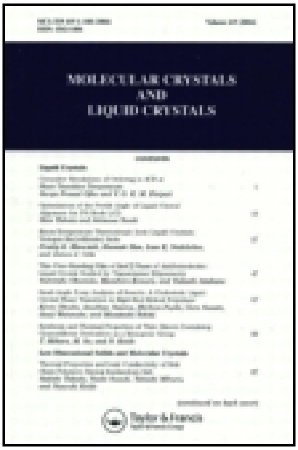

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Cubic D Phase of 4′-n-Pentadecyloxy-3′-Nitrobiphenyl-4-Carboxylic Acid

Shoichi Kutsumizu [a] , Takanari Yamaguchi [b] , Ryuji Kato [c] , Tatsuya Ichikawa [c] & Shinichi Yano [c]

[a] Instrumental Analysis Center, Gifu University, Gifu, 501-1193, Japan

[b] Tsukuba Research Laboratory, Sumitomo Chemical Co., Ltd., 6 Kitahara, Tsukuba. Ibaraki, 300-3266, Japan

[c] Faculty of Engineering, Gifu University, Gifu, 501-1193, Japan

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Cubic D Phase of 4'-*n*-Pentadecyloxy-3'-Nitrobiphenyl-4-Carboxylic Acid

SHOICHI KUTSUMIZU[a], TAKANARI YAMAGUCHI[b],
RYUJI KATO[c], TATSUYA ICHIKAWA[c] and SHINICHI YANO[c]

[a]*Instrumental Analysis Center, Gifu University, Gifu 501-1193, Japan,* [b]*Tsukuba Research Laboratory, Sumitomo Chemical Co., Ltd., 6 Kitahara, Tsukuba, Ibaraki 300–3266, Japan and* [c]*Faculty of Engineering, Gifu University, Gifu 501–1193, Japan*

The phase behavior of 4'-*n*-pentadecyloxy-3'-nitrobiphenyl-4-carboxylic acid (ANBC-15, where "15" corresponds the number of carbons in the alkoxy groups) was investigated by differential scanning calorimetric, polarizing optical microscopic, infrared spectroscopic and dynamic viscoelastic (DVE) measurements. ANBC-15 has a critical alkoxy chain length for exhibiting the cubic D (CubD) phase in ANBC series, and the virgin sample of ANBC-15 shows the CubD phase on heating, but the appearance of the CubD phase in the second heating depends on the turnover temperature of the preceding heating. Such instability of the CubD phase was also observed by isothermal frequency scans of DVE, which reveals the existence of a crossover of the storage and loss modulus curves, reflecting a structural fluctuation of the CubD phase in ANBC-15. The instability of the CubD phase of ANBC-15 is suppressed by mixing 25 mol % of ANBC-16, resulting in an enantiotropic CubD phase.

Keywords: Cubic D phase; fluctuation; 4'-*n*-alkyloxy-3'-nitrobiphenyl-4-carboxylic acids

INTRODUCTION

In 1957, Gray et al. [1] first synthesized a homologuos series of 4'-*n*-alkoxy-3'-nitrobiphenyl-4-carboxylic acid (ANBC-*n*, *n* is the number of carbons in the alkoxy groups) and the polymorphism of the hexadecyloxy (ANBC-16) and of the octadecyloxy (ANBC-18) derivatives was investigated by Demus et al. [2,3] They found an optically isotropic mesophase between the optically anisotropic smectic C (SmC) and smectic A (SmA) phases for

ANBC-16 and between the SmC and the "structured liquid" (I_1) phases for ANBC-18. This phase was called the smectic D phase at that time and now labelled the cubic D (CubD) phase.[4] In 1994, other members, the n=17 and 19-22 members(, and very recently, the n=26 member,) of the ANBC-n homologues were studied by us [5], and it was shown that the CubD phase is enantiotropic between n=16 and 22 (and n=26) and its temperature region becomes wider from 22 K for n=16 to 57 K for n=22 with increasing the number of carbons, n, in the alkoxy chains, as shown in the top part of Fig. 1. On the other hand, the polymorphism of ANBC-15 is very complicated; the CubD phase takes place from 459 to 469 K *only* on the first and not on the subsequent heating processes. As readily seen in the bottom part of Fig. 1, the enthalpy value for the SmC to CubD transition on first heating plotted versus n may be extrapolated to zero at around n=14, which demonstrates that ANBC-15 has a critical alkoxy chain length for exhibiting the CubD phase and also suggests us that the CubD phase of ANBC-15 may have an instability or a structural fluctuation in itself. From this viewpoint, we re-investigated the polymorphism of ANBC-15. In this paper, we present the results of the differential scanning calorimetric (DSC) and thermogravimetric (TG) analyses, polarizing optical microscopic (POM) observations, dynamic viscoelastic (DVE), and infrared (IR) spectroscopic studies of ANBC-15. Some results will be published separately but in more detail [6].

