CHEMISTRY LETTERS, pp. 295-298, 1993.

Heat-Induced Structural Changes of Multibilayer Films of Benzylideneaniline- and Salicylideneaniline-Containing Ammonium Amphiphiles[1)]

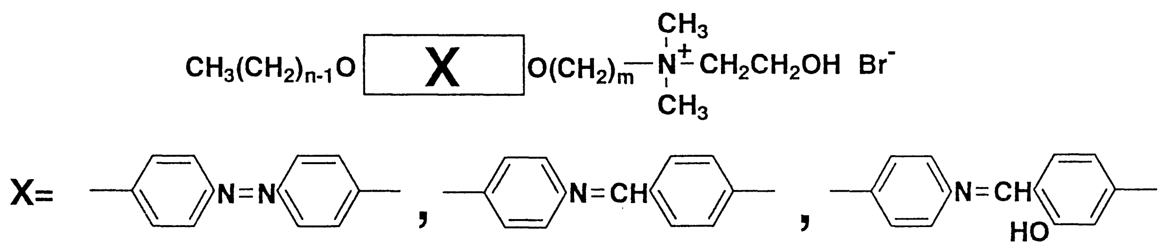
Taisei NISHIMI, Yuichi ISHIKAWA, Toyoki KUNITAKE,* Mari SEKITA,+ Guiqint XU,+ and Kenji OKUYAMA+

Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Fukuoka 812

+Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184

Cast films prepared from benzylideneaniline- and salicylideneaniline-containing ammonium amphiphiles at room temperature possess interdigitated bilayer structures. These molecular assemblies show various types of crystalline modifications above their transition temperatures.

Azobenzene-containing single-chain amphiphiles (**1**) form bilayer structures in water. These structures depend on their alkyl-chain lengths.[2)] For instance, an interdigitated structure was formed from **1**(8,10), as confirmed by X-ray diffraction studies of its cast multilayer[3)] and single crystal.[4)] In contrast, a tilted bilayer structure was found in the case of **1**(12,5).[5)] Interdigitated structures have been also confirmed for cast films of the corresponding benzylideneaniline (**2**)[6)] and salicylideneaniline (**3**)[7)] amphiphiles. It is thus presumed that the molecular organization in bilayers is determined by common features of the partial structure.



1 (n,m)=(8,10) **2** (n,m)=(8,10) **3** (n,m)=(8,10)

The interdigitated structure of the azobenzene bilayer is converted to other assemblies thermally or by contact with water.[8] Such a crystal-crystal transformation can be used to develop novel bilayer-based functions. In this paper, we describe heat-induced structural changes of bilayers **2** and **3**.

Syntheses of the component amphiphiles are described elsewhere.[6] Cast films of **2** and **3** were prepared from their 20 mM aqueous dispersions. Self-supporting, colorless (**2**) or yellow (**3**) films were obtained by slow casting on Teflon sheets at room temperature. X-Ray diffraction (XRD) (instrument, Rigaku RAD-R-32) of these films were measured at every 5 °C from room temperature to 170 °C. The temperature of the specimen was raised with a heating rate of 1 °C/min and kept constant for 5 min to attain equilibration before X-ray irradiation.

Figure 1 shows DSC thermograms (instrument, Rigaku, DSC 8232) of the cast films obtained at a heating rate of 10 °C/min. Complex endothermic behaviors were observed; peaks at 140 °C, 150 °C, 160 °C, and 170 °C for **2** and at 120 °C, 150 °C, and 180 °C for **3**.

The XRD curves of the cast films at various temperatures are shown in Figs. 2 and 3. These patterns are ascribed to four species. The first species observed at low temperatures are typical of the interdigitated structure with a weak 1st order peak and a very strong 2nd order peak. The long spacings are about 39 Å, which is close to their molecular lengths estimated from their CPK models. Moreover, these films show blue shifts in absorption spectra, which indicates the formation of the parallel chromophore packing (so-called "H-aggregate"),[9] consistent with the interdigitated structure.

