FTIR ATR Analysis for Microstructure and Water Uptake in Poly(methyl methacrylate) Spin Cast and Langmuir–Blodgett Thin Films

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ABSTRACT: Spin cast and Langmuir–Blodgett (LB) films of atactic PMMA [poly(methyl methacrylate)] were studied at 25 °C by FTIR ATR (Fourier transform infrared spectroscopy, attenuated total reflection) spectroscopy before and after annealing at 140 °C and after contact with water vapor or liquid. The dichroic ratios of the carbonyl groups revealed that the average molecular orientations of the films remained unchanged upon annealing and also upon exposure to water. However, annealing helped avoiding cracks which appeared in the nonannealed film after contacting liquid water. The absorbances of individual water bands (of the non-hydrogen-bonded monomers, hydrogen-bonded dimers, larger clusters, and associated chains of water) were determined by detailed spectral analysis and compared with a one-dimensional Fickian model. The absorbance data for the annealed spin cast film of thickness of 5.4 μm showed poor fit to the one-dimensional Fickian diffusion model, but the apparent diffusion coefficient, D_{app}, ranged from 5×10^{-10} to 4×10^{-11} cm^2/s. The process of film hydration was found to precede the transfer of bulklike water. For the annealed LB and spin cast films of thickness of 0.1 μm, D_{app} ranged between 10^{-13} and 10^{-15} cm^2/s. It was estimated from ATR carbonyl band intensities that the thin films were about 44% more dense than the thick film, indicating that they had a tighter structure with fewer structural defects or voids. Having more hydrophobic and less rough surface, the LB film showed a longer initial delay in liquid water transport than the spin cast film of the same thickness.

Introduction

Thin PMMA [poly (methyl methacrylate)] films have been studied extensively in the past 15 years for their potential applications as materials for barriers, membranes, microlithography, and optical applications.[1-5] Because controlling the film quality is important for these applications, many workers have reported on the use of various microscopic and spectroscopic techniques for probing pinholes, defects, grain boundaries, etc.[1-5] Important characteristics of quality are the porosity and the permeability of the films to water and other vapors or liquids.

Several techniques have been developed for studying the water transport in PMMA films. In most cases, the sorption kinetics and volumetric changes of PMMA were determined by measuring the weight of the water uptake. Turner reported that sorption dynamics departed from Fick's law.[6] IR and NMR spectroscopy have been used to probe the diffusion of water in polymers.[7-9] Davydov et al.[10] studied the permeability of polyurethane film with respect to water vapor by infrared spectroscopy. Grinsted et al.[11] used NMR imaging to study the sorption–desorption cycle of water and methanol into PMMA rods. Kuan et al.[4,5] reported that spin cast films of PMMA have considerably higher pinhole densities than the LB films. Water transport depends of course on the film quality. Little attention has been given, however, on how the processing method affects the microstructure and the transport properties of these thin films.[7,12]

This article focuses on the FTIR ATR analysis of thin PMMA films made by spin casting or by LB deposition, to obtain a realistic comparison of the two methods. The FTIR ATR spectroscopy is an excellent tool for quantitatively analyzing the microstructural features of dry and wetted films, estimating the water content, and for probing the transport rate of water through the films. This approach can also be useful for studying other penetrants transported through organic thin films.

Two different film thicknesses were produced for studying their differences in regard to the film microstructure, water uptake, and water content. Because microfiltration or ultrafiltration membranes can range from about 1 to 20 μm in thickness,[13] films of about 5 μm were prepared by the spin casting method for evaluating the performance of this polymer as a membrane. By using thick films, one can reduce the IR water signal at the initial measurements after liquid water is placed on top of the film, because the decaying evanescent electric field of the IR beam cannot probe the water on top of the film, but can probe the water in the film. Thus, for thick films one can observe only the transient water uptake, and for thin films one also observes the water on top of the film. Thinner films, of thickness $l = 0.1$ μm, were prepared by the LB and spin casting methods. For an overall evaluation of the film as either a membrane or a barrier material, the dynamics of the water uptake of these two thin films and the thick films was followed.

Experimental Section

Materials. The atactic poly(methyl methacrylate) was obtained from Eastman Kodak; it was polydisperse with $\overline{M}_w = 101\,000$ and $\overline{M}_n = 48\,300$. Polymer films were cast from a chloroform solution (HPLC grade from Aldrich). All water used (DI) was purified using a Milli-Q 4-bowl system, from Millipore Corp., and had an initial resistivity of 18 MΩ/cm.

Spin Casting. Films were cast on the ATR crystals with a spin coater (Model 1-EC101D-R485, Photo-Resist Spinners, Garland, TX). For producing films of about 5.4 and 0.1 μm thickness, respectively, solutions of 200 and 5 mg/mL in chloroform were applied to the entire surface of the ATR crystals. Spinning for 1 min was done at 1000 and 500 rpm, respectively. All films were dried at room temperature for 1 h before they were examined.

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