Ia3d-cubic phase and its thermal transition to and from an *Im3m*-cubic phase of BABH-*n*

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BABH-*n*は剛直なコアとその両側にアルキル鎖（その炭素数を*n*とする）をもち，鎖長と温度に依存して異なる対称性(*Ia3d*, *Im3m*)のキュービック相を発現する．特に，*Im3m*型相はサーモトロピック系特有の凝集構造をもつ．本研究では，これらの相形成の鎖長依存性と温度依存性を，主に小角X線散乱と赤外分光により検討，比較整理した．本発表では，短鎖系（*n*=5-13）と長鎖系（*n*=15-22）の*Ia3d*型相の分子凝集構造の違いについて議論し、異なる対称性(*Ia3d*, *Im3m*)のキュービック相間の相転移に対して時分割測定の結果を報告する．

1 Introduction

Thermotropic cubic (Cub) mesophase of bicontinuous type is of much interest in that both local mobility and a three-dimensionally periodic molecular arrangement are realized by relatively simple rod-like molecules. 1,2-bis(4'-*n*-alkoxybenzoyl)hydrazine is such a Cub-phase forming molecule, which is composed of a rigid aromatic core at the center and a flexible alkyl tail at each end. The molecule is designated as BABH-*n* with *n* being the number of carbon atoms in the alkyl tail. The BABH-*n* exhibits two types of Cub phases, depending on temperature *T* and alkyl chain length *n*.[1)] One is the *Ia3d* phase which is commonly known in lyotropic and block copolymer systems as well as in thermotropic ones, usually called gyroid (G). Another type has the symmetry *Im3m*, whose observation is at this stage restricted in thermotropic systems. For this phase, we proposed that a doubled P (PP) structure first introduced by Góźdź and Hołyst[2)] is a suitable model,[3)] but a more sophisticated model was recently proposed by Zeng, Ungar and Clerc.[4)] The molecular organization in the *Im3m* phase is, however, still subject to debate, because transformation of this phase to and from other phases including the *Ia3d*-G phase remains unanswered.

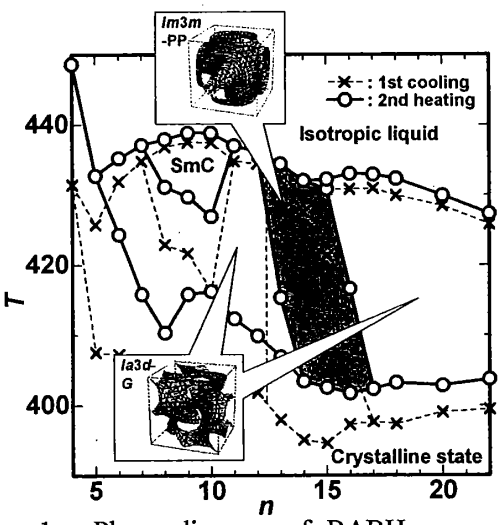

Fig. 1. Phase diagram of BABH-*n*. as a function of temperature *T* and alkyl chain length *n*. Interface models of *Ia3d*-G and *Im3m*-PP phases are shown.

2 Results and Discussion

2.1 Phase diagram and Cub-to-Cub transition

Fig. 1 is the phase diagram finally established. One feature is that the *Ia3d* phase region is divided into two regions with *n* = 5-13 and *n* = 15-22 and between them the *Im3m* phase region intervenes. In the next

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section, we compare the molecular organizations of two *Ia3d*-Cub phases formed by the short-chain and long-chain members. Second feature to note is that when temperature is elevated, the n = 13 member undergoes an *Ia3d*-G to *Im3m*-PP phase transition at 415 K, whereas the n = 15 and 16 members show the reverse transition from the *Im3m*-PP to *Ia3d*-G phases at 431 K and at 417 K, respectively. From topological point of view, those thermally-induced Cub-to-Cub transitions are quite interesting, and a preliminary time-resolved SAXS result for the n = 13 member is also presented and discussed.

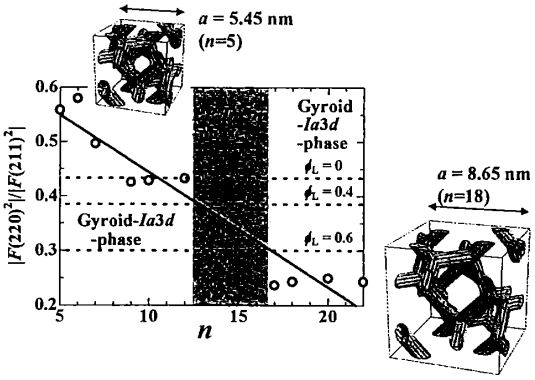

Fig. 2. Plots of the relative intensity of the (220) reflection with respect to the (211) reference peak as a function of n, which are compared with three values (broken lines) calculated by Garstecki and R. Hołyst[6] for the volume fraction (ϕ_L) of the layer decorating the G surface. The solid line is a guide for the eye.

2.2 Molecular organization of short-chain *Ia3d* and long-chain *Ia3d* phases

As described in our preceding paper[5] and shown in Fig. 2, by examining how the relative intensity of (220) reflection with respect to the (211) reference peak varies with n, we can conclude that the 'alkyl chain on G-surface' remains stable against a large variation in the chain length from n = 5 to 22, with an intermission of the *Im3m* phase region of n = 13-16 (grey region in Fig. 2). In other words, 3-by-3 networks (grey rods in schematic illustration) in both short-chain and long-chain *Ia3d* phases are composed of aromatic cores and the core-core aggregation is essential for the Cub phase formation in thermotropic systems. It is noted that in lyotropic systems, two components exchange their role when the volume fraction ϕ of one counterpart is changed beyond ϕ = 0.5.

When we consider the molecular organization in more detail, two competitive mechanisms are shown to be mainly operated; and the first mechanism, the preferential orientation of arranging all long axes of the aromatic cores parallel to each other, favors the bundle-type micelles in the short-chain *Ia3d* phase, while the second contribution, micro-segregation between the aromatic cores and alkyl chain parts of the molecules, plays a dominant role in long-chain *Ia3d* phase.

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