The 2nd species were found at temperatures near the 1st large endothermic peaks. Their XRD patterns display strong 1st order and 3rd order peaks, which correspond to long spacings of about 44 Å. These XRD patterns are very similar to that of **1** which has been attributed to the tilted bilayer structure (so-called "J-aggregate")[8]. The 3rd and 4th species observed at higher temperatures have long spacings of 59 Å and 63 Å, respectively. Since these spacings are longer than their molecular lengths (39 Å), these species must possess bilayer structures of which tilt angles are different. They show only three XRD peaks, suggesting poor structural regularities. Some differences between transition temperatures obtained by DSC and XRD seem to

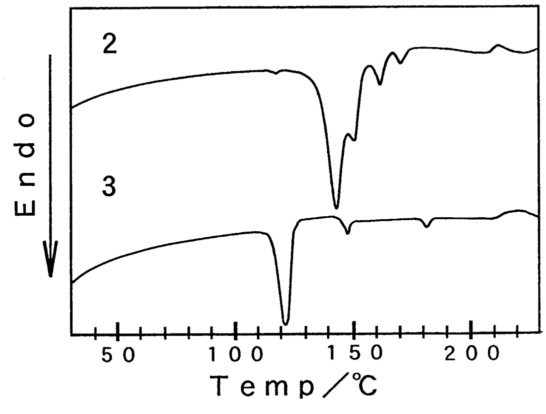


Fig.1. DSC thermograms of cast films of **2** and **3**.

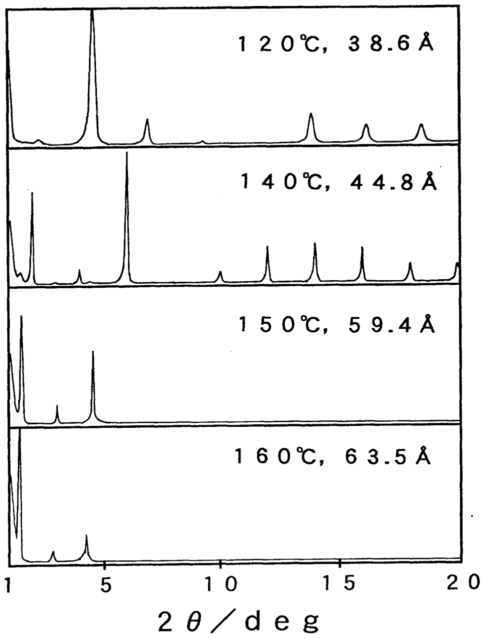


Fig.2. Heat-induced changes in XRD patterns of cast film of **2**.

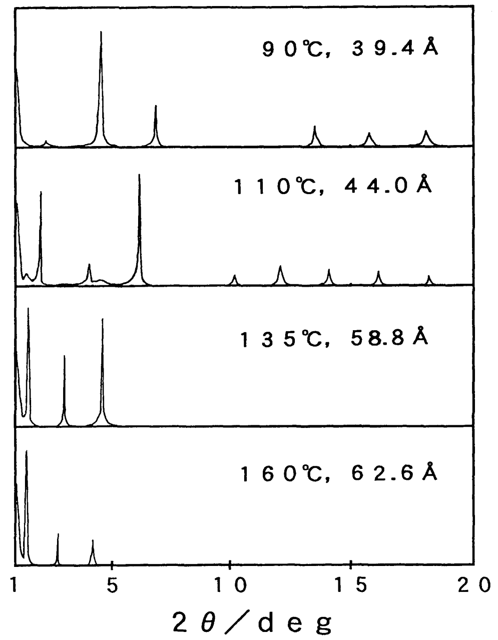


Fig.3. Heat-induced changes in XRD patterns of cast film of **3**.