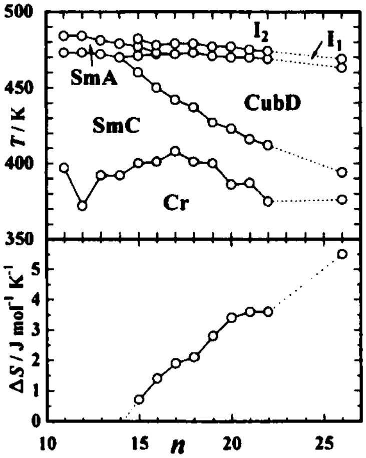

FIGURE 1. Plots of phase transition temperatures (in the top) and the SmC to CubD transition entropy (in the bottom) against carbon number of the alkoxy groups (n) in ANBC homologues.

Experimenral

All ANBC-n homologues were prepared according to the established method [1]. Characterization was done using the following instruments: Nikon Optiphoto-pol XTP-11 polarizing optical microscope equipped with a

Mettler FP-82 hot stage, Seiko Denshi SSC 5000 system containing both DSC-210 calorimeter and TG analysis instrument (TG/DTA-300), a Perkin-Elmer system 2000 IR spectrometer equipped with a heated cell and a controller (S.T. Japan 0019-201 and 0019-200). The DVE measurements were carried out by using a Rheometric Dynamic Stress Rheometer DSR and a Rheometric RDS-II.

Results and Discussion

As reported previously, the phase behavior for ANBC-n homologues with $n \leq 14$ and $n \geq 16$ is little dependent on the thermal cycles, except the appearance of a metastable phase called S_4 on cooling [3], and for $n \geq 16$ the CubD phase takes place enantiotropically and reproducibly on the repeated thermal cycles up to around 500 K [5]. On the contrary, the polymorphism for the n=15 homologue is very complicated and was found to be strongly influenced by the thermal cycle used, which will be described elsewhere [6] but briefly mentioned here: When a fresh sample of ANBC-15 that was recrystallized from the solution was heated up to 503 K, the sample showed three liquid crystalline phases, the SmC (399-459 K), the CubD (459-469 K) and the SmA (469-475 K) phases, and a "structured liquid" labelled I_1 (475-479 K), before showing the isotropic liquid labelled I_2 at 479 K, but on the subsequent cooling and heating processes, the CubD phase disappeared; for example, ANBC-15 showed the SmC (398-464 K) and SmA (464-474 K) phases on the third heating, where another feature of ANBC-15 (and the higher ANBC-n homologues), i.e., the presence of the I_1 phase, was maintained regardless of exhibiting the CubD phase. When the turnover temperature in the higher temperature side was lowered to around the CubD-SmA phase transition temperature, the CubD phase appeared repeatedly thereafter on both heating and cooling processes. Hence, it was suggested that the appearance of the D phase is strongly dependent on the temperature maximum experienced before [6].

Here, one might pointed out the possibility of decomposition of the samples at high temperatures. The thermogravimetric analyses were performed for ANBC-14, -15, and -16. All three homologues started degrading slowly above 500 K, but showing less than 2 % of weight losses at 550 K, by 70 K higher than the clearing temperatures. Until 500 K, the losses were only 0.5 % or less, and it is noted that no difference was observed among the three, where only ANBC-15 shows the complicated phase behavior mentioned above and ANBC-16 shows an enantiotropic CubD phase. Furthermore, we compared to each other the infrared spectra at room temperature for three ANBC-15 samples with different thermal histories; a fresh sample, the sample heated up to 470 K (at around the CubD-SmA phase transition temperature) and still capable to exhibit the CubD phase, and the sample that was heated up to 503 K not to show the CubD phase thereafter. The comparison showed no difference among the three, and for example, the hydrogen-bonded C=O stretching at 1689 cm^{-1}, benzene ring C=C stretching at 1608 cm^{-1}, and NO_2 asymmetric stretching bands at 1537 cm^{-1} were not changed in shape and intensity by heating up to 503 K, although that heating largely affects the phase behavior of ANBC-15. Consequently, these results clearly indicate that decomposition is not a reason for the complicated polymorphism of ANBC-15.

