

A Fluorescence Spectra of Polydiacetylene Monolayer at the Air-Water Interface

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Abstract

Fluorescence spectra from the polydiacetylene indicates the information of completeness of π -conjugated chains and relaxation process in the crystal. So, it is reasonable to compare the fluorescence spectra of polydiacetylene bulk crystals with monolayers at the air-water interface which is free to mechanical stress. For this purpose, we built a fluorescent microscopic optical system for the *in-site* determination of polarized fluorescence from the monolayer crystals.

Key words : Polydiacetylene, fluorescence spectra, π -conjugated chains, LB films, spherulitic spiral structure, Photon counting

1. Introduction

Diacetylene has attracted significant interest due to the fact that π -conjugated chains can be formed by solid-state polymerization.¹⁻³⁾ Despite of organic substances, the material can form a single crystal with high crystallinity, and easily polymerize through the UV irradiation. Since polydiacetylene (PDA) possesses substantially long π -conjugated chains, one may expect application to the nonlinear optical material and optical solid state devices.

Theory showing that one-dimensional systems of conjugated π -electron should have large third-order nonlinear susceptibility, and that the magnitude of this nonlinearity is largely dependent on the conjugation length.

Until now, however, that the extended π -conjugation is not enough. Langmuir-Blodgett monolayers are of particular interest since well defined thin film structures can be fabricated from highly polarizable organic amphiphilic-molecules. The physical properties of the LB films on a substrate strongly depend on the surface structure and the imperfection, so a

preparation of large single-crystal domains of one monolayer on a water surface is strongly desired for a variety of applications. Experiments to align the main chain of the PDA in the monolayer at the air-water interface were attempted. Consequently, uniformly oriented large domains of over 20 mm \times 5 mm were prepared when the area of water surface was slowly increased by moving a barrier after the highly concentrated solution was spread on a small water surface.⁴⁾

The polymer crystals of diacetylene possess the long π -conjugated chains. Nevertheless, it is known that the PDA derivative crystals reveal very low electric conductivity ($10^{-10} \sim 10^{-16} \Omega^{-1} \cdot \text{cm}^{-1}$) resistivity.⁵⁾ The reason of this was not known, and the attempt to doping were not succeed. It is reasonable to study the fluorescence of PDA to estimate the completeness of π -conjugated chains. I attempt to determine the relationship between the morphological structure of PDA and fluorescence spectra. For this purpose, we built an optical system for the *in-site* determination of polarized fluorescence from the monolayer crystals.

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2. Experimental

2.1 Materials and equipment

The amphiphilic diacetylene derivative, 10, 12-pentacosadiynoic acid ($\text{CH}_3-(\text{CH}_2)_{11}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_8-\text{COOH}$), was used. By using benzene as a solvent (10^{-2}M) a large domain of diacetylene can be formed. To stabilize the monolayer structure, we added CdCl_2 of $2.5\times 10^{-4}\text{M}$ into the subphase. The pH of the subphase was adjusted to 6.8 by adding NaHCO_3 .

Figure 1 shows the schematic illustration of trough and measurement systems. A small Langmuir trough (spreading area: $250\text{ mm}\times 75\text{ mm}$, depth: 5 mm) was specially designed to have an oblique edge where the developing solution is trapped.⁶⁾ Monolayer at the air-water

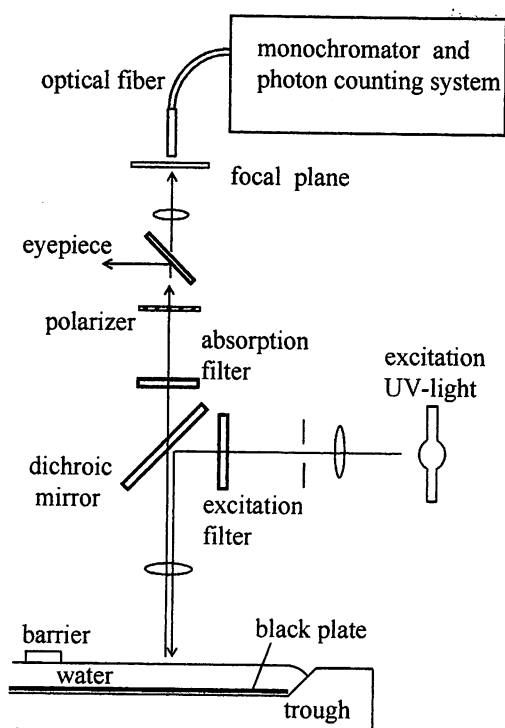


Fig. 1. Schematic diagram of the observation and measurement system of the monolayer at the air-water interface: Langmuir trough with moving barrier, measurement systems consisting of optical microscopes were mounted on individual baseplates to prevent vibration.

