

Electric Field-Induced Cubic Phase in 4'-*n*-Docosyloxy-3'-nitrophenyl-4-carboxylic Acid

Shoichi Kutsumizu,^{*,†} Makoto Yamada,[†] Takanari Yamaguchi,[‡] Katsufumi Tanaka,[§] and Ryuichi Akiyama[§]

Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan, Tsukuba Research Laboratory, Sumitomo Chemical Co., Ltd., 6 Kitahara, Tsukuba, Ibaraki 300-3266, Japan, and Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan

Received October 18, 2002; E-mail: kutsu@cc.gifu-u.ac.jp

Molecules composed of two incompatible parts, aliphatic versus aromatic, hydrophobic versus hydrophilic, or soft versus rigid, form a variety of aggregation structures and are often called soft materials.¹ 4'-*n*-Docosyloxy-3'-nitrophenyl-4-carboxylic acid, denoted as ANBC-22, is such a compound, consisting of a nitrophenyl-carboxylic acid core and a long alkoxy tail.^{2–10} ANBC-22 exhibits two kinds of liquid crystalline phases, a lamellar-like smectic C (SmC) and a three-dimensionally (3-D) ordered cubic (Cub) phase,^{6,7,9,10} at elevated temperatures, where the dimerized ANBC-22 is the basic aggregation unit (see Chart 1); in the Cub phase, the ANBC-22 dimers aggregate into rod-shaped micelles, which join 3-by-3 or 6-by-6 to form a 3-D network structure with space group *Ia3d* or *Im3m*.¹⁰ While in polycatenar systems a mismatch between the cross-sectional areas of the two incompatible parts is a principal origin of the destabilization of the SmC layer structure, the nature of the transition in the present system is not so well described, and other intermolecular interactions are very likely to be of importance.^{1,10,11}

A fascinating feature of the soft materials is that their aggregation structure changes sensitively in response to the physical external stimuli (temperature, electric field, shear deformation, etc.). An application of nematic liquid crystals to the display devices uses this feature. We focus attention on the SmC to Cub phase transition of ANBC-22, at which the storage modulus (G') and viscosity jump by 3 orders of magnitude,⁷ but the SmC and the Cub phases are energetically close and the transition enthalpy between them is 1.6 kJ mol⁻¹.^{6,9} If the transition can be controlled by an external stimulus, a new application to the stress transferring device would be open. Here, we report the influence of an alternating-current (AC) electric field on the SmC phase for the ANBC-22. We found the formation of an electric field-induced Cub phase at temperatures 4–10 K below the zero-field SmC to Cub phase transition temperature.

ANBC-22 was prepared according to the method of Gray et al.² The influence of the AC electric field application on the transition was examined by the polarizing optical microscopic (POM) observation. The samples were inserted into the indium-tin-oxide (ITO) coated cells of 4 μ m thickness in the isotropic liquid state, and then the cells were placed in a Mettler FP82 hot stage, to which an AC electric field (field strength $E = 100\,000$ V cm⁻¹) was applied. The frequency was 1–100 kHz.

In the inset of Figure 1, two representative photos observed under crossed polarizers are shown: (A) at 127.0 °C, 2 min after the application of 10-kHz electric field E , and (B) at 123.3 °C, 60 min

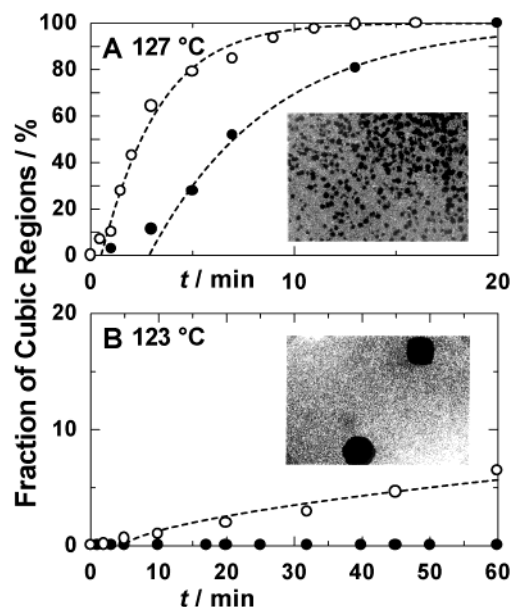
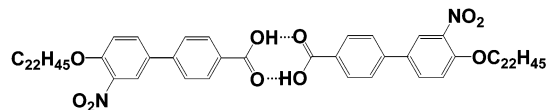


