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CHANGE OF ELECTRONIC ABSORPTION SPECTRA OBSERVED THROUGH HEATING EVAPORATED THIN FILMS OF A DIACETYLENE COMPOUND

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Abstract A vapor-deposited thin film of *N*-[4'-(5"-hydroxypenta-1",3"-diynyl)-benzylidene]-4-octyloxyaniline, which is one of the diacetylene compounds, demonstrated a drastic change of its electronic absorption spectrum characterized by the absorption edge being expanded to the near-infrared region, associated with heating its substrate above 100 °C. X-ray diffraction patterns of the film revealed that there are three different stages for the film at temperatures elevated through heating. As it has been confirmed that the molecule concerned suffers no chemical change through the heat treatments, those observed phenomena can be understood to be induced by a characteristic change in intermolecular electronic interaction via modification of molecular aggregation forms caused by substrate heating.

INTRODUCTION

Solid state polymerization of diacetylenes has drawn much attention, while conditions for their polymerization reactions are rather restricted.[1] To extend such reactivities of diacetylenes, *N*-[4'-(5"-hydroxypenta-1",3"-diynyl)benzylidene]-4-octyloxyaniline (C_8BADAOH) (see Figure 1) was designed as a diacetylene monomer open to liquid-crystalline states[1] and has been studied on its polymerization under heating in the liquid-crystalline state as well as in the crystalline state.[2]

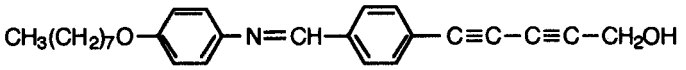

FIGURE 1 Molecular structure of C_8BADAOH.

On the other hand, we have recently made evaporated thin films of C_8BADAOH in the thickness of about 100 nm to examine the possibility of its thermal polymerization in such films, and, as a result, we have observed a notable behavior different from the polymerization as presented in this paper.

EXPERIMENTAL

C_8BADAOH with a mesogenic core of benzylidene(4-octyloxy)aniline moiety was prepared by the condensation of 4-octyloxyaniline and 4-(5'-hydroxypenta-1',3'-diynyl)benzaldehyde.[4] The obtained compound was separated using gel permeation chromatography and purified by repeated recrystallization from chloroform and, as occasion demands, by vacuum sublimation which competes with thermal reaction to a large extent.

C_8BADAOH thin films in the thickness of 40–300 nm were vapor-deposited at high deposition rates onto quartz glass plates at room temperature in the vacuum of 10^{-3} Pa. Such films were heated at intervals on a hot plate or in an electric oven at different temperatures including the temperature range 110–130 °C at which polymerization reactions are confirmed to occur in the bulk of C_8BADAOH.[3,5] Effects of these heat treatments to the thin films were examined using electronic absorption spectra, X-ray diffraction (XD) patterns, infrared (IR) absorption spectra and electron diffraction (ED) patterns, where each measurement was carried out at room temperature.

RESULTS AND DISCUSSION

Experimental results of differential scanning calorimetry (DSC) and XD for the bulk C_8BADAOH indicate that there are four different phases in the temperature range from room temperature up to about 150 °C: crystal I, crystal II, smectic and nematic phases, among them transition temperatures are determined as 96, 115 and 123 °C in order.[5]

X-ray Diffraction Patterns and Electronic Absorption Spectra

A C_8BADAOH as-deposited film showed an electronic absorption spectrum almost similar to that of a solution cast film; positions of spectral features were in good agreement with each other, however, their relative intensities were slightly different between the two spectra. On the other hand, an XD pattern of the film, which is characterized by three peaks corresponding to interplanar spacings of 29.7 (s), 15.0 (m) and 7.5 (w) Å was different from each pattern of powder XD for crystal I (at 25 °C), II (at 102 °C) and smectic (at 106 °C) phases of the bulk C_8BADAOH,[5] where s, m and w indicate that the peak intensities are strong, middle and weak, respectively. As an XD peak of a thin film deposited on a flat substrate corresponds to a spacing between periodic planes parallel to the substrate surface, an oriented molecular film usually demonstrates its XD pattern different from the powder pattern of the same material. However, the differences in the XD pattern noted above are not limited to the relative intensities but are recognized much in the peak positions. A molecular aggregation form

in the evaporated thin film could therefore be different from that of each phase in the bulk.

