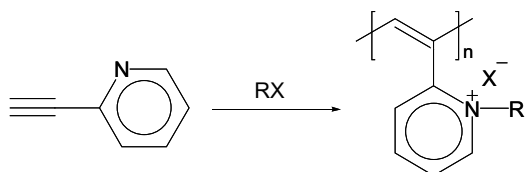
Substituted ionic polyacetylenes (P2EPy-R) with various alkyl chain lengths were prepared by spontaneous polymerization of 2-ethynylpyridine quarternized with 1-bromohexane, 1-bromododecane, 1-bromo-octadecane and HCl as described in the literature [22–24]. The structures of P2EPy-R are depicted in Scheme 1 and Table 1.

2.4. Preparation of nanocomposite films via layer-by-layer deposition

The exfoliated saponite particles were used as a polyanion and P2EPy-R as a polycation. The multilayer nanocomposite films were obtained by the layer-by-layer deposition method as described [20]. The overall process of layer-by-layer deposition consisted of a cyclic repetition of the following steps: (1) dipping the substrates (Chemsolv® treated glass or Nafion® film) into the amphiphilic polyelectrolytes solution for 1 min, (2) rinsing with methanol and drying under a stream of nitrogen, (3) dipping into an aqueous dispersion of the exfoliated saponite nanoparticle for 1 min and (4) final rinsing with deionized water and drying under a stream of nitrogen.

2.5. Characterization and measurement

The UV–vis absorption spectra were recorded by a Perkin–Elmer Lambda 9 UV–vis spectrophotometer. X-ray diffractograms were obtained using Cu K α ($\lambda = 1.5405 \text{ \AA}$) radiation with a Philips 3-kW



Scheme 1. Preparation of substituted ionic polyacetylenes by spontaneous polymerization of 2-ethynylpyridine with alkyl halides.

Table 1
Types of polyacetylenes (P2EPy-R)

Sample	R	X
P2EPy-C0	H	Cl
P2EPy-C6	C ₆ H ₁₃	Br
P2EPy-C12	C ₁₂ H ₂₅	Br
P2EPy-C18	C ₁₈ H ₃₇	Br

X-ray generator and vertical diffractometer. The morphology of the self-assembled micelles was investigated by atomic force microscopy (Park Scientific, CA) operated in the non-contact mode using a standard silicon nitride in ambient air. The monolayer samples for AFM were prepared on the mica surface by dipping for 1 min followed by washing and drying.

The measurement of water vapor transmission rate (WVTR) [25] of multilayer nanocomposite film was measured using a dynamic moisture permeation cell (DMPC). The flow rate was 2 mL/min and the relative humidity was 95% at 30 °C.

3. Results and discussion

3.1. Hydrophobic barrier: effect of molecular ordering of P2EPy-R

The amphiphilic polyacetylenes, P2EPy-R were prepared by spontaneous polymerization of 2-ethynylpyridine in the presence of alkyl halide (RX) as shown in Scheme 1. The UV–vis absorption spectra of the polymers dissolved in methanol is shown in Fig. 1. The positively charged P2EPy-R was deposited on the exfoliated nanoparticles by the layer-by-layer assembly method. UV–vis absorption spectroscopy of the nanocomposites [20] indicates that the maximum absorbance of the polymers increased linearly with deposition cycles (Fig. 2).

UV–vis absorption spectroscopy of the (P2EPy-R/saponite) nanocomposite films showed the absorption maximum of P2EPy-R at 450 nm was red-shifted to 471 and 502 nm as the alkyl chain length increased (Fig. 3). This indicates that the polyacetylenes tend to be more ordered with increasing alkyl side chains, resulting in increased π – π interaction of the conjugated polymer chains on the flat surface of the aluminosilicate nanoplates.

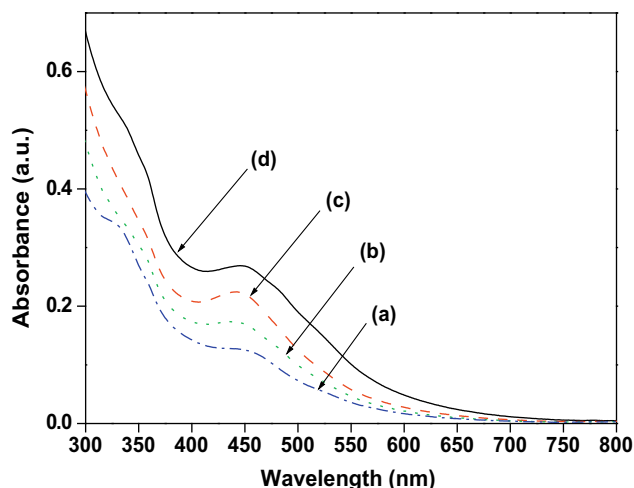


Fig. 1. UV–vis spectra of P2EPy-C0 (a), P2EPy-C6 (b), P2EPy-C12 (c), and P2EPy-C18 (d) dissolved in MeOH. ($\lambda_{\text{max}} = 435\text{--}445 \text{ nm}$).

Download English Version:

<https://daneshyari.com/en/article/821767>

Download Persian Version:

<https://daneshyari.com/article/821767>

[Daneshyari.com](https://daneshyari.com)