Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Investigation of the Orientation of Amphiphiles in Langmuir-Blodgett Films Using IR Spectroscopy

Mutsuyoshi Matsumoto [a] & Masaki Shimomura [a]

[a] National Institute of Materials and Chemical Research, Tsukuba, 305-8565, Japan

Version of record first published: 24 Sep 2006

To cite this article: Mutsuyoshi Matsumoto & Masaki Shimomura (2000): Investigation of the Orientation of Amphiphiles in Langmuir-Blodgett Films Using IR Spectroscopy, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 207-210

To link to this article: http://dx.doi.org/10.1080/10587250008024901

Mol. Cryst. Liq. Cryst., 2000, Vol. 349, pp. 207-210
Reprints available directly from the publisher
Photocopying permitted by license only

Investigation of the Orientation of Amphiphiles in Langmuir-Blodgett Films Using IR Spectroscopy

MUTSUYOSHI MATSUMOTO and MASAKI SHIMOMURA

National Institute of Materials and Chemical Research, Tsukuba 305–8565, Japan

A facile method for investigating the orientation of amphiphiles in the LB films using IR transmission and reflection-absorption spectroscopy (RAS) was presented. This method does not require the estimation of the enhancement factor in the RAS measurements or that of the difference in quantities of the molecules in the LB films on different substrates. The application of the present method to the actual LB films gave better results compared with the conventional method.

Keywords: LB films; IR; orientation

INTRODUCTION

Langmuir-Blodgett (LB) technique has been used for the fabrication of ultrathin films with the structures defined at the molecular level. The packing and orientation of the amphiphiles have been investigated using IR spectroscopy[1-4]. In particular, the combination of transmission and reflection-absorption spectroscopy (RAS) provides important information on the orientation of the alkyl chains of the molecules in the films. In this paper, we will report on a facile method for the estimation of the molecular orientation in the LB films.

EXPERIMENTAL

The preparation of hybrid LB films of dihexadecyldimethylammonium (DHA^+) and MoS_2 is described in the previous paper[5].

RESULTS AND DISCUSSION

We focus on the intensities of the CH_2 symmetric and antisymmetric stretching modes because the transition moments of these bands are perpendicular to each other and are also perpendicular to the chain axis of the hydrocarbon.

Figure 1 shows Cartesian coordinates (X, Y, Z) for expressing the orientation of the molecule. X-Y plane is chosen as the surface of the substrate and Z axis is parallel to the film normal. The vector $\underline{P}$ shows the direction of the chain axis of the hydrocarbon. $\underline{M}_1$ and $\underline{M}_2$ are the transition moments of the CH_2 symmetric and antisymmetric stretching modes, respectively. $I_s/I_{as} = M_1^2/M_2^2$ where I_s and I_{as} are absorbance of the CH_2 symmetric and antisymmetric stretching modes in the IR spectra of unoriented molecules, respectively. The value I_s/I_{as} can be obtained experimentally by measuring the intensities of the two bands in the IR spectra of the powder or solution sample.

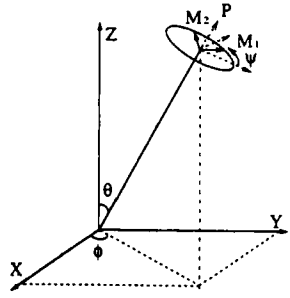

FIGURE 1 Space coordinates for expressing the orientation of the amphiphile.

The ratios of $I_{R,s}/I_{R,as}$ and $I_{T,s}/I_{T,as}$, which can be independently obtained from RAS and transmission measurements, respectively, are expressed as

$$I_{R,s}/I_{R,as} = (I_s/I_{as}) \langle \sin^2\theta\cos^2\psi \rangle / \langle \sin^2\theta\sin^2\psi \rangle \quad (1)$$

$$I_{T,s}/I_{T,as} = (I_s/I_{as}) \langle\cos^2\theta\cos^2\psi + \sin^2\psi\rangle/\langle\cos^2\theta\sin^2\psi + \cos^2\psi\rangle \quad (2)$$

where $I_{R,s}$ and $I_{R,as}$ are absorbance of the CH_2 symmetric and antisymmetric stretching modes in the RAS spectra, and $I_{T,s}$ and $I_{T,as}$ are absorbance of the CH_2 symmetric and antisymmetric stretching modes in the transmission spectra of the LB films. When $\underline{M}_1$ and $\underline{M}_2$ are distributed homogeneously with respect to the vector $\underline{P}$, that is, when the alkyl chain can freely rotate around its axis, we can not obtain any information on the angle θ because both of $I_{R,s}/I_{R,as}$ and $I_{T,s}/I_{T,as}$ are equal to I_s/I_{as} according to Eqs. (1) and (2).