Figure 1. Growth behavior of the Cub regions of ANBC-22 as a function of time (t) taken after the application of an AC electric field E at a frequency of 1 kHz (●) and 10 kHz (○) (field strength $E = 100\,000$ V cm⁻¹): (A) at 127.0 °C and (B) at 123.3 °C. Broken curves are best fits based on the Avrami equation (see text). In each graph, the optical microscopic photo under crossed polarizers is shown as an inset: (A) 2 min and (B) 60 min, after the application of 10-kHz E .

Chart 1



after the application of the same field. The two temperatures are in the SmC region on heating if $E = 0$, that is, ca. 6 and 10 °C below the zero-field SmC to Cub transition temperature ($T_{\text{SmC-Cub}} = 133$ °C on POM), respectively. In both photos, the major part is a bright, birefringent texture (schlieren texture), where the SmC phase is formed. The remaining areas are completely black, consistent with the optically isotropic Cub phase. The boundaries of these areas are sharp, and in (B) the shape is square-like or hexagon-like. The shape reflects the envelope of each single domain, which is possible only when the growth of the organization is very slow.⁸ Such features are characteristic of the Cub phase formation.^{4,5}

The growth behavior of the Cub regions as a function of time (t) taken after the application of E is shown in Figure 1. Even in the zero-field condition $E = 0$, the growth of the Cub phase of

[†] Gifu University.
[‡] Sumitomo Chemical Co.
[§] Kyoto Institute of Technology.

ANBC-22 at 133 °C is relatively slow, and the transition takes several seconds. On the other hand, the completion of the field-induced SmC to Cub transition required more time, at 127.0 °C in (A), 10 min at 10 kHz and 20 min at 1 kHz. Furthermore, at 123.3 °C in (B), the transition induced proceeded at a much slower rate, and even after 60 min, only 6% of the SmC phase was converted at 10 kHz; at 1 kHz, no induction was observed. At 117.5 °C, ca. 16 °C below $T_{\text{SmC-Cub}}$, much farther below than the above two cases, no induction was observed in the time interval of 90 min under the application of 1-kHz E or 100-kHz E .

The kinetics of the growth behavior of the Cub phase is well described by the Avrami equation,¹² which is given as

$$f = 100 \times (1 - \exp(-[(t - t_0)/\tau]^n))$$

where f is the fraction of the Cub regions (in %), t is the time after the application of E (in min), t_0 is the early stage period, τ is the time constant (which corresponds to the time for 63.2% accomplishment), and n is the Avrami index. The best-fits are shown as broken curves in Figure 1: at 127.0 °C in (A), $t_0 = 2.9$ min, $\tau = 6.0$ min, and $n = 1.0$ at 1 kHz, and $t_0 = 0.5$ min, $\tau = 2.8$ min, and $n = 1.05$ at 10 kHz; at 123.3 °C in (B), $\tau = \infty$ at 1 kHz, and $t_0 = 5$ min, $\tau = 5000$ min, and $n = 0.63$ at 10 kHz. The good applicability of the equation implies a nucleation-growth mechanism in the Cub phase formation. A similar observation but under $E = 0$ was reported for both the hexagonal to Cub and the Cub to lamellar phase transitions in a lyotropic system, the hexaethylene glycol mono- n -dodecyl ether (C_{12}EO_6)/water binary system.¹³

