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Ion-Induced Bicontinuous Cubic and Columnar Liquid-Crystalline Assemblies of Discotic Block Codendrimers

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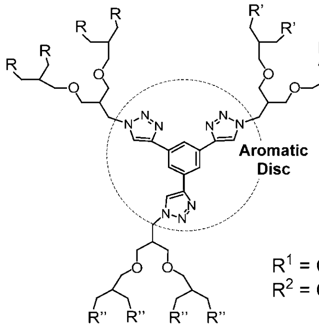
Block codendrimers, sometimes known as hybrid or Janus dendrimers, in which two constitutively different dendrons are covalently bound at the center, have recently received much attention as a new class of self-assembling soft materials. Several block codendrimers displayed liquid-crystalline (LC) properties in the melt. These contain mostly mesogenic dendrons, for example, Percec-type poly(benzyl ether) dendrons, as their basic building unit.[1] Meanwhile, despite several reports suggesting the synthesis of block codendrimers carrying nonmesogenic dendrons,[2] to date, only two examples have displayed a lamellar-type LC morphology (Lam) in the melt.[3] Therefore, further research needs to be undertaken to elucidate the bulk assembling behavior of the unexplored block codendrimer system.

Discotic liquid crystals, composed of a rigid aromatic core and flexible alkyl chains, are another type of self-assembling soft material. Due to the stacking of anisotropic disclike cores, they are well known for forming columnar LC phases. However, triphenylene discogens with ionic-liquid pendants, as recently reported by the Aida group, frustrated this common structure–LC morphology correlation.[4] In addition to a hexagonal columnar LC phase (Col$_{hex}$), the discogens revealed a bicontinuous cubic (Cub$_{bi}$) LC phase, consisting of two continuous cylindrical networks. For the generation of the Cub$_{bi}$, the ionic interaction of the ionic-liquid pendants was suggested as one of the major parameters.

In this context, we designed amphiphilic molecules, referred as "discotic block codendrimers", which may be considered as either block codendrimers or discotic molecules. These molecules are based on a rigid aromatic disc connected to two types of 2nd generation aliphatic polyether dendrons: one (A) is made up of hydrophilic tri(ethylene oxide) (TEO) coils, and the other (B) of hydrophobic tetradecyl chains. Using the systematic combination of these two dendrons, we prepared two discotic block codendrimers (A_2B and AB_2). As a notable feature in the discotic block dendrimer design, we used a triazole-based aromatic disc to bridge the dendrons. This is because, in terms of synthesis, the aromatic 1,2,3-triazole can be obtained by a straightforward click reaction.[5] Herein, we report the ion-induced LC behavior of the discotic block codendrimers. In particular, we highlight the generation of an unprecedented Cub$_{bi}$ LC phase and the tuning of its microstructures (i.e., cylindrical core and matrix).



A_2B : $R = R' = R^1$, $R'' = R^2$
AB_2 : $R = R^1$, $R' = R'' = R^2$

$R^1 = CH_3O(CH_2CH_2O)_2CH_2CH_2O-$
$R^2 = CH_3(CH_2)_{12}CH_2O-$

The preparation of the discotic dendrimers began with the convergent synthesis of the hydrophilic and -phobic 2nd generation aliphatic polyether dendrons with the hydroxyl focal group, as described in previous publications.[6] The hydroxyl group of each dendron was converted into an azide group by sequential tosylation and azidation reactions (Scheme S1 in the Supporting Information). The aromatic core precursors, that is, mono-H and di-H, were prepared by the Sonogashira reaction (Scheme S2 in the Supporting Information).[7] Copper(I) bromide and 2,2′-dipyridyl were used as reagents for the click reaction.[8] The azide-terminat-

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ed dendron (B-N_3) was first coupled with the core precursors, because the resulting compounds (B_1-I and B_2-I) could then be clearly distinguished from the reactant dendron in the column chromatography (Scheme S3 in the Supporting Information). The iodine groups of the first clicked intermediates were changed into ethynyl ends. Subsequently, the hydrophilic dendrons (A-N_3) were attached, producing discotic block codendrimers A_2B and AB_2. The obtained dendrimers were characterized by ^{1}H, and ^{13}C NMR spectroscopy, elemental analysis, gel permeation chromatography (GPC), and MALDI-TOF MS. All experimental data fit well with the designed molecular structure (see the Supporting Information).

The thermal properties of the discotic block dendrimers were analyzed by polarized optical microscopy (POM) and differential scanning calorimetry (DSC), and are summarized in Table S1 in the Supporting Information. No LC phase was observed in any of the block codendrimers. From the thermal data, we may consider that the degree of mixing between hydrophilic and -phobic blocks in the dendrimer architecture is greater than that in linear–linear block copolymers. This speculation is consistent with recent theoretical work by Pickett and Rios, which predicted that there would be difficulty in obtaining a strongly segregated regime in block codendrimers.[9]

It is well known that ion-doping in PEO-containing block copolymers enhances microphase separation,[10] and we also wanted to test this. Therefore, we prepared ion-doped samples with A_2B and AB_2. For each block codendrimer, we made two samples with different lithium concentrations per ethylene oxide ($[Li^+]/[EO]$). All ion-doped samples from the block codendrimers revealed ordered structures in the melt, as supported by the DSC, POM, small- and wide-angle X-ray scattering (SAXS and WAXS) techniques.

