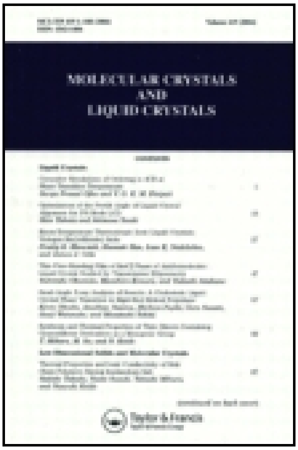

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Adsorption of Poly(γ-Substituted α-, L-Glutamate) on Aluminum Surface: Atr and Mo Approaches

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Adsorption of Poly(γ-Substituted α, L-Glutamate) on Aluminum Surface: Atr and Mo Approaches

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To examine possible adsorptive mechanism of polyglutamates on the aluminum surface, ATR-FTIR (attenuated total reflectance-Fourier transform infrared) spectrometer and MO (molecular orbital) calculation were used. Expected C=O stretching shift due to the chemical binding was not observed even in less-substituted glutamate polymers. ATR studies suggest: (1) the interaction between Al surface and polyglutamates is driven by physical adsorption, and (2) the interaction between the hairy rod polymer and solid substrate is governed by the intercrossing of side chain pendent groups.

Keywords: polyglutamate; hairy rod; polymer adsorption; ATR-IR

INTRODUCTION

There have been many considerable interests to construct polypeptide on solid substrates. Making out the nature of physisorption or chemisorption between polymer and solid surfaces is an essential to understand the adsorptive pattern and disposition of outmost layers. The materials used in this experiment were PLG, PBLG, PELG, PHLG, and PSLG, which refer to poly-L-glutamic acid, benzyl, ethyl, hexyl, and stearyl substituted L-glutamate, respectively. They were composed of the helical backbone-rigid rodlike part and the aliphatic side chain-flexible ordering, that have the character of lyotropic liquid crystalline. Self-assembled layers of PSLG and PBLG featured different morphologies; adsorption from very dilute solutions in THF produced small globules of polymers on hydrophilic mica surface, and from concentrated solutions produced "anchovies in the net" or "flower structures."[1] Structural characteristics depend on two aspects; *interdigitation* of side chains due to the hydrophobic interaction and *adsorption* of rodlike molecules on solid surface. In the present work, we have used molecular orbital calculation and attenuated total reflectance-Fourier transform infrared spectroscopy to provide information about the interaction between glutamate polymers and solid surface.

EXPERIMENTAL

Materials: Each polymer was purchased from Sigma Chemical Co. and determined the polydispersity and molecular weight by viscometry and light scattering. Spectroscopic grades of THF and chloroform were purchased from Aldrich and used to make spreading solution for the Langmuir-Blodgett deposition. PSLG was synthesized by Leuchs' method as described elsewhere.[2] Aluminum plate was cleaned by the H_2O, H_3PO_4, HNO_3 as in reference.

Sample Preparation: Self assembly of polypeptide on aluminium was carried out by exposing the plate to the polymer solutions for time period ranging from 3 to 30 hrs, washing the sample with a corresponding pure solvent, drying it in a laminar hood. Monolayer of polyglutamate was prepared by Lauda LB trough using dipping the plate or lowering the water level methods described in details elsewhere.[2]

Instrument: Mid-infrared spectra of polymer adsorbates were recorded on a Bio-Rad FTS-6000 interferometer using a single reflection diamond ATR and operating at a resolution of 4 cm^{-1}. The ATR accessory used a 2mm x 2mm square diamond that was brazed into a tungsten carbide disk and transfer optics were optimized to obtain a maximum throughput. The cryogenic MCT was used as a detector and spectra were taken in dry nitrogen purging.

