Phase Structure and Phase Transition Mechanism for Light-Induced \( \text{la}3\text{d}-\text{Cub} \) Phase in 4'-\( n \)-Docosyloxy-3'-nitrobiphenyl-4-carboxlic acid / Ethyl 4-(4'-\( n \)-Docosyloxyphenylazo)benzoate Binary Mixture

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4'-\( n \)-alkoxy-3'-nitrobiphenyl-4-carboxlic acid (denoted as ANBC-\( n \), where \( n \) denotes the number of carbon atoms in the alkoxy group) is a representative thermotropic cubic (Cub) mesogen which forms two kinds of bicontinuous Cub phases, \( \text{la}3\text{d} \) and \( \text{Im}3\text{m} \) types, in addition to conventional smectic C (SmC) liquid crystal (LC) phase.\(^{[1]}\) Recently, our group first achieved the reversible switching between the SmC and \( \text{la}3\text{d} \)-Cub LC phases by UV/VIS light irradiations for mixtures composed of ANBC-22 and ethyl 4-(4'-\( n \)-docosyloxyphenylazo)benzoate (AZO-22).\(^{[2]}\) Interestingly, in this case, the generation of the cis isomers increases the phase dimensional order from the 1D SmC to the 3D Cub phases. In other words, the bent molecules of AZO-22 seem to stabilize the Cub phase. How does the AZO-22 work on the formation of the Cub phase? Moreover, how is the phase structure of the light-induced Cub phase related with that of the thermally induced one? The structure of the light-induced \( \text{la}3\text{d} \)-Cub LC phase was investigated in detail using grazing-incidence X-ray diffraction (GI-XRD) and FT-IR spectroscopy, to elucidate the phase transition mechanism at the molecular level.

In Figure 1, the lattice constant, \( a \), for the light-induced Cub phase is plotted against temperature together with that for the thermally induced one. The \( a \) for light-induced Cub phase agrees fairly well with the extrapolated value from the temperature dependence of the \( a \) for the thermally induced Cub phase. The FT-IR analysis also showed that the UV irradiation shifts the peak positions towards their extrapolated wavenumbers that would be displayed by the thermally induced Cub phase at the temperature. These results indicate that both the molecular state and periodic structure realized by the irradiation may be regarded as the “postulated” state and periodic structure of thermally induced Cub phase at the temperature. This leads to a conclusion that the \( \text{trans} - \text{cis} \) photoisomerization of the azobenzene derivatives in the mixture gives rise to destabilization of the SmC phase with layered structure, alternatively favoring the formation of the Cub phase with twisted molecular arrangement (Figure 2).

References:

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