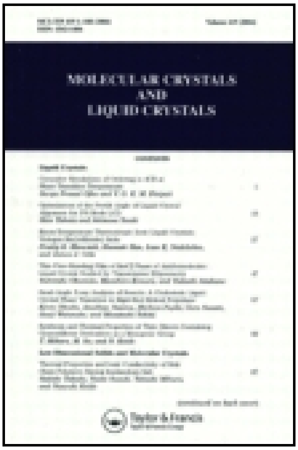

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UPS AND XANES STUDIES OF PHOTOPOLYMERIZATION OF LONG-CHAIN DIACETYLENE COMPOUNDS

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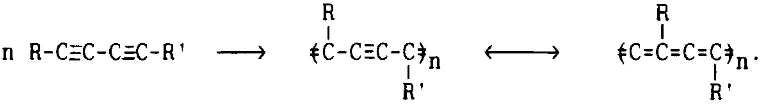
Abstract Photopolymerization process was studied by UV photoelectron spectroscopy (UPS) and X-ray absorption near edge (XANES) spectroscopy for long-chain diacetylene tricosa-10,12-diynoic acid and its Cd salt in the form of oriented evaporated films and Langmuir-Blodgett films, respectively. The UPS results revealed a large reduction of ionization energy due to the pi-band formation. The XANES results also showed spectral changes caused by the formation of pi* band.

INTRODUCTION

Many diacetylenes R-C≡C-C≡C-R' polymerize by UV irradiation to form polymers with conjugated pi electron system as



$$n\ \mathrm{R{-}C{\equiv}C{-}C{\equiv}C{-}R'} \longrightarrow \left(\underset{\mathrm{R'}}{\overset{\mathrm{R}}{\mathrm{C}}}\mathrm{{-}C{\equiv}C{-}}\mathrm{C} \right)_n \longleftrightarrow \left(\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{=}C{=}C{=}}\underset{\mathrm{R'}}{\mathrm{C}} \right)_n .$$

(Acetylenic) (Butatrienic)

This reaction proceeds in various states such as single crystals,[1] Langmuir-Blodgett (LB) films,[2] and evaporated films.[3] Besides this unique polymerization procedure, possible use of their large nonlinear optical coefficients of these systems attracts much attention.[4]

In this work, we report the studies of the electronic structure of long chain diacetylene compound tricosa-10,12-diynoic acid (R = $CH_3(CH_2)_9$, R' = $(CH_2)_8$) and its Cd salt in thin films prepared by vacuum evaporation[5] and LB technique,[6,7] respectively. The occupied and unoccupied states were examined using UV photoelectron spectroscopy (UPS) and X-ray absorption near edge structure (XANES) spectroscopy.

EXPERIMENTAL

The sample of tricosa-10,12-diynoic acid was purchased from Dojin Chemical. Evaporated films were formed on NESA glass substrates to about 10 nm (UPS) and 100 nm (XANES) thickness. For preparing LB films, the monolayer was spread on an aqueous subphase containing 3 x 10^{-4} M $CdCl_2$ and 5 x 10^{-5} M $KHCO_3$, and the multilayers were deposited at 15 mNm^{-1} and 15 ^{o}C to a thickness of 5 layers (UPS) and 20 layers (XANES) on Cu discs (UPS) or NESA glasses (UPS and XANES) by the vertical dipping method. Also we examined films prepolymerized in the monolayer state on water and then transferred to NESA glass substrate. Polymerization was caused by irradiation from a Xe lamp or a D_2 lamp.

The UPS spectra were measured using either monochromatized H_2 discharge or Xe I resonance discharge (Cd salt). Energy analysis was performed using a retarding-field type electron energy analyzer.[8]

The XANES spectra were measured in the C1s absorption edge region at the beamline 11A of National Institute for High Energy Physics (KEK-PF) using a Grasshopper monochromator in the total electron yield mode. The energy resolution was 0.3-0.7 eV.

RESULTS AND DISCUSSION

UPS

In Fig. 1 we show the UPS spectra of evaporated tricosa-10,12-diynoic acid before and after polymerization by the Xe I resonence line ($h\nu$ = 8.42 eV). The abscissa is the binding energy (ionization energy) relative to the vacuum level. The ionization threshold energy I_{th} is determined from the right hand onset to be 7.0 eV. After polymerization, both blue and red forms show similar spectra, with I_{th} of 5.2 and 5.1 eV, respectively, which are much smaller than that of monomer.