Calculations: The geometry optimization and vibrational frequencies of glutamate polymer on $Al(OH)_3$ were obtained using Hartree-Fock and density functional theory (DFT) B3LYP methods with 3-21G* and 6-31G* basis sets from the Gaussian 94 program.[3] Full geometry optimization of binding complex was compared with the molecule in bulk with C=O stretching mode. Every frequency value was corrected using scale factor.[4]

RESULTS AND DISCUSSION

ATR spectra of the LB monolayer, the self assembled layer, and the pellet of PELG are shown in Figure 1(a). The peak at 1730 cm^{-1} is assigned to the C=O stretching, indicating the presence of free carbonyl. Two discernible peaks at 1651 and 1543 are combination band from the backbone. Assuming the chemical binding between the –OH of aluminum hydroxide and C=O of outside of hairy rod polymer, there should be shifted to a lower force constant of C=O stretching.

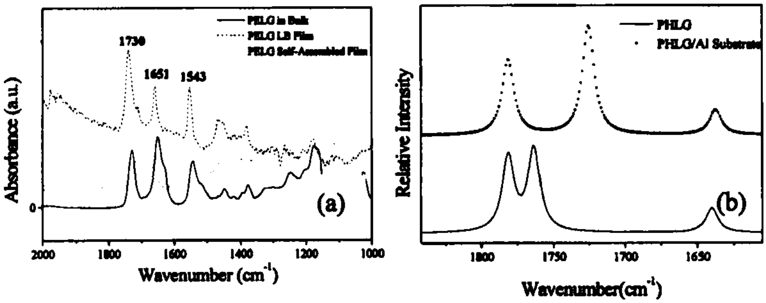

FIGURE 1. (a) Actual ATR spectra of PELG prepared by LB and self-assembled layer on Al_2O_3. (b) Simulated ATR spectrum from MO calculation which is expected by assuming the chemical bond of PELG on Al_2O_3. Shifted band is coming from the side chain -C=O.

The spectrum, however, shows no dramatic shift of the C=O stretching. MO calculation predicts ~30 cm^{-1} shift by chemical binding between the side chain rod-like polymer and the aluminum hydroxide, Figure 1(b). The shifted band in Figure 1(b) is the C=O stretching from the side chain. The ATR spectrum of self-assembled PLG on Al plate shows intensity change at C=O stretching and shift of adsorption band between the range of 1000-1800 cm^{-1}. A change in the IR band profile of PLG on aluminum oxide is explained by a canted head group (mono-dentate) or a symmetrically bonded head group (bi-dentate)[5] The substituted side chains, however, prevent the approach of the active site on the solid surface. The length of ethyl, hexyl, and stearyl substitutions is longer than the distance between the OH of aluminum and C=O of polyglutamte, 2.047Å. Hexyl and benzyl substituted polyglutamtes also have the same ATR trends as the PELG. The long side chain of PSLG

(Figure 2(a)) is less effected by the Al surface than that of short side chain polymers. The interaction between the domain structure and Al surface is strong: repeated AFM scans with modest force, ~100nN, lead to no damage of the polymer layer. General picture for the association of surface attached molecules is determined by the interplay of the interaction between polymer backbones and the interaction between the side chains. The dipole-dipole interaction of short side chains governs the process of adsorption on solid surface and the interaction of the side chains are the main driving force for the long side chain polyglutamates. ATR studies suggest: (1) the interaction between Al and polyglutamates is driven by physical adsorption, and (2) the interaction of the polyglutamate on Al surface is mostly governed by the side chain intercrossing. Figure 2(b) indicates the short chain glutamates (top) in which the dipole-dipole interactions are dominant, and long side chain polymers (bottom) in which the side chains are intercrossed.

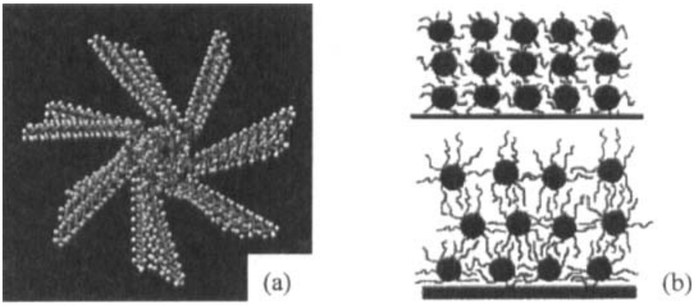

FIGURE 2. (a) Molecular modeling of PSLG with 14 repeating units. (b) adsorption model of short (top) and long (bottom) side chain glutamate polymers.

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