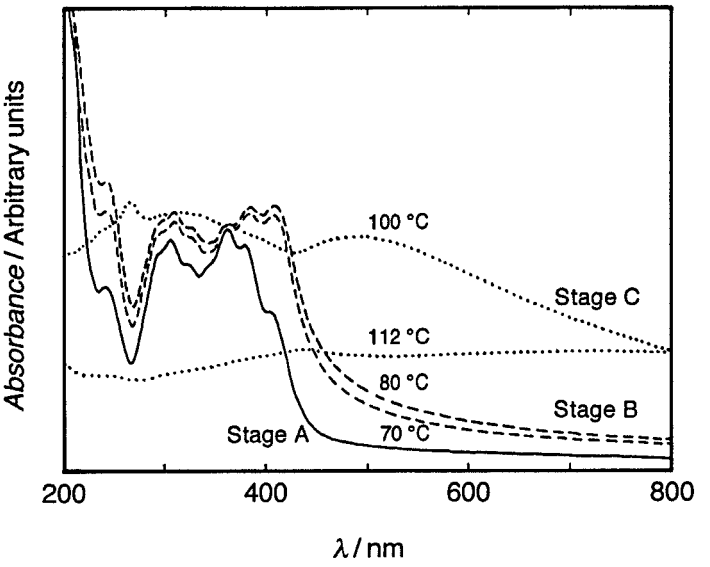

FIGURE 2 Electronic absorption spectra of C8BADAOH evaporated thin films after heating at temperatures written beside respective spectra except for the bottom one, the spectrum of as-deposited film.

Electronic absorption spectra of the evaporated thin films were recorded after every intermittent heat treatment at several temperatures. Heat treatment at 70–80 °C caused a small shift of spectral features at the maximum wavelength region, and, in particular, the absorption peak at the maximum wavelength λ_{max} shifted from 400 to 410 nm, as shown in Figure 2. However, further spectral change was not observed for prolonged heating at the same temperatures as above. The XD pattern of thus-heated films changed remarkably from that of as-deposited films: The three peaks above disappear thoroughly and, in place of them, two peaks corresponding to interplanar spacings of 20.5 (m) and 10.3 (w) Å reveal themselves, moreover, a small bump corresponding to 4.5 Å is often recognized. These changes in the XD pattern are exhibited in Figure 3.

The results obtained for C8BADAOH evaporated thin films heat-treated at about 110 °C appear to be noteworthy. Such heating induced an eminent change of electronic absorption spectra with notable red shifts of the spectral feature and/or the absorption edge at the maximum wavelength region: such spectral shifts reached over the visible light region to the near-infrared one with the prolonged heating, though their absorption

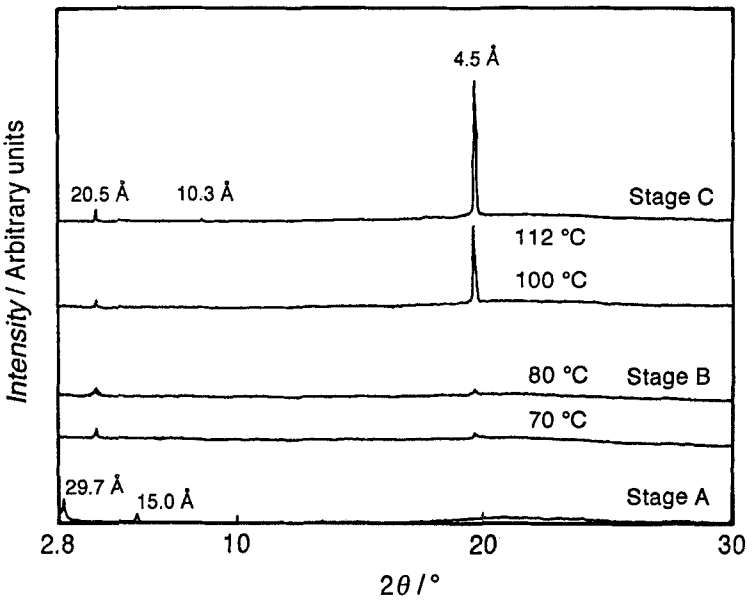

FIGURE 3 X-ray diffraction patterns of C8BADAOH evaporated thin films after heating at temperatures written beside respective spectra except for the bottom one, the pattern of as-deposited film.

