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Heat-induced Crystal Transformation of Synthetic Bilayer

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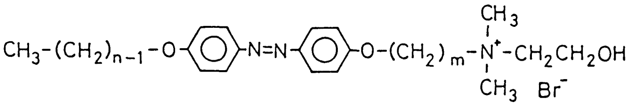
The side-by-side arrangement of azobenzene chromophores (H-aggregate) in the self-supporting cast films of $C_8AzoC_{10}N^+Br^-$ changes to the head-to-tail arrangement by heating above 115 °C (J'-aggregate) and by cooling below 60 °C after annealing above 115 °C (J-aggregate). The J-aggregate changes further to the original H-aggregate by absorbing water molecules in the atmosphere.



$C_nAzoC_mN^+Br^-$
(n=12,10,8,6; m=10,8,6,5,4,2)

Totally synthetic bilayer-forming amphiphiles have become important because of their structural characteristics, such as molecular orientation and phase transition. A series of azobenzene-containing amphiphiles, $C_nAzoC_mN^+Br^-$, shows several types of chromophore aggregation states depending on the number of carbon atoms in the tail (n) and spacer (m) parts of the hydrophobic chain.[1)] The head-to-tail (J-like) aggregation between adjacent chromophores, detectable as a bathochromic shift in the absorption spectra, was found in the single crystals and aqueous dispersion of $C_nAzoC_5N^+Br^-$ (n=12, 10, 8, and 6). Their detailed crystal structures were determined by the X-Ray single crystal analyses and bore out the J-like aggregation of azobenzene chromophores at the atomic level[2,3)] (Fig.1). While the side-by-side (H-) aggregates, in which adjacent azobenzene chromophores are aligned in parallel fashion, shows a hypsochromic shift in the absorption spectra. This was observed for $C_8AzoC_{10}N^+Br^-$ and $C_6AzoC_{10}N^+Br^-$. The X-Ray analysis of the ordered and self-supporting cast films, prepared from aqueous bilayer dispersion of $C_8AzoC_{10}N^+Br^-$, revealed the plausible bilayer structure in which amphiphilic molecules are normal to the bilayer surface and arranged in parallel fashion with interdigitating azobenzene chromophores[4,5)] (Fig.2). In this paper, we report the heat-induced crystal transformation of the cast films of $C_8AzoC_{10}N^+Br^-$, associated with the rearrangement for azobenzene chromophores.

Figure 3 shows differential scanning calorimetry (DSC) curves of cast films prepared from the aqueous solution of $C_8AzoC_{10}N^+Br^-$. The bilayer structure of the original compound ((1) in Fig.3) has been known as the interdigitating H-aggregate. It has two endothermic transitions at 115 °C and 177 °C. From the observation under the polarizing microscope at various temperature, the latter transition temperature was found to be the melting point. The X-Ray diffraction pattern taken at 130 °C ((2) in Fig.3) showed Debye-rings due to the latteral repetitions of the azobenzene moieties and alkyl chains, which indicating that the transition at the lower temperature was not a crystal-liquid crystal transition as usually observed for amphiphilic compounds, but a crystal-crystal transition. In the second run, the transition temperature at 115 °C shifted to 60 °C, while the higher transition temperature (melting point) showed no change (Fig.3). The X-Ray diffraction pattern from the specimen above 60 °C (2') showed exactly the same intensity distribution as that from the state (2). On the other hand, the X-Ray pattern from the specimen at room temperature (3) after heating above 115 °C was very different from that of the original (1), but quite similar to that from the state (2). After this specimen was kept in a high humidity atmosphere, the DSC curve showed the same profile as that of the first run, which suggesting that the molecular arrangement in the specimen changed to the H-aggregate by humidity.