This reduction of 1.7 eV in I_{th} can be understood with the lower half of the energy correlation diagram in Fig. 2. The pi electronic states of the diacetylene monomer are composed of doubly degenerate bonding (π_1) and antibonding (π_2)combinations of the pi HOMO of acetylene. On polymerization, the $2p_z$ orbitals vertical to the molecular plane form delocalized pi band, with the top (π_t) 1.7 eV higher than the HOMO of diacetylene. In the acetylenic form, which is known to be the case at least for the blue form,[9] the 2p orbitals in the molecular plane at each triple bond form localized pi bond (π_n). With the known splitting 2.4 eV[10] between the $_1$ and $_2$ orbitals of diacetylene, and assuming a symmetric band, the total width of the pi band is estimated to be 5.8 eV. The similarity of I_{th} excludes the possibility of red form being in the butatrienic form, in which I_{th} is expected to be 0.5 - 1.0 eV higher than in the acetylenic form.[11-13]

Very similar results were obtained for the LB films of the Cd salt. The value of I_{th} changes from 6.7 eV in the monomer to 5.1 eV in the polymer both in blue and red states. The small difference from the neutral acid may be due to the Madelung energy in the ionic Cd salt.

XANES

In Fig. 3 we show the wide scan C1s spectrum of an evaporated film of tricosa-10,12-diynoic acid before and after polymerization. The real

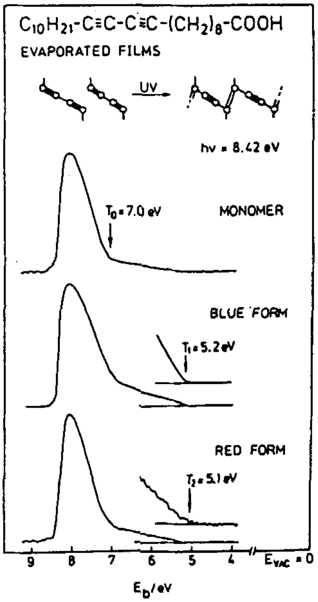


FIGURE 1. Change of the UPS spectra on photopolymerization. (a) monomer, (b) blue form of polymer, and (c) red form of polymer. Arrows indicate the ionization threshold energies.

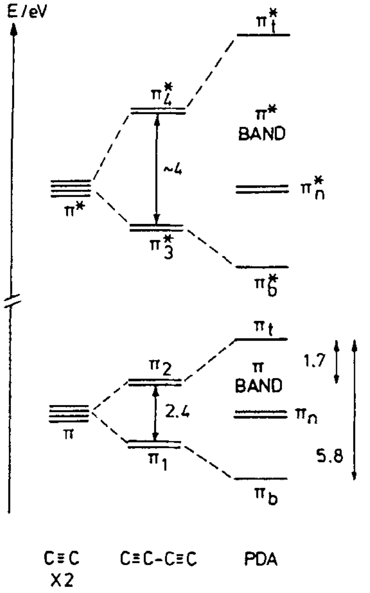
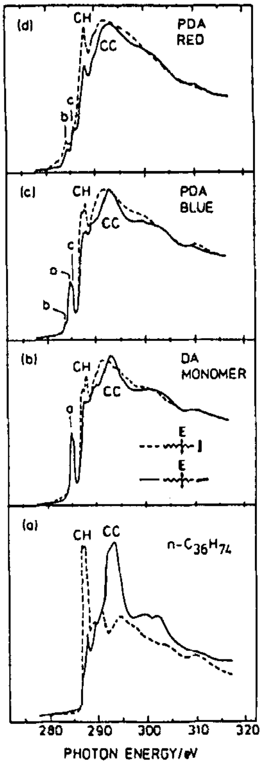


FIGURE 2. Energy level diagram of acetylene, diacetylene, and polydiacetylene. Lower and upper halves correspond to the occupied and vacant sates, respectively.

and broken lines correspond to the grazing and normal incidence of photons, with the electric vector almost vertical and parallel to the substrate surface. The spectra in the high energy region aove 286 eV are dominated by the excitation in the alkyl part as seen from the good correspondence with the spectra of evaporated long chain alkane n-$CH_3(CH_2)_{34}CH_3$ (Fig. 3(a)),[14] in which molecules are known to stand vertical to the substrate. The features in Fig. 3(a) are assigned to the excitation from the C1s orbital to the antibonding sigma orbitals localized at the CH and CC bond,[15] as indicated in the figure.