intensities decreased gradually. These changes are clearly shown also in Figure 2. In accordance with such changes, XD patterns of those films demonstrated a simple change that a diffraction peak corresponding to an interplanar spacing of 4.5 Å, which was observed faintly in the pattern of the films heated at 70–80 °C and yet rather hard to be assigned on the basis of the powder pattern of C8BADAOH, grew up on and on with decreasing two peaks to be the same as observed for the films heated at 70–80 °C as the heat treatment at about 110 °C was prolonged. An example of such XD patterns is exhibited in Figure 3.

Thus, an evaporated thin film of C8BADAOH is understood to undergo three stages with increasing heat-treatment temperature: the stage A is just as-deposited state and the stages B and C can be realized after heated at 70–80 °C and at about 110 °C, respectively. The three stages observed for the film could not necessarily correspond to thermodynamically stable states, while no change in the electronic absorption spectrum was affirmed for the film heated below 70 °C and heat treatments above 120 °C caused changes much similar to those observed for the film in the stage C. Bearing this in mind, we will examine the characteristics of the three stages in more detail using other experimental results of the film. In particular, as the stage C appears to be rather unique

state, most discussion will be given to this state.

The drastic spectral change mentioned above was common to all films in the stage C, that is, the behavior was independent of their thickness. This observation excludes the possibility of spectral change to be caused by an extrinsic or trivial phenomenon, such as interference of light by the film. Besides, although the position of absorption maximum or absorption edge in the long wavelength region moves over the visible light region with prolonged heating of the film in the stage C as pointed out above, it is brought to an end, which is examined to depend on the film thickness, after a heat treatment for a long enough time.

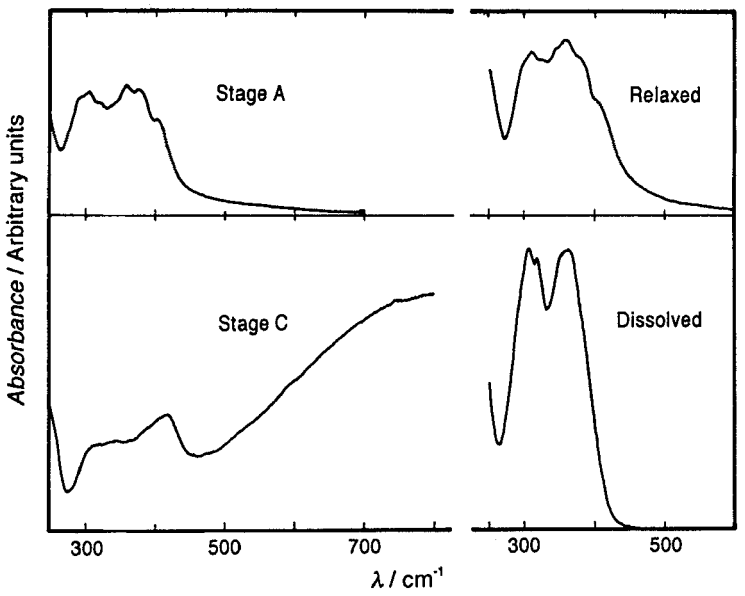

FIGURE 4 Electronic absorption spectra of a C8BADAOH evaporated thin film. As-deposited film in the stage A was heated at 115 °C to give a stage C film and a 'relaxed' film was made after dripping a little solvent onto it and evaporating the solvent, further, a 'dissolved' solution obtained by washing the relaxed film out from the substrate.