interface was inspected with fluorescence microscope. The Nomarsky differential interference microscope and polarizing microscope could be used to confirm the surface structure of the monolayer on the water surface. The optical images of the monolayer were almost not detectable due to the strong light reflected from the bottom of the trough. This difficulty was overcome by placing an anti-reflection black plate at the bottom of the trough and using an object lens with low numerical aperture. Besides these methods, complete flatness of the water surface allowed observation with sufficiently high contrast. Microscopes were set up on a baseplate that could be moved in the horizontal direction, so that it was possible to observe the monolayer over the entire trough surface. To reduce vibration on the water surface, the entire apparatus was mounted on individual plates. To detect the direction of polymerization that is parallel to the conjugated chain direction, fluorescence emitted from the PDA monolayer was observed. Fluorescence excited by the UV irradiation (G excitation, λ : about $470\sim 550\text{ nm}$, B excitation, λ : about $420\sim 480\text{ nm}$) from the PDA monolayer is polarized in the direction of the conjugated main chain. After passing through the polarizing plate, the fluorescent light creates images on the focal plane (area: $35\times 24\text{ mm}$). Fluorescent light of about 3% areas of the focal plane was measured by grating monochromator which was connected to fluorescence microscope. Photon counting measurement system was adopted in order to detect the weak fluorescence emission.

Preparation of the monolayers were done in a clean room under yellow cut. The temperature during the preparation process was kept at about 18°C and the humidity at about 60%.

2.2 Procedures

Prior to the deposition of developing solution onto the subphase, to obtain a clean water surface we wiped out the subphase by the barrier which was driven by a magnetic force. Then we deposited the diacetylene solution

onto the subphase surface. The solution deposited to the trapping place gradually migrated from the oblique edge and eventually covered the subphase surface. By the use of such a developing method, the subphase surface was covered with radial-type domains. Note that the volume of the solution, hence the number of diacetylene molecules, was adjusted so as to form a monolayer on the subphase surface. Even just after the development of the solution, crystallization immediately occurs in the monomer monolayer. The polymerization was performed by exposing the monolayer to a low-pressure mercury lamp ($\lambda = 254\text{nm}$). Before the polymerization, the crossed Nicol polarized microscope is useless for the observation of surface structure of the diacetylene monolayer, since no conjugated chain is formed in the monolayer. Interestingly, it is found that an observation scheme consisting of illumination by circular polarized light and detection by linear polarized light can reveal the surface structure of the diacetylene monomer monolayer. Thereby, we can carry out direct and successive observations of the surface morphology of the monolayer both in the monomer and polymer states.

3. Results and Discussion

Figure 2 shows the polarizing micrograph of two-dimensional spherulitic spiral structure after polymerization. The barrier moved from right to left. The water surface is filled with elongated large domains originating from the spherulitic structures. A spiral molecular orientation was observed near the origin of the long domains, but it became a unidirectional structure far from the origin. The Two-dimensional crystallized area in which the polymer chains align parallel to each other spread over $20\text{mm} \times 5\text{mm}$. It is apparent that the initial crystallization takes place on the narrow rectangular water surface (at the right edge of the trough) where an excess of spreading solution exists, and then the growing structure were

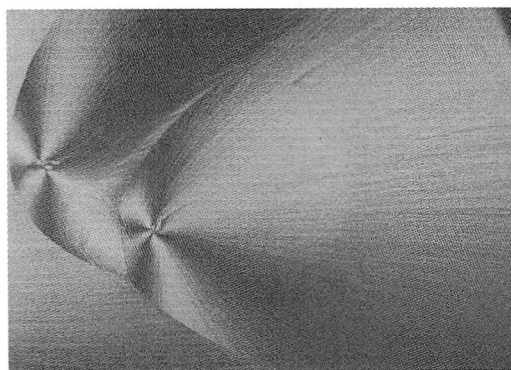


Fig.2. Polarizing micrograph of two-dimensional spherulitic spiral structure after polymerization.

