Chromatic Phase and Molecular Packings of Polydiacetylene Langmuir-Blodgett Films

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Molecular packings of polydiacetylene (PDA) Langmuir-Blodgett (LB) film in various chromatic phases such as blue, red and bluish-green forms have been clarified by the electron diffraction analysis for the first time. Spectroscopic properties - molecular packings relationships for the chromatic phases of PDA LB film indicate that the chromatic phase of PDA is strongly dependent on its molecular packing in the crystal phase.

Polydiacetylenes(PDAs) are expected to be one of excellent candidates for the third order nonlinear optical materials, because of their large third order nonlinear optical susceptibility and their ultrafast response. The nonlinear optical properties of PDAs are strongly dependent on their electronic structures related to their π-electron orbitals along the conjugated main chains.[1] The electronic structure of PDA is evaluated by its visible light absorption spectroscopic properties reflecting the magnitude of the lowest transition energy between two energy levels, *i.e.*, band gap. It has been reported that PDAs have two spectroscopically distinct phases designated as the blue form and the red one according to their colors.[2] The blue and the red forms show the exciton absorption peaks around the wavelength of 640 nm and 540 nm in the Visible absorption spectrum, respectively. The difference in the electronic structures for these two forms has been explained in terms of the effective delocalization length of π-electron.[3] That is, the red form is thought to have a shorter delocalization length of π-electron than the blue form, as expected from the wavelength of the absorption peaks, 640 nm and 540 nm. The effective delocalization length of π-electron has been attributed to the degree of lattice strain on a conjugated PDA main chain, since the lattice strain on a main chain can disturb the conjugation of π orbitals along the series of alternate single, double, single and triple bonds, consisting an acetylenic main chain.[3] Based on this interpretation, the wavelength of the absorption peak of PDA should shorten consistently with an increase of lattice strain. In the case of the blue-to-red phase transition, however, a shortening of the wavelength of the absorption peak was not observed, but both an appearance of the absorption peak for the red form and a disappearance of the absorption peak for the blue form was observed. This apparently indicates that the interpretation on the lattice strain mentioned above is not correct. It was also reported that the absorption peak at the wavelength of 704 nm was detected upon photopolymerization of the annealed Langmuir-Blodgett (LB) film of cadminium 10,12-tricosadiynoate.[4] The new spectroscopic phase was designated the bluish-green form. The electronic structure of the bluish-green form has been remained unrevealed as yet. Therefore, in order to obtain the PDA LB films with superior nonlinear optical characteristics, it is of great importance to investigate the electronic natures to determine these chromatic phases. In this letter, molecular packings of the blue, the red and the bluish-green forms for the polymerized cadmium 10,12-tricosadiynoate LB films have been clarified by the electron diffraction (ED) analysis for the first time. A electronic nature specifying the chromatic phase of PDA was proposed.

A benzene solution of 10,12-tricosadiynoic acid was prepared at the concentration of 2.0×10^{-3} mol.l^{-1}. The solution was spread on the water subphase containing 4.0×10^{-4} mol.l^{-1} of $CdCl_2$ and 5.0×10^{-5} mol.l^{-1} of $KHCO_3$ at the subphase temperature of 286 K.[4] The monolayer formed on the water surface was transferred onto the SiO substrate at the surface pressure of 35 mN·m^{-1}. The hydrophilic SiO substrate was prepared by vapor-deposition of SiO onto a Formvar-covered electron microscope grid (200-mesh) for ED analysis. The number of transferred monolayers for the LB film was 19. Polymerization of the LB film on the SiO substrate was carried out by UV light irradiation (UL1-5EB-6A, Ushio Co., Ltd.) in N_2 atmosphere. The PDA blue form was prepared by photopolymerization of the monomeric LB film. The PDA red form was obtained by heating the blue form up to the temperature of 353 K. Also, for the preparation of the bluish-green form, the monomeric LB film was pre-annealed at 323 K for 1 hr before photopolymerization of the LB film. The Visible absorption spectra of the LB films were obtained using a Shimadzu MPS-2000. ED patterns were taken with a Hitachi H-7000 electron microscope, which was operated at an acceleration voltage of 75 kV. The spot size of electron beam was 2 μm in diameter.

Figures 1(a), (b) and (c) show the Visible absorption spectra of the PDA LB films in the blue, the red and the bluish-green forms. The blue form has the main absorption peak at 640 nm and the phonon sideband at ca. 580 nm. On the other hand, the red form has the main absorption peak at 540 nm and the sideband at 500 nm. Furthermore, the absorption peak at 704 nm and the

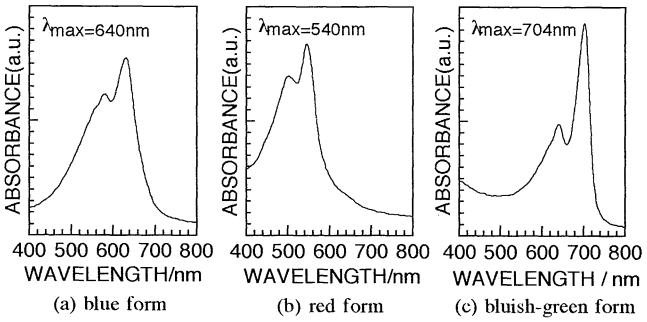

Figure 1. Visible absorption spectra of the PDA LB films in various chromatic phases.