To check the possibility of polymerization in the film of the stage C, we examined the electronic absorption spectra of a 'relaxed' film obtained after dripping a little solvent onto the film of the stage C and evaporating it and also of its 'dissolved' solution obtained by washing it out from the substrate. As these spectra shown in Figure 4 were in good agreement with those of a solution cast film and a liquid solution, respectively, it was confirmed that the drastic change in the spectrum of the stage C film is not induced by polymerization, so that it appears to be caused by formation of a specific

intermolecular ordering realized only in the evaporated thin film via the heat treatment at 110 °C.

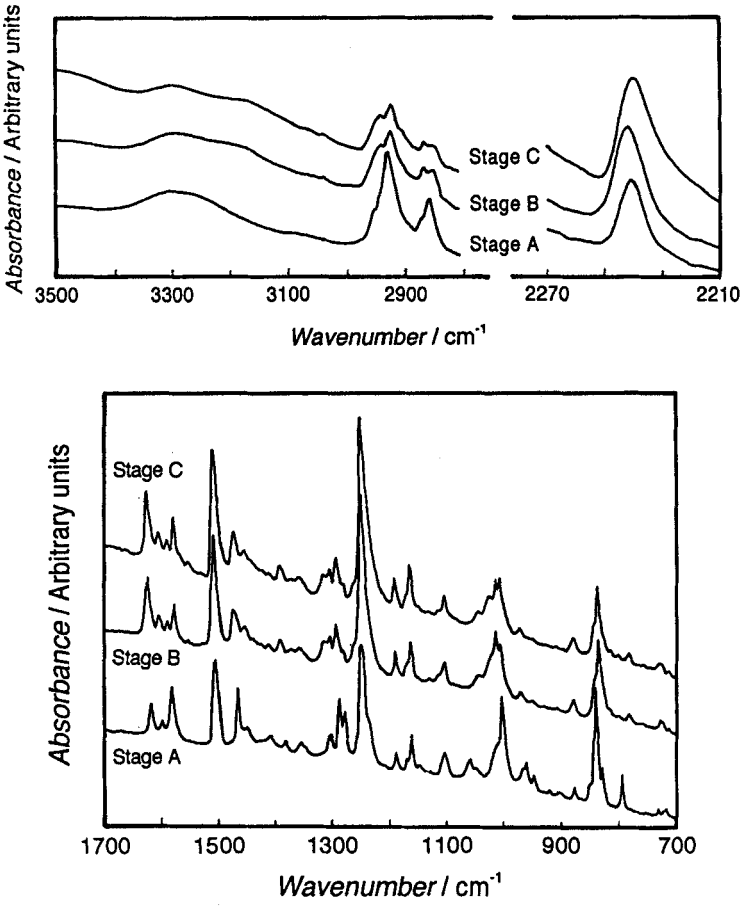

FIGURE 5 Infrared absorption spectra of C_8BADAOH evaporated thin films in the three stages.

Infrared Absorption Spectra

Infrared absorption spectra of the films in the three stages were compared with one another to obtain information on any structural differences among them. In the whole measured spectral range from 3500 to 700 cm^{-1} in wavenumber, spectra for the stages B and C agree with each other in general, while they are certainly different from that for the stage A. This indicates that microscopic structures of a C_8BADAOH molecule are more changed in the transition of the stage from A to B than in that from B to C.

A new absorption feature appeared at about 3200 cm^{-1} and a red shift with a decreased intensity of a spectral band observed between 3000 and 2800 cm^{-1}, which is

assigned to the C–H stretching mode of alkyl chains, are noted through the transition from A to B in the high wavenumber region. The former feature indicates an additional type of hydrogen bond is formed in the stage B film, while a similar feature is observed in the IR spectrum of the bulk C_8BADAOH in the crystal I phase,[5] and the latter spectral change appears to be due to a conformational change of alkyl chains[6] to all-*trans* form with making their orientation parallel to the substrate surface.

The increasing intensities of both absorption peak at about 2240 cm^{-1} which is to be assigned to an anti-symmetric stretching of C≡C–C≡C[3] and the peak at about 1620 cm^{-1} which is assigned to a C=N stretching for the transition to the stage B indicate the increase of molecular-chains oriented parallel to the substrate. The absorption band located between 1600–1450 cm^{-1} to be assigned to vibrational modes of the skeleton of a benzene ring changes notably on going from the stage A to B to suggest a significant conformational change around the *N*-benzylideneaniline part of the molecule.