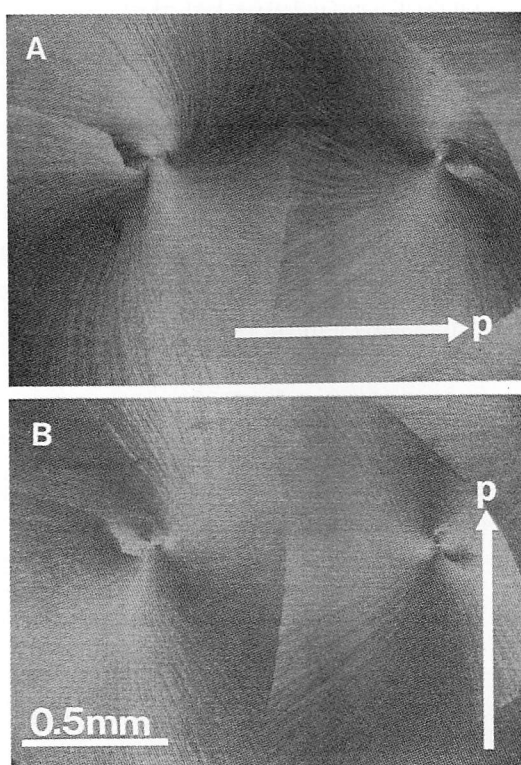


Fig.3. Fluorescent microscopic view observed by the excitation by B excitation. (λ : about $420 \sim 480\text{nm}$) It revealed that there are two kinds of spirals with left and right-handed directions.

moved to the left along with surface expansion.

Figure 3 shows the fluorescent microscopic view observed by the excitation of polarized ultraviolet light. It revealed that there are two

kinds of spirals with left and right-handed directions. Then the monodomains having different orientations of conjugated chains originate from the radial growth structures with left and right-handed spirals. The direction of the conjugated main chain in the PDA monolayer was determined from the polarized fluorescent light emitted from each domains. This spherulitic structure unique to the fast crystallization of organic molecules has been reported and discussed.⁷⁾

In a PDA backbone, two extreme types of conjugation are possible, i.e., the acetylene type structure $(=C-C\equiv C-C=)_n$ and butatriene type electric structure $(-C=C=C-C-)_n$. The PDA in this study must have butatriene type structure because the fluorescences from the acetylene type structure was hardly observed because it's low quantum efficiency (below 10^{-6}). Moreover, it was confirmed that only $\pi-\pi^*$ transition concerns the electrical phenomena and photo absorption or emission near visible wavelength region.

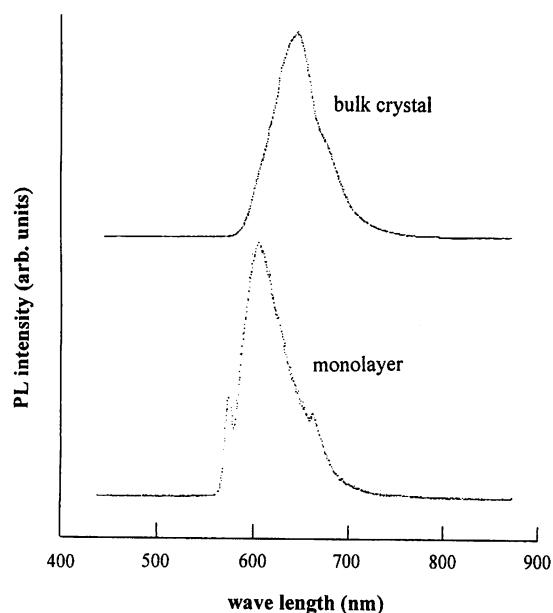


Fig.4. Polydiacetylene fluorescence spectrum of monolayer at the air-water interface. For comparison, the spectrum from the bulk crystal was shown.

Figure 4 shows the PDA fluorescence spectra of monolayer at the air-water interface. For comparison, the spectrum from the bulk crystal was shown. It is apparent that there are somewhat differences between two spectrum profiles, i.e., 612nm peak in monolayer and 650nm in bulk crystal. The energy gap of polydiacetylene $\pi-\pi^*$ band was estimated about 3eV. However, the excitation photon energy in this measurement was 2.3 ~ 2.6 eV, then, the only X-exciton band or A-exciton band may be excited. The observed spectra were supposed to shifted downward to selftrapped excitation band energy.⁵⁾ The difference of two spectral features may be due to the sample inhomogeneity. Therefore, this observation suggests that a slight modification of the electronic states of monolayer and bulk crystal.

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