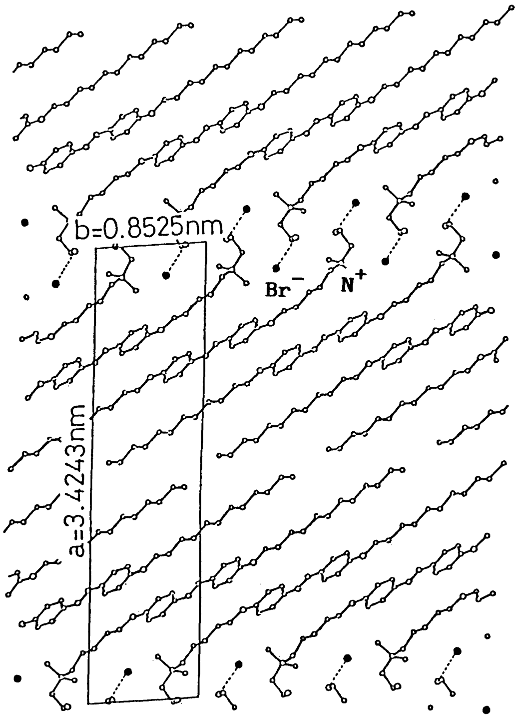


Fig.1. J-like aggregation of the chromophores in the single crystal of $C_{12}AzoC_5N^+Br^-$.

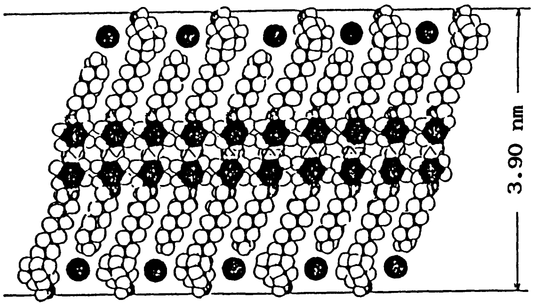


Fig.2. H-aggregation of the chromophores in the cast film of $C_8AzoC_{10}N^+Br^-$.

Figure 4 shows the absorption spectra of cast films of $C_8AzoC_{10}N^+Br^-$. The numbers in Fig.4 correspond to those in Fig.3. The isolated azobenzene chromophore shows an absorption maximum at 355 nm. While the original specimen (1) and the specimen (4) obtained by keeping (3) in a high humidity atmosphere showed the extreme hypsochromic shift (λ_{max}= 300 nm), which suggesting the parallel orientation of the transition dipoles (H-aggregate). On the other hand, the cast films above 115 °C (2) and the films below 60 °C after annealing above 115 °C (2') showed the bathochromic shifts (360-370 nm) in absorption spectra, indicating a head-to-tail orientation of transition dipoles (J-like aggregate). The drastic colour change from pale yellow to deep orange was observed for both the crystalline powder and the cast film as heating above 115 °C on a hot stage. The deep orange colour remained even after cooling the specimen below 60 °C.

The X-Ray intensity distribution based on the repetition of bimolecular layer

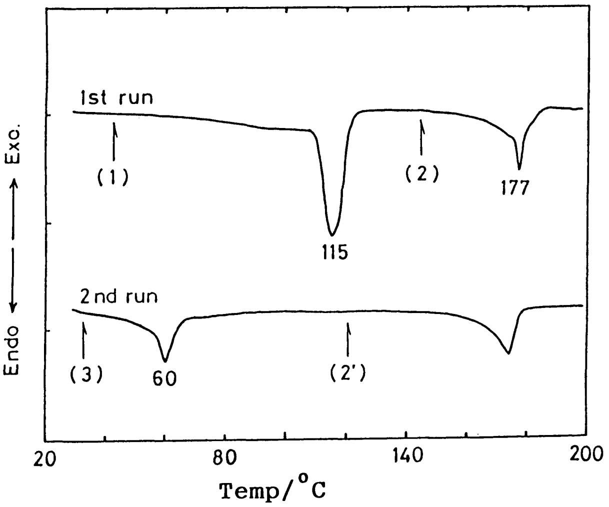


Fig.3. DSC curves of the cast films of $C_8AzoC_{10}N^+Br^-$. The scale on the ordinates corresponds to 2.9 mJ s^{-1}.

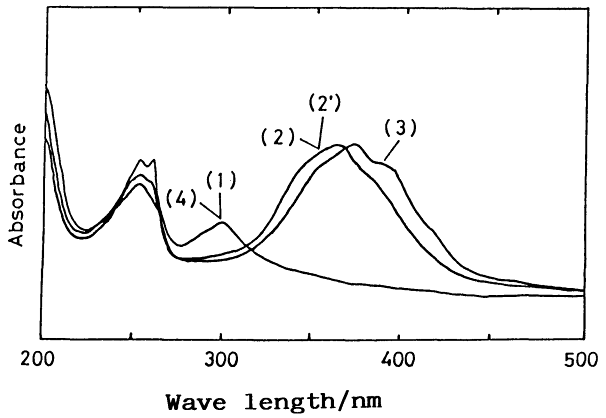


Fig.4. Absorption spectra at various states of $C_8AzoC_{10}N^+Br^-$. The numbers correspond to those in Fig.3.
The specimen (4) was obtained by keeping (3) in a high humidity atmosphere.