Further, both anti-symmetric and symmetric stretching modes of C(aromatic)–O–C at about 1250 and 1050 cm^{-1}, respectively, exhibit red shifts from the stage A to B; through the same transition, the band at about 1300 cm^{-1} to be assigned to C–O stretching and O–H deformation modes of a hydroxymethyl group appears to have a blue shift, and an out-of-plane deformation mode of a C(aromatic)–H bond at about 860 cm^{-1} shows a notable change in its lineshape. These behaviors suggest a molecular conformational change with a change of the angle C(aromatic)–O–C and the hydrogen bond at the terminal of a molecule and also with increasing face-to-face configuration between its phenyl groups and the substrate.

Additional Experimental Results

Other experimental results to be described below will be useful for the discussion on the concerned change of electronic spectra with heating a C_8BADAOH evaporated film. First, no fluorescence emission spectrum have been observed for the films of all stages. Secondly, a thin film in each stage was tried to be removed from the substrate and the electronic and IR absorption spectra have been measured for a KBr pellet made from the film. No electronic absorption feature in the long wavelength region has been observed for all the pellet, and each obtained spectrum agrees with one another and almost corresponds to that of the evaporated film in the stage A, while relative intensities among spectral features are in rather good agreement with those for a cast film.

On the other hand, the IR spectrum of the pellet made from the stage A film has been noted to be not so different from those of the pellets from the films in the other stages: the spectral feature reflecting hydrogen bonds in the range from 3400 to 3100 cm^{-1} are common to the three pellets and in fairly good agreement with that of the

evaporated film in the stage A, and their bands assigned to vibrations of the skeleton of a benzene ring appears to be similar to those in the spectra of the evaporated films in the stages B and C, while both anti-symmetric and symmetric stretching modes of C(aromatic)–O–C for the three pellets are different in the spectral features from those for the evaporated film in each stage.

Finally, the electron diffraction pattern, a peak of which corresponds to a spacing for the in-plane periodicity in a thin film, have shown a peak corresponding to 4.5 Å as such a spacing for the film transferred onto a metal mesh, but only for the film prepared from the evaporated film in the stage A. This suggests that in terms of the 4.5 Å periodicity observed by either XD or ED in the alternate cases the molecular orientation in the stage A film is in almost perpendicular relation to that in the stage C film.

Supposed Outline of the Changes Observed

A brief consideration of the change in the molecular aggregation form and the electronic state of the evaporated film of C_8BADAOH through heating at about 110 °C will be described below. In the stage A film C_8BADAOH molecules could have an orientation almost perpendicular to the substrate surface and may be bound by hydrogen bonds with each other to form the 4.5 Å spacing as an in-plane periodicity in the film. By heating the film at 80–90 °C those molecules could tend to lie down on the substrate to form an aggregation characteristic of the stage B, where an additional hydrogen bond is created, accompanied with their conformational changes in the parts of *n*-octyl chain, phenol ether and/or *N*-benzylideneaniline. Besides, several studies show that conformational changes of *N*-benzylideneaniline derivatives lead to several tens nm of their spectral red shifts at most.[7–9]

Further heating at about 110 °C has brought the film to the stage C which appears to be even more specific to the evaporated thin film of C_8BADAOH than the stage B. In the stage C, an ordered structure suggested by a periodic spacing of 4.5 Å normal to the substrate surface has remarkably been growing with the increase of heating time and such a behavior reminds us of the crystal growth in general. The drastic change in the electronic absorption spectrum mentioned above is observed only for the evaporated thin film in this stage. The additional hydrogen bond formation might take an important role in this spectral change: a dimeric molecular aggregation and/or a network structure to be formed through different kinds of hydrogen bonds could induce a characteristic electronic state of the film. To such an electronic state a local charge-transfer interaction may have some contribution, since the C_8BADAOH molecule could be regarded as a molecule which has both electron-donating and -accepting parts in the same molecule.

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