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Heavily Retarded Transition from Smectic C to Cubic Phase in Liquid-Crystalline 4′-n-Docosyloxy-3′-nitrobiphenyl-4-carboxylic Acid

Shoichi Kutsumizu[1)], Eiji Funai[2)] and Shinichi Sakurai[2)*]
[1)]Department of Chemistry, Faculty of Engineering, Gifu University,
1-1 Yanagido, Gifu 501-1193, Japan
[2)]Graduate School of Engineering, Kyoto Institute of Technology,
Matsugasaki, Sakyo-ku, Kyoto, Kyoto 606-8585, Japan

Cubic (Cub) mesophases have attracted great attention because of their self-organization of simple rodlike molecules into a complex aggregation structure with cubic symmetry. The 4′-*n*-docosyloxy-3′-nitrobiphenyl-4-carboxylic acid (ANBC-22, where "22" represents the number of carbon atoms in the alkoxy group) is such a Cub phase-forming compound. It exhibits the following phase sequence upon heating: smectic C (SmC) → Im3m-Cub → Ia3d-Cub → isotropic liquid. The low temperature three phases are considered to be basically made up by layered aggregates of the ANBC-22 molecules, but having different degrees of dimensionality; the SmC phase is a one-dimensionally ordered phase, whereas the two Cub phases are three-dimensionally ordered ones. The Ia3d-Cub phase is widely seen in thermotropic and lyotropic liquid crystals and block copolymers, often called gyroid, but the Im3m-Cub phase is at present limited in the thermotropic liquid crystals. The phase transition behavior has been investigated by several techniques such as differential scanning calorimetry, adiabatic calorimetry, polarizing optical microscopy, dynamic viscoelasticity, and small-angle X-ray scattering (SAXS). Nevertheless, like other soft materials, little is understood about the transition kinetics and detailed mechanisms of the transformation from the SmC to Cub phases and from one Cub phase to another. We report herewith heavily retarded transition from SmC to Cub phase in ANBC-22, as revealed by SAXS using PF, BL-9C and 15A.

The most important and unexpected finding is that even at a temperature 8 K below the SmC to Cub phase transition temperature ($T_{SmC\text{-}Cub} \approx 408$ K) determined previously for the compound, the Cub phase grows, after a very long induction period (several hours). The SAXS measurements revealed the formation of an *Im*3*m*-type Cub phase at the temperature (Fig. 1(c)). It is suggested that the "true" transition temperature, which is difficult to determine precisely, exists around 396 K. The time-dependence of the *Im*3*m*-type Cub phase growth was analyzed using the Avrami theory, implying the nucleation and growth mechanism mainly governing in the SmC to Cub phase transformation. The fact uncovered is that between 408 and 396 K, the SmC to Cub transformation is virtually prohibited by the strongly limited nucleation, for which it was further found that the electric field promotes the nucleation of the Cub phase in the temperature region where the Cub phase is potentially more stable than the precursory SmC phase.

* shin@kit.jp

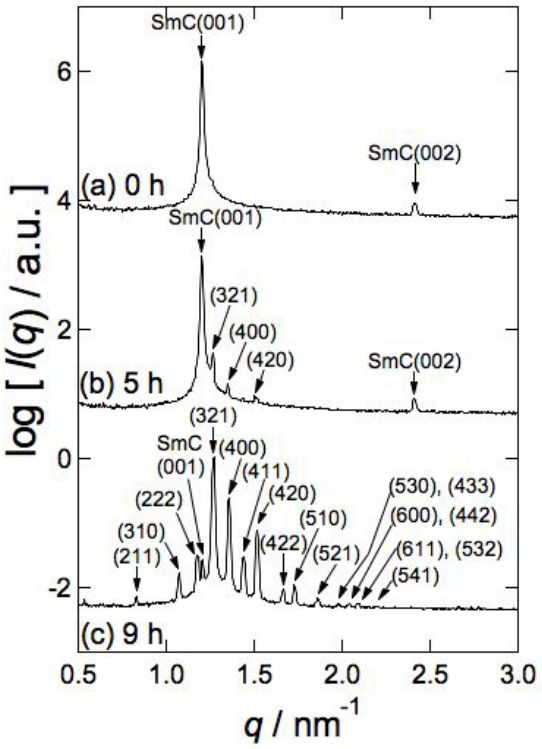

Figure 1 Time evolution of the SAXS profiles of ANBC-22 about 7 K below $T_{SmC\text{-}Cub}$: (a) initial state, (b) after 5 h, and (c) after 9 h.