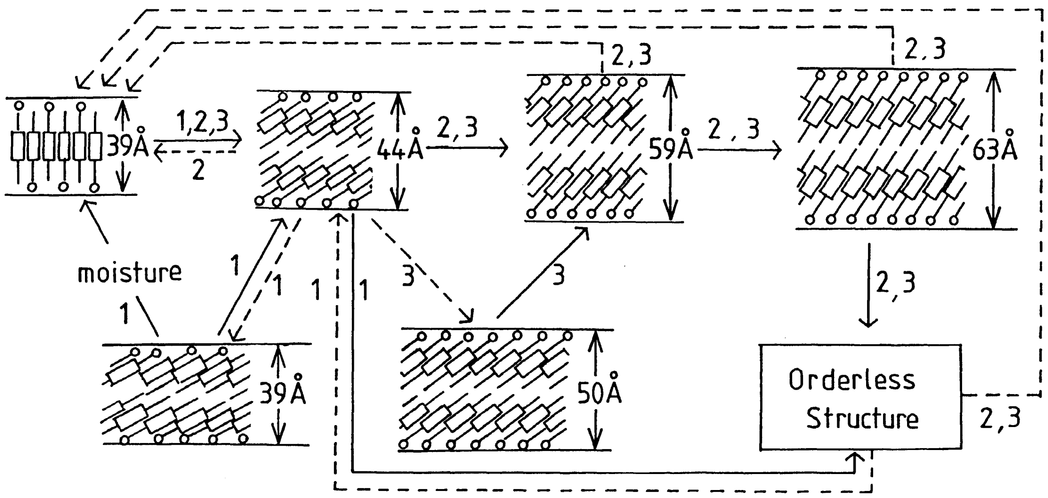


Fig.4. Schematic illustrations of structure transformations of cast films of **1**, **2**, and **3**.
————: heating process, -----: cooling process.

arise from the heating device for XRD.

In the case of azobenzene-containing bilayer **1**, new crystalline modifications were obtained by cooling below T_C after heating above T_C. This is not the case with the benzylideneaniline-containing bilayer. The three species observed at high temperatures return to the original interdigitated structure upon cooling. On the other hand, salicylideneaniline-containing bilayer **3** shows more complex behavior. The species which have 59 Å and 63 Å layer thicknesses regenerate the 39 Å-species after cooling to room temperature, but the 44 Å-species is transformed to a new 50 Å-species with an absorption maximum at 345 nm at room temperature. These phase transition phenomena are schematically summarized in Fig. 4.

In conclusion, we demonstrated that there were some common features in the mode of structural transformation of cast multibilayer films among three single-chain amphiphilies. These features would be useful for designing molecular assemblies with novel photoactive,[10] metal-binding[11] and electronic[12] functions.

We are grateful to Mr. M. Isayama of Molecular Architecture Project, Research Development Corporation of Japan for X-ray diffraction measurement at varying temperatures.

References

1) Contribution No. 962 from the Department of Chemical Science and Technology.
2) M. Shimomura, R. Ando, and T. Kunitake, Ber. Bunsenges. Phys. Chem., 87, 1134 (1983).
3) T. Kunitake, M. Shimomura, T. Kajiyama, A. Harada, K. Okuyama, and M. Takayanagi, Thin Solid Films, 121, L89 (1984).
4) G. Xu, K. Okuyama, and M. Shimomura, Mol. Cryst. Liq. Cryst., 213, 105 (1991)
5) K. Okuyama, H. Watanabe, M. Shimomura, K. Hirabayashi, T. Kunitake, T. Kajiyama, and N. Yasuoka, Bull. Chem. Soc. Jpn., 59, 3351 (1986).
6) T. Nishimi, Y. Ishikawa, and T. Kunitake, Polym. Prep. Jpn., 39, 893 (1990).
7) Y. Ishikawa, T. Nishimi, and T. Kunitake, Chem. Lett., 1990, 165.
8) K. Okuyama, M. Ikeda, S. Yokoyama, Y. Ochiai, Y. Hamada, and M. Shimomura, Chem. Lett., 1988, 1013.
9) M. Kasha, "Spectroscopy of the Excited State," ed by B. D. Bartolo, Plenum Press, New York(1976), p.337
10) M. D. Cohen and G. M. J. Schmidt, J. Phys. Chem., 66, 2242 (1962).
11) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, Prog. Inorg. Chem., 7, 83 (1966).
12) J. D. Wright, "Molecular Crystals," Cambridge Univ. Press (1987), Chap. 6 and 8.

(Received October 5, 1992)