Determination of molecular orientations in Langmuir–Blodgett films by polarized Fourier transform IR attenuated total reflection and transmission spectroscopy

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Abstract

New methods for evaluating the molecular orientations using polarized Fourier transform IR spectroscopy are presented. When used together, the attenuated total reflection and the transmission modes can provide detailed orientation information of simple and complex Langmuir–Blodgett (LB) systems. The methods were applied to IR dichroic ratio data of cadmium stearate, atactic poly(methyl methacrylate) and isotactic (PMMA), and rigid-rod oligoimide LB multilayer films. The chain axes of the cadmium stearate films were uniaxially oriented at 37° on average. Orientations of PMMA LB films depended on the tacticity. Whereas uniaxial orientation was found for the methylene and the carbonyl stretching transition moments in the atactic PMMA films, biaxial orientation was indicated in the isotactic PMMA films. A least-squares analysis of the rigid-rod oligoimide data suggests that biaxial orientation is more probable than the single-crystal-type orientation. Orientation polydispersity, as characterized by a gaussian standard deviation, affects the dichroic ratio significantly, and hence affects the average orientation angle deduced from the data. The average orientation angles estimated with the conventional assumption of a single tilt angle for a uniaxial system are valid when the standard deviation is less than 0.2 rad (11.5°).

1. Introduction

The study of the molecular orientation of Langmuir–Blodgett (LB) films is important, since high molecular order uniquely distinguishes LB deposition compared with other processing methods of thin film [1]. Highly preferred molecular orientations are crucial for most of the current or potential applications of LB films such as non-linear optics, sensors, and membranes [2]. Polarized Fourier transform IR (FTIR) spectroscopy is an excellent tool for studying the molecular orientation, because it is non-destructive and quite specific. Many IR studies have used uniaxial orientation models, which may be adequate for materials of simple structure such as fatty acids [3]. Recently, LB films of more complex monomeric or polymeric molecules have been investigated [4–10]. IR dichroic ratios for such LB systems often exhibit deviations from the uniaxial orientation. Hence, the orientation evaluation may require more rigorous orientation models.

The present study deals with a new strategy of evaluating molecular orientations of LB films. New orientation equations are presented for polarized FTIR transmission spectroscopy. These equations provide more detailed orientation information when used with those for the attenuated total reflection (ATR) mode. The strategy is applied to the dichroic ratio data on cadmium stearate and atactic poly(methyl methacrylate) (PMMA) LB films. Literature data on isotactic PMMA [8] and rigid-rod oligoimide [9] LB films are also analyzed using the new method and compared with previous analyses. Finally, the effects of orientation distribution (or orientation polydispersity) on interpreting the dichroic ratios are discussed.

2. Orientation models for polarized Fourier transform IR spectroscopy

2.1. General theory

The molecular coordinates (*a*, *b*, and *c* axes) and the laboratory cartesian coordinates (*x*, *y*, and *z* axes) for IR experiments are shown in Fig. 1(a). The *z* axis is along the surface normal of the film (ATR and transmission modes), and also along the propagation direction of the IR beam in the transmission mode. The *x* axis is along the IR beam propagation direction of the ATR mode. The *y* axis is along the direction of s polarization for both modes. For the transmission mode, the p polarization is defined to be along the *x* axis. For the ATR mode the p polarization lies in the plane of incidence (*Oxz* plane) with an incidence angle of 45°. When the molecular orientation configuration allows a definition of a straight chain axis, the following

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