The formation of the field-induced Cub phase was dependent on the frequency of the applied field, and as shown in Figure 1, or easily seen from the value of τ , the higher frequency induces the evolution more effectively. This rules out the possibility of the Joule heating effect due to ionic impurities. The Cub to SmC transition temperature (116 °C), measured on cooling from 137 °C at a rate of 0.5 K min^{-1} , was not affected by the application of E . This observation and the very slow evolution of the Cub phase under E , as compared with at $T_{\text{SmC-Cub}}$ under $E = 0$, both reflect that the bulk temperature of the sample is not changed with E .

Although the mechanism of this field effect is not clear at present, a plausible origin is the coupling with the large dipole moment (4.2 D) of the NO_2 side group. The AC electric field E would enhance the molecular motion within the SmC layers, introducing a nucleating perturbation which enables the Cub phase formation in a temperature region below the $T_{\text{SmC-Cub}}$.

Another feature of the field-induced Cub phase growth is that once the growth starts, it does not stop, although the evolution became slightly slow, after the removal of the applied E . Moreover, the temperatures at which the field-induced transition was realized are limited (at this stage) within the temperature region where the supercooled Cub phase can exist as a metastable phase on cooling. Because the SmC and Cub phases are energetically in close vicinity, these observations are considered to reflect a possible dominance for kinetic factors in the transition behavior.⁵ In other words, the recorded transition temperature between the SmC and Cub phases of this system under $E = 0$ is some temperature that derives from a mix of thermodynamic and kinetic factors. Thus, it may be said that at a certain temperature range below the $T_{\text{SmC-Cub}}$, the applied field overcomes the kinetic barrier to the transition.

As mentioned, the SmC to Cub phase transition of ANBC-22 brings about a dramatic jump of the storage modulus G' .⁷ Thus, the effect of AC electric field application on the viscoelastic behavior is of much interest. At 131 °C, 2 °C below $T_{\text{SmC-Cub}}$, a small oscillatory shear strain with an angular frequency of 9.42

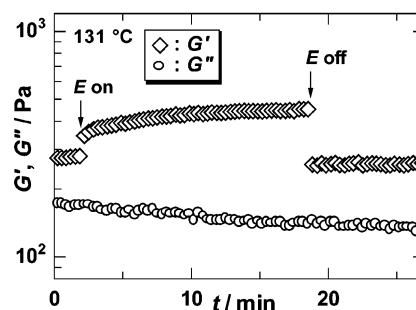


Figure 2. Effect of an AC electric field (E) on the storage modulus (G') and loss modulus (G'') at 131 °C. The frequency and strength of E were 10 kHz and 200 000 V cm^{-1} , respectively, and the frequency and amplitude of the shear strain were 9.42 rad s^{-1} and 0.12, respectively.

rad s^{-1} was applied to the sample (thickness: 200 μm), and the dynamic moduli were recorded as a function of time, where an AC electric field E of 200 000 V cm^{-1} at a frequency of 10 kHz was applied and then removed. The result is shown in Figure 2, demonstrating that the application of E gives rise to a gradual increase in G' , which quickly recovers to the original value in response to the removal of the E . In contrast to the jump at $T_{\text{SmC-Cub}}$ under $E = 0$, the increase of G' was not so large. This result is reasonable considering that the bulk storage modulus is not influenced substantially in the intermediate stage of the Cub phase growth such as its 50% accomplishment. Rather, it is worth noting that the response of the G' is almost reversible with the application and removal of the E . Probably, it is the presence of the small oscillatory shear strain, which stabilizes the SmC layer structure, that leads to this significant feature different from the POM observation mentioned above.

In conclusion, we found the first example of field-induced Cub phases. We hope our finding opens a new page in the field of Cub mesophases science and gives a route for future applications such as the stress transferring devices.

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