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

Thermal Behavior of One-Layer Langmuir-Blodgett Films of 2-Pentadecyl-7,7,8,8-Tetracyanoquinodimethane Studied by Ultraviolet-Visible and Infrared Spectroscopies

Shin-Ichi Morita [a], Katsuhiro Nichogi [b] & Yukihiro Ozaki [a]

[a] School of Science, Kwansei-Gakuin University, Nishinomiya, 662-8501, Japan

[b] Advanced Materials Reseach Laboratory, Matsushita Research Institute Tokyo, Inc, Higashimita, Tama-ku, Kawasaki, 214-8501, Japan

Version of record first published: 24 Sep 2006

To cite this article: Shin-Ichi Morita, Katsuhiro Nichogi & Yukihiro Ozaki (1999): Thermal Behavior of One-Layer Langmuir-Blodgett Films of 2-Pentadecyl-7,7,8,8-Tetracyanoquinodimethane Studied by Ultraviolet-Visible and Infrared Spectroscopies, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 337:1, 325-328

To link to this article: http://dx.doi.org/10.1080/10587259908023443

Mol. Cryst. and Liq. Cryst., 1999, Vol. 337, pp. 325-328
Reprints available directly from the publisher
Photocopying permitted by license only

Thermal Behavior of One-Layer Langmuir-Blodgett Films of 2-Pentadecyl-7,7,8,8-Tetracyanoquinodimethane Studied by Ultraviolet-Visible and Infrared Spectroscopies

SHIN-ICHI MORITA[a], KATSUHIRO NICHOGI[b] and YUKIHIRO OZAKI[a]

[a]*School of Science, Kwansei-Gakuin University, Nishinomiya 662–8501, Japan and* [b]*Advanced Materials Reseach Laboratory, Matsushita Research Institute Tokyo, Inc, Higashimita, Tama-ku, Kawasaki 214–8501, Japan*

Thermal Behavior of one-layer Langmuir-Blodgett (LB) films of 2-pentadecyl-7,7,8,8-tetracyanoquinodimethane (pentadecyl-TCNQ) has been investigated by use of infrared (IR) and ultraviolet-visible (UV-Vis) spectroscopies. An IR transmission spectrum of the film shows gradual temperature-dependent changes below the melting point of the film, and then gives dramatic spectral changes near the melting point. Temperature-dependent UV-Vis spectral changes of the film indicate that the morphological changes occur in domains of the film, and that absorption bands in the 320–560 nm region arising from the π-π^* transition of the chromophore consist of at least three components due to different forms of chromophore aggregation. More active state of the alkyl-chain, hexagonal state, seems to be a trigger for the morphological changes in the domains.

Keywords: Langmuir-Blodgett films; infrared spectroscopy; thermal behavior; tetracyanoquinodimethane

INTRODUCTION

Thermal behavior of Langmuir-Blodgett (LB) films has been a matter of keen interest not only from the point of basic science but also from the point of practical application of organic conductive devices. We have been

investigating thermal behavior of LB films of 2-alkyl-7,7,8,8-tetracyanoquinodimethane (alkyl-TCNQ) by use of infrared (IR), ultraviolet-visible (UV-Vis) spectroscopy, and atomic force microscopy [1]. Recently, it was found by the Nomarski microscope that the morphological variation into the spherical-like domain occurs from 85 to 90 °C [2]. Moreover, infrared analysis indicated that pre-melting phenomenon takes place around 90 °C before the melting point (around 120 °C). The purpose of the present study is to provide new insight into the pre-melting and melting phenomena of a one-layer LB film of pentadecyl-TCNQ by use of IR and UV-Vis spectroscopies.

EXPERIMENTS

A CaF_2 plate was put under water before preparing Langmuir films of pentadecyl-TCNQ. The one-layer LB films consisting of two molecular monolayers were fabricated by transferring the Langmuir films by lifting the plate vertically under the surface pressure of 10 mNm^{-1} [1]. Instrumentations to obtain the IR and UV-Vis spectra and temperature control system were the same as those described previously [1]. The spline-4 algorithm in GRAMS/386 software (Galactic Industries Co.) was used to interpolate the spectra mathematically.

