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Thin Solid Films 263 (1995) 134–144

thin solid films

Microstructure and water transport in spin cast films of poly(hexylmethacrylate azobenzene-sulfone)

Peter Sutandar, Dong June Ahn[1], Elias I. Franses*

School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-1283, USA

Received 22 September 1994; accepted 21 February 1995

Abstract

Spin cast films of poly(hexylmethacrylate azobenzene-sulfone) (PHMA-AS) with a thickness of 7.5 μm were studied at 25°C by Fourier transform infrared attenuated total reflectance spectroscopy before and after annealing at 140°C, and before and after contact with water vapor or liquid. Spectral analysis of the hydrocarbon and water bands was used to probe the changes in the film microstructure after these treatments. Slight orientation changes were detected in the hydrocarbon region after hydration. No changes were observed, however, in the dichroic ratios of the carbonyl and the chromophore groups of the PHMA-AS films. These groups had average tilt angles of 62° and 69°, respectively, from the surface normal. The addition of side chains consisting of a spacer and a chromophore group to the backbone of PMMA makes the film a better barrier material for water, as it absorbs less water vapor and less liquid water. The density of the sorbed water at 89% relative humidity was estimated to be 0.006 g per cm^3 of polymer. Initially water permeated fast, as non-bulk-like water, through film defects before diffusing more slowly, as bulk-like water, throughout the film. The estimated total density of liquid water absorbed by the film was 0.05 g per cm^3 of polymer. The in-situ transport data suggest transport mechanisms more complex than the one-dimensional Fickian diffusion, evidently due to the complex microporous structure of the films.

Keywords: Coatings; Fourier transform infrared spectroscopy; Polymers; Water

1. Introduction

Films with chromophores chemically attached to poly methylmethacrylate (PMMA) are candidates for non-linear optical materials [1–4]. The film's optical and microstructural qualities are important for such applications. Various studies have been made to test their thermal, mechanical, and chemical stability [1,5]. The film microstructure has been investigated by non-linear optical methods, which probe the chromophore orientation, and by Fourier transform infrared spectroscopy (FTIR) and other methods [1–3,6–8].

This article focuses on using FTIR attenuated total reflectance (ATR) spectroscopy for studying thick spin cast films of PHMA-AS, or PMMA with azobenzene sulfone chromophore side chains, which are used to impart non-linear optical properties to the film [1]. The results are compared with those for thick spin cast films of PMMA [9]. PHMA-AS films turn out to be less hydrophilic than PMMA films. The FTIR ATR spectroscopy is an excellent tool for quantitatively probing several microstructural features of the films, either dry or wetted with water. Water content and transport rate were studied for their relevance to possible barrier or membrane applications, and to provide overall measures of film quality.

2. Experimental details

2.1. Materials

The atactic poly(hexylmethacrylate azobenzene-sulfone) (PHMA-AS) was obtained from Eastman Kodak ($\bar{M}_w = 89\,000$ and $\bar{M}_n = 38\,600$). The polymer actually consists of a PMMA backbone with chromophore groups attached through a $(CH_2)_6$ spacer to each ester group. Its structure is schematically drawn in Fig. 1 (top). Polymer films were cast from a chloroform solution (HPLC grade from Aldrich). All

* Corresponding author.

[1] Present address: Center for Advanced Materials, Lawrence Berkeley Laboratory, MS66-200, Berkeley, CA 94720, USA.