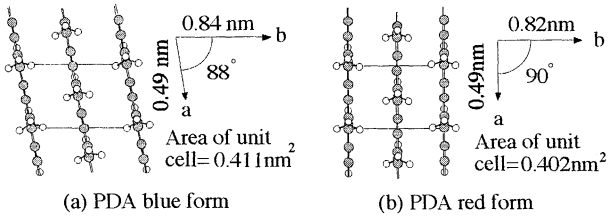

Figure 2. Schematic molecular packings of the PDA LB films in the blue and the red forms.

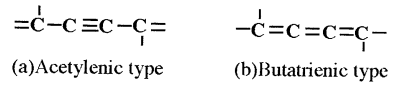

Figure 3. The two resonance backbone structures of the PDA.

sideband at 640 nm were observed in the Visible absorption spectrum of the bluish-green form. The ED patterns of the PDA LB films in each form exhibited crystalline spots.

Figures 2(a) and (b) show the schematic molecular packings of the PDA LB films in the blue and the red forms, respectively. Side chains along a PDA chain are not shown in the schematic drawing for simplification. The two-dimensional (2D-) lattice parameters, the *a* and the *b* axes lengths, the areas of the unit cells and the *a*-*b* axes angles are shown in Figure 2. These possible molecular packings were calculated from the ED patterns so that the repeating unit distances of main chain along the *a* axis agree with 0.49 nm for the acetylenic backbone structure calculated by the *ab* initio method.[5] Though the two resonance backbone structures, that is, the acetylenic and the butatrienic types as shown in Figure 3 have been predicted for the PDA derivatives, the resonance backbone structure of PDA in only both the blue and the red forms was determined to be the acetylenic type based on the ultra-violet photoelectron spectroscopic analysis.[6] The molecular packings of the PDA blue and red forms took 2D- oblique and rectangular crystal systems, respectively. This means that the conjugated main chains are inclined-stacked with respect to the translational lateral-chain axis *i.e.*,*b*-axis in the case of the blue form, while the conjugated main chains in the red form are stacked perpendicular to the *b*-axis. This relationship between molecular packing and spectroscopic property of PDA is similar to that of dye molecule with a large electric dipole transition moment along its long axis. A number of dye molecules have two characteristic exciton energy levels attributed to its distinct packings of the molecules, the so-called j-aggregate and h-aggregate.[7] Figure 4 illustrates the schematic molecular packings of the j-aggregate and the h-aggregate for the dye molecules. In the case of the j-aggregate, the dye molecules are inclined-stacked with respect to the translational lateral axis. On the other hand, the dye molecules in the h-aggregate are perpendicularly stacked to the translational lateral axis, as shown in Figure 4. The h-aggregate has the higher exciton energy level than the j-aggregate. The difference in the exciton energy level between the j- and the h-aggregates of the dye molecules can be explained in terms of the electrostatic interaction of transition moment among adjacent molecules.[7] Therefore, the difference in the spectroscopic property (exciton energy level) between the blue and the red forms of PDA might be attributed to their molecular packings, *i.e.*, the stacking manner or the orientation of the main chains, since the PDA chain also has the large electric transition dipole moment along the conjugated

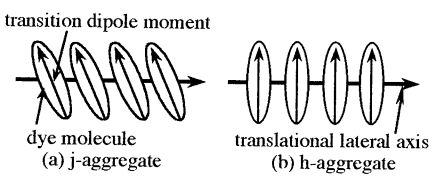

Figure 4. Schmatic molecular packings of the j-aggregate and the h-aggregate.

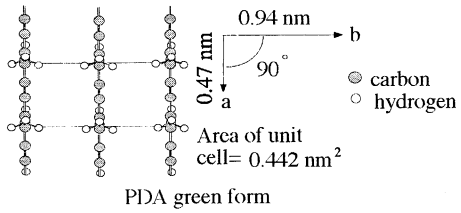

Figure 5. Schematic molecular packings of the PDA LB films in the bluish-green form.

main chain.

Figure 5 shows the schematic molecular packings of the PDA main chain in the bluish-green form. Molecular packings of the bluish-green form could be determined unconditionally, since the ED pattern for the bluish-green form exhibited 2D- monoclinic crystal lattice. Though the conjugated main chains in the bluish-green form were perpendicularly stacked to the *b*-axis (the translational lateral axis), the repeating unit distance of the main chain was 0.47 nm of which magnitude was apparently different from 0.49 nm of the blue and the red forms. This indicates that the resonance backbone structure of the bluish-green form might be the butatrienic type rather than the acetylenic type as shown in Figure 3, since the repeating unit distance for the butatrienic type is predicted to be 0.483 nm on the basis of the *ab* initio calculation.[5] This also means that the bluish-green form has the energy level of the ground state that is different from those for the blue and the red forms.

In conclusion, the difference in the spectroscopic properties of PDA in the three different forms could be elucidated in terms of the PDA molecular packings. The PDA blue and red forms have the acetylenic type main chains with different stacking manner causing the difference in the exciton energy level between two forms. On the other hand, the bluish-green form has the butatrienic type main chain. The electronic natures of the PDAs are strongly dependent on their resonance backbone structures and also, the stacking manners of the main chains.

References and Notes

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