

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 Gózdź and Hołyst²⁾ 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.

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

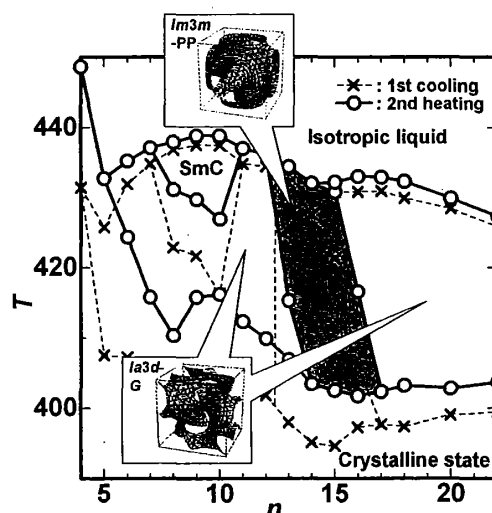


Fig. 1. Phase diagram of BABH-*n*. as a function of temperature *T* and alkyl chain length *n*. Interface models of *Ia3d*-G and *Im3m*-PP phases are shown.

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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.

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

As described in our preceding paper⁵⁾ 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 $\phi = 0.5$.

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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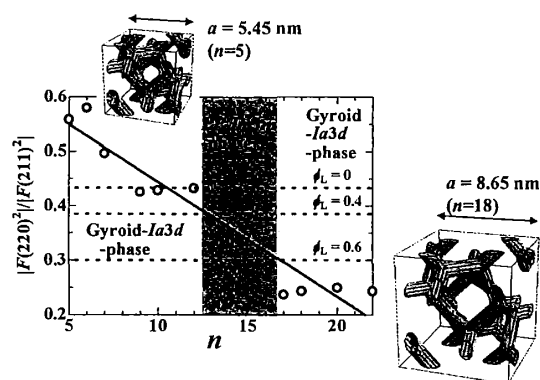


Fig. 2. Plots of the relative intensity of the (220) reflection with respect to the (211) reference peak as a function of n , which are compared with three values (broken lines) calculated by Garstecki and R. Holyst⁶⁾ for the volume fraction (ϕ_L) of the layer decorating the G surface. The solid line is a guide for the eye.