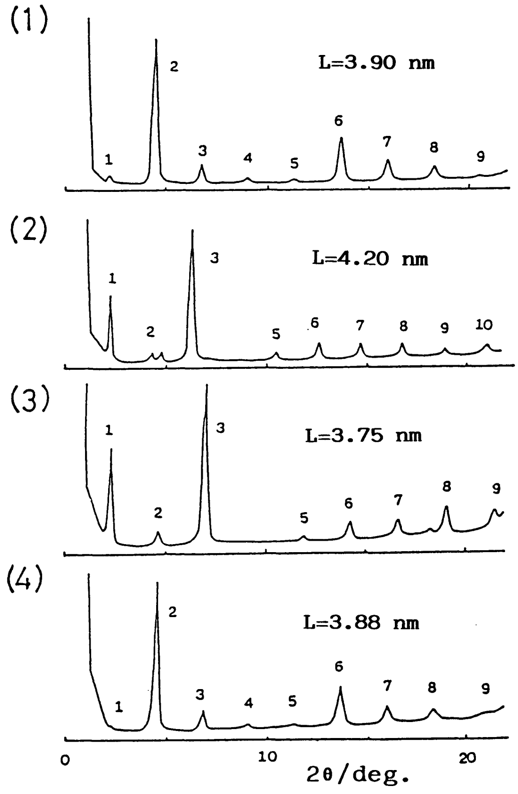


Fig.5. X-Ray diffraction curves for various states of $C_8AzoC_{10}N^+Br^-$. (The numbers in parentheses correspond to those in Figs.3 and 4.) The number for each reflection corresponds to the order of diffraction with the long period L.

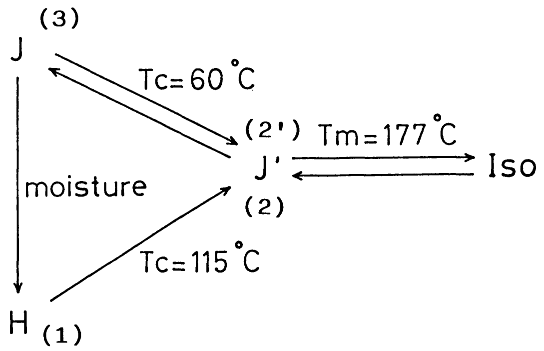


Fig.6. Schematic phase diagram of $C_8AzoC_{10}N^+Br^-$. The numbers correspond to those in Figs.3 and 4.

in the lamella structure for the several states in Fig.3 are shown in Fig.5. By using intensity distribution of the original specimen (1), we have proposed the plausible bilayer structure (Fig.2) consistent with the hypsochromic shift in the absorption spectra. Although the long period (L) are different by about 0.5 nm, the overall profiles of (2) and (3) are quite similar to each other, that is, fairly strong first order reflection, weak 2nd and strong 3rd order reflections. The molecular arrangements for both specimens, therefore, are seemed to be the similar J-like aggregates as suggested from the bathochromic shifts in the absorption spectra (Fig.4). After keeping the specimen at 85%RH in 24 hours, the diffraction curve (4) showed the same kind of the profile as that of the original (1).

Taking into account of the above observations, the phase transitions of cast films of $C_8AzoC_{10}N^+Br^-$ summarizes in Fig.6. The interdigitated H-aggregate changes to the J'-aggregate by heating above 115 °C. By heating further, the J'-aggregate melts at 177 °C. While, by cooling below 60 °C, it changes to the J-aggregate which has a further shift in the absorption spectrum. The processes between $J' \rightleftharpoons$ isotropic and $J' \rightleftharpoons J$ were reversible and depending on temperature. The J-aggregate changes to the H-aggregate by absorbing water molecules, that is, by humidity in the atmosphere surrounding the specimens. This process is irreversible. The rate of this transformation varies depending on the relative humidity and the thickness of the specimen. If the specimen is kept in dry, no phase transition occurs.

In order to clarify the bilayer structures of the J'- and J-aggregates, we are analysing X-Ray diffraction patterns (edge view) including wide angle region and searching the plausible bilayer model from the intensity distributions shown in Fig.5.

References

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