If we assume that all the molecules have the same orientation, the above equations are reduced into the following[5].

$$I_{R,s}/I_{R,as} = (I_s/I_{as})\,(1/\tan^2\psi) \quad (3)$$

$$I_{T,s}/I_{T,as} = (I_s/I_{as})\,(\cos^2\theta+\tan^2\psi)/(\cos^2\theta\tan^2\psi+1) \quad (4)$$

The main advantages of this method is that the estimation of the following two critical parameters is not necessary: (i) enhancement factor in the RAS measurements[2,4] and (ii) difference in quantities of the molecules in the LB films on different substrates.

Figure 2 shows $I_{T,s}/I_{T,as}$ normalized to I_s/I_{as} as a function of θ for several values of ψ according to Eq. (4). When ψ is 45°, this value is unity irrespective of the angle θ. This means that the determina-

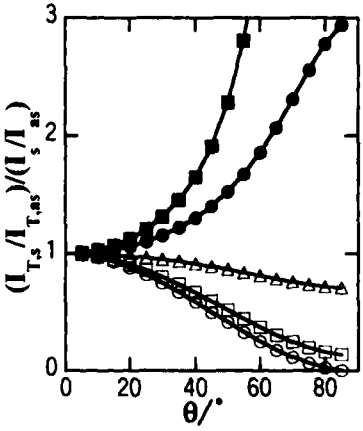

FIGURE 2 $I_{T,s}/I_{T,as}$ normalized to I_s/I_{as} as a function of θ according to Eq. (4). ○:ψ=0°, □:ψ=20°, △:ψ=40°, ●:ψ=60°, ■:ψ=80°.

tion of the angle θ entails large errors when ψ is around 45°.

The orientation of DHA^- depended on the subphase concentration of MoS_2[5]. The tilt angle θ of the hydrocarbon of DHA^- was obtained using the present and the conventional method[2,4]. The results are summarized in Table 1. The interlayer spacing obtained from XRD[5] was also reduced into the tilt angle and shown in the last line.

TABLE 1 Tilt angle θ of the hydrocarbon of DHA^- in the LB films

MoS_2 conc. ($g\ L^{-1}$)	0.12	0.33	0.68
Present method[5]	53	64	63
Conventional method	20	23	41
XRD	56	66	70

It is clear that the present method gives better agreement with the results of XRD compared with the conventional method.

In summary, this study shows that the orientation of amphiphiles in the LB films can be obtained without estimating the enhancement factor in the RAS measurements or the difference in quantities of the molecules in the LB films on different substrates. The present treatment is particularly important in that the latter factor affects the results significantly but is usually not explicitly considered due to the difficulty in the estimation of the amount of molecules in the LB films for RAS measurements.

References

[1] J. F. Rabolt, F. C. Burns, N. E. Schlotter and J. D. Swalen, *J. Chem., Phys.*, **78,** 946(1983).
[2] J. Umemura, T. Kamata, T. Kawai and T. Takenaka, *J. Phys. Chem.*, **94**, 62(1990).
[3] M. Shimomura, K. Song and J. F. Rabolt, *Langmuir*, **8,** 887(1992).
[4] R. Azumi, M. Matsumoto, S. Kuroda and M. J. Crossley, *Langmuir*, **11.** 4495(1995).
[5] Y. Taguchi, R. Kimura., R. Azumi, H. Tachibana., N. Koshizaki, M. Shimomura, N. Momozawa, H. Sakai, M. Abe and M. Matsumoto, *Langmuir,* **14**, 6550(1998).