The infrared spectroscopy is also useful for investigating the dissociation of hydrogen-bonded COOH groups, and the C=O carbonyl stretching absorption is resolved into two vibrational modes, vibration of monomeric COOH groups ($\nu(C{=}O)_{monomer}$) at around 1730 cm^{-1} and that of hydrogen-bonded COOH groups ($\nu(C{=}O)_{dimer}$) at around 1690 cm^{-1}, by using curve-fitting procedure. Our previous work[7] used Lorentz function, but in this work, Gauss-Lorentz function was used to get better fitting for all three ANBC-*n* homologues. The molar fraction values of hydrogen-bonded COOH groups were estimated by using the integrated absorbances of two components on the basis of a reasonable assumption that the molar extinction coefficient of the $\nu(C{=}O)_{monomer}$ band is equal to that of the $\nu(C{=}O)_{dimer}$ band. Fig. 2 plots molar fraction values of hydrogen-bonded COOH groups as a function of temperature for ANBC-14, -15, and -16, where the measurements for ANBC-15 were done on both first and second heating processes and the latter process does not include the CubD phase. The results show that the temperature dependence of the molar fraction value of hydrogen-bonded COOH groups is the same for all three on the first heating. On the second heating, ANBC-15 showed a little higher value in the SmA phase region than others in the same temperature region, but this difference is not so beyond the errors; the difference would be diminished but remains in the isotropic liquid states. Therefore, we were not able to derive a definite conclusion from this IR result, although this may

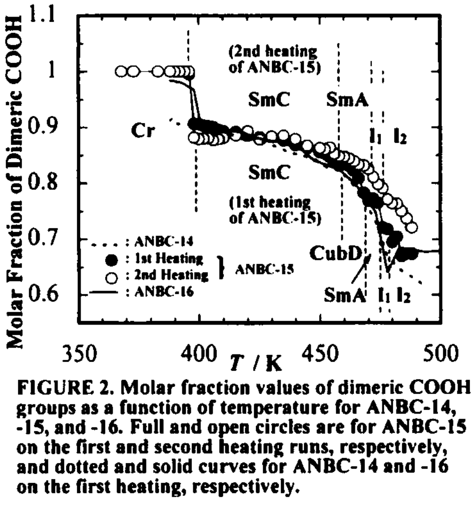

FIGURE 2. Molar fraction values of dimeric COOH groups as a function of temperature for ANBC-14, -15, and -16. Full and open circles are for ANBC-15 on the first and second heating runs, respectively, and dotted and solid curves for ANBC-14 and -16 on the first heating, respectively.

suggest that a reduced dissociation of hydrogen-bonded COOH groups on the second heating is partly related to the disappearance of the CubD phase.

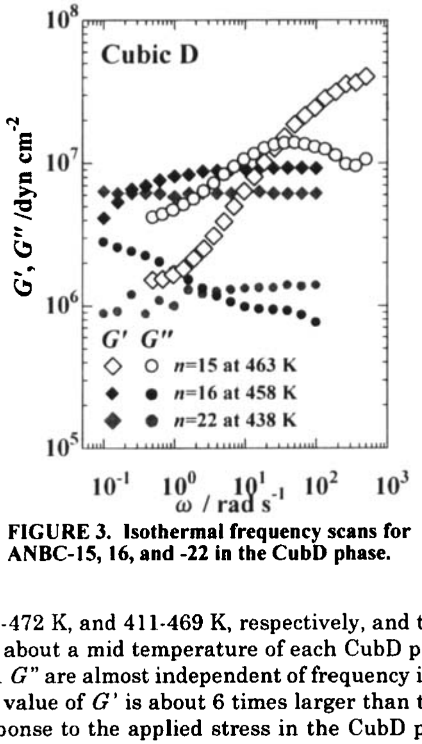

FIGURE 3. Isothermal frequency scans for ANBC-15, 16, and -22 in the CubD phase.