The anisotropy of the monomer spectrum in Fig. 3(b) is much less than that of vertically standing alkane, and even than that of Ca arachidate LB film, for which Outka and Stoehr[16] estimated the tilt angle of 33°. This corresponds to the estimation of about 44° from X-



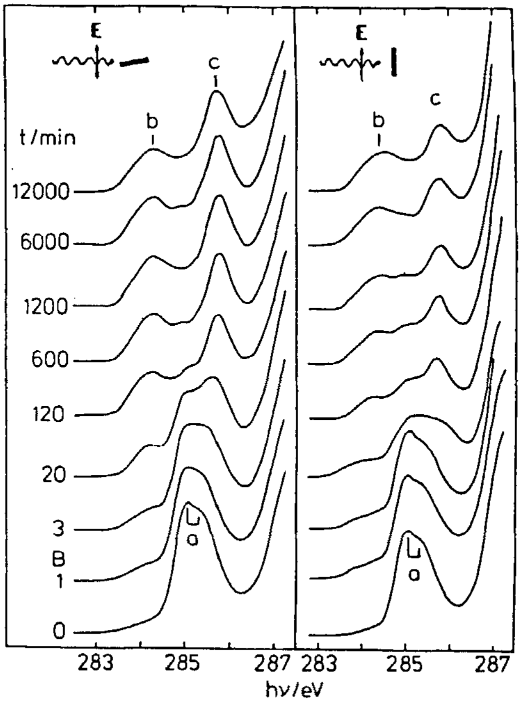


FIGURE 3. Change of the wide scan C1s XANES spectra of an evaporated film of the neurtral acid. (a) n-$C_{36}H_{74}$ as a reference, (b) monomer, (c) blue form polymer, and (d) red form polymer.

FIGURE 4. Change of the XANES spectra in the C1s → pi* excitation region. UV irradiation time is shown for each curve.

ray diffraction for the monomer film. On polymerization, anisotropy does not change significantly, while the fine features are smeared out. Correspondingly, X-ray diffraction intensity is decreased, indicating disorder formation in the film.

The spectra in the region below 286 eV corresponds to the excitation to the pi* levels. The spectral change in this region on polymerization is shown in Fig. 4, for grazing and normal incidence. The anisotropy is small, indicating inclination of unsaturated parts to the substrate surface. The monomer spectrum at the bottom shows a single peak with doublet structre. On UV irradiation, it changes into two peaks. This change is explained using the upper half of Fig. 2, with the knowledge that the excitation to a delocalized pi* system tends to concentrate to the bottom of the pi* system due to the core hole effect.[17] The monomer peak corresponds to the excitation to the lower unoccupied MO (π_3). The low and high energy peaks in the polymer spectra are due to the excitations to the lower edges of the two independent pi* systems, $\pi^*{}_b$ and $\pi^*{}_n$, respectively. These spectra have two isosbestic points at 284.6 and 285.6 eV, indicating that the polymerization is continuous, without specific intermediate state even around 5 minutes irradiation, which corresponds to the blue form.

These results were also directly examined by MO calculations in the CNDO/S formalism using equivalent core approximation.[17] The simulated spectra confirm the above-stated assignments. Further, they indicate that the doublet feature of the monomer spectrum may correspond to the excitations of 2 inequivalent carbon sites, with the the inner carbon correspond to the lower energy excitation.

For LB films, qualitatively similar results were obtained for the alkyl part, but the results for the excitation to the pi* orbitals were differernt for the films polymerized after transferring to the substrate. Firstly, the blue form film were converted into the red form during the XANES measurements, making the measurement of the blue form impossible. Secondly, the appearance of the two peaks is not so clear as in the evaporated film and the reproducibility of the spectrum was poor, as seen in the spectrum in Fig. 5(a). This suggests incomplete polymerization, possibly due to disorder in the transferred films. On the other hand, films prepolymerized on water was in already in the red form, and showed similar spectrum to the evaporated film.

Corresponding incomplete and complete polymerization was also suggested by the visible absorption for the films on NESA glass substrates.

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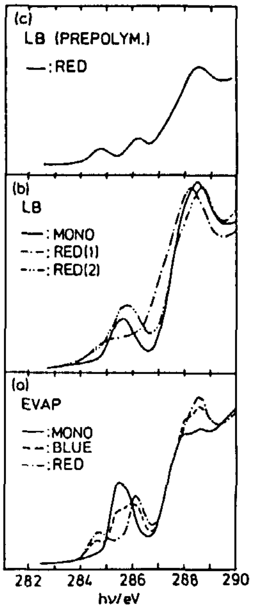

FIGURE 5. Comparison of the C1s→ pi* XANES spectra of (a) evaporated film, (b) LB film polymerized after transfer (2 samples), and (c) LB film prepolymerized on water.

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