RESULTS AND DISCUSSION

Figure 1 shows temperature-dependent IR spectra in the 3000-2800 cm^{-1} region of a one-layer LB film of pentadecyl-TCNQ. Bands near 2920 and 2848 cm^{-1} are assigned to CH_2 antisymmetric and symmetric stretching modes of the alkyl chain, respectively. The antisymmetric stretching band is split into two. We selected the CH_2 symmetric stretching band at 2850 cm^{-1} to investigate the

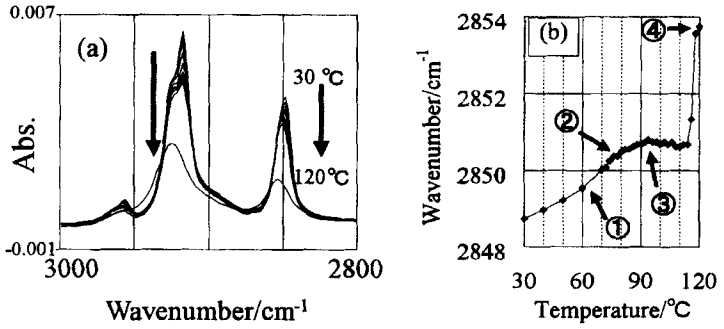

FIGURE 1 (a) Temperature-dependent IR spectra in the 3000-2800 cm^{-1} region (b) Temperature dependence of the peak-top position of the CH_2 symmetric stretching band

thermal behavior of the alkyl-tail because of the less overlapping by other absorption bands. Moreover, the interpolation technique was applied to the band to determine the position of the peak. Figure 1 (b) shows temperature dependence of the peak-top position, calculated from the interpolation technique. We have succeeded in showing some point of inflection. We assign point ① to the changing point to hexagonal subcell packing from another subcell packing, where the nearest zigzag plane of the alkyl-chain packed perpendicular each other, point ② to the starting point of the morphological change of plate-like domain into spherical-like domain, region ③ to the stabilized state as a spherical-like domain, and region ④ to the liquid state. This suggests that the hexagonal subcell packing of the alkyl-chains occurs around 60 ℃ by taking thermal energy. This different kind of environment of alkyl-chains from the lower temperature region (30 to 50 ℃) may be a driving force to build-up another domain structure.

Figure 2 depicts UV-Vis spectra of a one-layer LB film of pentadecyl-

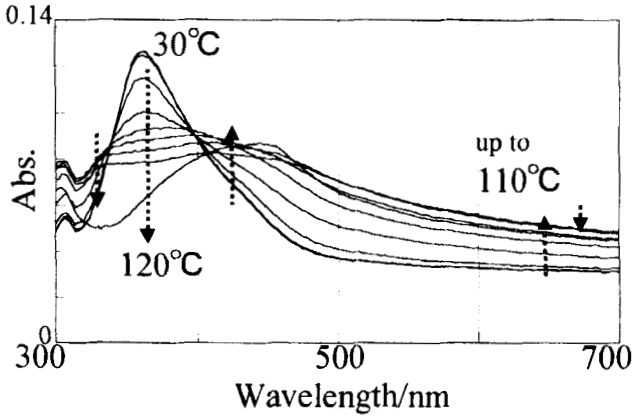

FIGURE 2 Temperature-dependent UV-Vis spectra

TCNQ over a temperature range of 30-120 °C at increments of 10 °C. The baseline of the UV-Vis spectrum shifts up with temperature increase up to 110 °C. It indicates that the number of the domains, whose size is comparable to the wavelength of the visible light (about 1μm), increases. Another distinct feature in Figure 2 is that there are, at least, three components in the absorption bands in the 320-560 region originated from the π–π* transition. It is noted that the intensity of a band at 363 nm, due to the stacked form [1], is more sensitive to the thermal stimulus, and that its thermal behavior is similar to the variation of a CH_2 scissoring band near 1465 cm^{-1} in the IR spectra. It is likely that more active thermal movement in the hexagonal state leads to decrease the 363 nm component and also likely that its movement seems to be a trigger into spherical-like domain structure.

References

[1] Y. Wang, K. Nichogi, S. Terashita, K. Iriyama, Y. Ozaki, *J. Phys. Chem* **100,** 368 (1996).
[2] K. Nichogi, S. Morita, Y. Ozaki to be published.