Dynamic viscoelastic (DVE) invesigations are useful to get an insight into the structure and dynamic properties of the CubD phases for ANBC-*n* series, as reported previously; the isochronal measurement results showed that the *G'* values of the CubD phase for *n*=16 and 22 are very high and 10^6-10^7 dyn cm^{-2} at an angular frequency of 6.28 rad s^{-1}, 10^3 times larger than the corresponding values of the SmC and SmA phases [8]. Hence, the CubD phase is much more stiff than the SmC or SmA phases with layer structures, reflecting the three-dimensional network structure constructed by rod-like micelles, as proposed by the Tardieu and Billard's interpenetrating jointed (IPJR) model with space group *Ia3d* [9]. Fig. 3 shows isothermal frequency scans in the CubD phase for three ANBC-*n* homologues with *n*=15, 16, and 22; the temperature regions of the CubD phase of the *n*=15, 16, and 22 members are 459-469 K, 450-472 K, and 411-469 K, respectively, and the measurement temperatures are about a mid temperature of each CubD phase region. For *n*=22, both *G'* and *G"* are almost independent of frequency in the range 10^{-1}-10^2 rad s^{-1}, and the value of *G'* is about 6 times larger than that of *G"*, showing a solid-like response to the applied stress in the CubD phase. The relation *G'* > *G"* is also seen for the CubD phase for *n*=16, but unlike in the CubD phase for *n*=22, the difference between *G'* and *G"* is diminished towards zero with reducing frequency below 10^1 rad s^{-1}. The most interesting feature is seen for *n*=15, which shows a crossover of the *G'*-frequency and *G"*-frequency curves; the crossover frequency (ω_c) is ~4×10^1 rad s^{-1}, below which *G'* < *G"* is obtained. Returned to the data for *n*=16, extrapolating both *G'*-frequency and *G"*-frequency curves towards the lower frequency side provides a crossover point at ~5×10^{-2} rad s^{-1}, much less than the ω_c value for *n*=15. The existence of the crossover frequency ω_c and *G'* < *G"* in the lower frequency side in ANBC-15 means that when the cycle of applied stress is faster than the frequency of ω_c, the cubic structure acts as a "solid" while it acts as a "liquid" for slower stresses than ω_c. In other words, the cubic structure of ANBC-15 fluctuates in the time scale of ω_c. Clearly, such phenomenon is closely connected with the fact that the alkoxy chain length of ANBC-15 is critical for exhibiting the CubD phase.

Finally, we would like to show that instability of the CubD phase of ANBC-15 is suppressed by mixing a small amount of ANBC-16. The contact method using POM under crossed polarizers showed complete mixing of two CubD phases of ANBC-15 and -16 without boundaries. Fig. 4 is the isobaric phase diagram for the binary system ANBC-15/ANBC-16, which is based on the second heating DSC results. As the molar fraction of ANBC-15 increases, the temperature region of the CubD phase becomes gradually narrower, eroded by both high (SmA) and low (SmC) temperature phase regions, but it is noted that the binary mixture containing 75 mol % of ANBC-15 shows an enantiotropic CubD phase on the second and third heating/cooling runs, indicating that the instability of the CubD phase of ANBC-15 is suppressed by mixing 25 mol % of ANBC-16. This is another aspect of fluctuated cubic structure of ANBC-15.

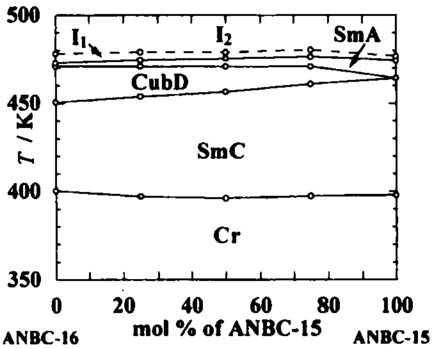

FIGURE 4. Isobaric phase diagram of the binary system of ANBC-16/ANBC-15. Phase transition temperatures are taken for the second heating process.

In summary, this report uncovered the instability and fluctuated nature of the CubD phase of ANBC-15 mainly using DSC and DVE measurements. In ANBC-*n* series, the chain length of the alkoxy groups is a key factor for exhibiting the CubD phase, and in ANBC-15, it is critical. Thus, the CubD phase has a fluctuated structure, which is characterized by the crossover frequency ω_c on DVE. As another aspect, the CubD phase is labile on the thermal cycle up to 503 K and replaced by the SmC and SmA phases on the second heating DSC. The lability, however, was suppressed by mixing 25 mol % of ANBC-16. We are currently progressing the X-ray diffraction studies for ANBC-15 and higher ANBC-*n* homologues and the results will be reported in the near future.

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