An ion-doped sample, A_2B-1 with $[Li^+]/[EO]=0.15$, melted at 15.7 °C, after which temperature two distinct LC phases were observed upon heating, followed by isotropization near 143 °C. The POM observation of the first entering LC phase showed no birefringence and high viscosity in the melt from the POM observation, reminiscent of a cubic phase. In contrast, upon heating, the second LC phase showed a birefringence, although this birefringence did not cover the whole area. To clarify the identities of both LC phases, we investigated their SAXS patterns. The SAXS data of A_2B-1 detected at 30 °C displayed two strong and four weak reflections, which can be indexed as the (211), (220), (420), (332), (422), and (431) planes of a cubic structure with space group $Ia3d$ (Figure 1a). From the observed d spacing of the (211) reflection, the best-fit value for the cubic lattice parameter was estimated to be 16.16 nm. On the other hand, above 80 °C, another LC phase was revealed. Its SAXS pattern detected at 100 °C showed two reflections with a q-spacing ratio of 1:2 (Figure S3 in the Supporting Information). By taking into account the hydrophilic volume fraction ($f=0.68$) and the wedge-type molecular structure, however, it could be considered that the (110) reflection of a 2D hexagonal columnar morphology (Col_{hex}) was missing, presumably due to a structural factor. In addition, a fanlike texture from the POM observation at 100 °C also suggests a hexagonal columnar LC phase (Figure S4 in the Supporting Information). From the primary (100) reflection, the intercolumnar distance (a) was calculated to be 6.96 nm. On the basis of the interpretation of the hexagonal columnar structure, we can speculate that the cubic LC phase in lower temperatures is a Cub_{bi} morphology. As the temperature increases, the steric repulsion between the majority TEOs would be greater than those between the minority tetradecyl chains, leading to the Col_{hex}. Therefore, we suggest that the cubic phase at lower temperatures is a Cub_{bi} rather than a micellar structure.

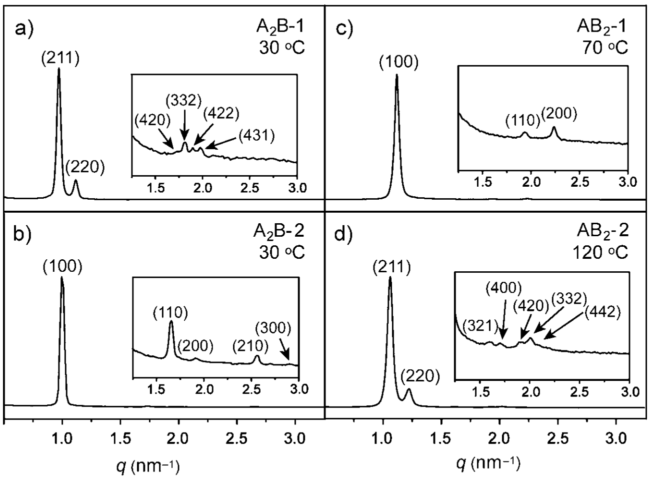

Figure 1. SAXS spectra for a) A_2B-1, b) A_2B-2, c) AB_2-1, and d) AB_2-2 at different temperatures plotted against the scattering wave vector, q ($=4\pi\sin\theta/\lambda$).

As the lithium concentration increased to $[Li^+]/[EO]=0.4$, A_2B-2 with $f=0.74$ also exhibited a Col_{hex}, which persisted up to the experimentally accessible temperature of 220 °C. In Figure 1b, the SAXS spectrum at 30 °C exhibited five reflections, which can be indexed as the (100), (110), (200), (210), and (300) planes of a Col_{hex}. In comparison to the Col_{hex} of A_2B-1, the intercolumnar distance (7.28 nm) of A_2B-2 is somewhat larger, which is attributed to the more added lithium salts.

On the basis of the hydrophilic volume fractions of A_2B-1 and A_2B-2, the outer matrix in the observed columnar structures must be composed of hydrophilic species, while hydrophobic dendrons occupy the inner cylindrical cores. In this way, the structural transformation from the Cub_{bi} to Col_{hex}, as a function of temperature or f, seems to be very reasonable. It can be explained that the expanded hydrophilic parts break up the interconnected hydrophobic cylindrical networks into cylinders as temperature or ion concentration increases.

By considering the stretched molecular length of 5.80 nm, the intercolumnar distances (6.96 and 7.28 nm for A_2B-1 and A_2B-2, respectively) and the spacing-filling requirement in the 2D columnar structure, a bilayered columnar assembly can be suggested as a suitable packing model because it avoids undesirable contact between the hydrophilic and -phobic regions (Figure 2c). By using the basis of the 4.6 Å thick column stratum (from the WAXS data in Figure 3a) and the relevant densities, the numbers of codendrimers per column cross-section of the Col$_{hex}$ were calculated to be approximately 3.1 and 2.8 for A_2B-1 and A_2B-2, respectively.[1b,13] The bilayered columnar structure differs from the orthogonal stacking of conventional discotic LCs, and this is attributed to the amphiphilic nature of the discotic block codendrimer.

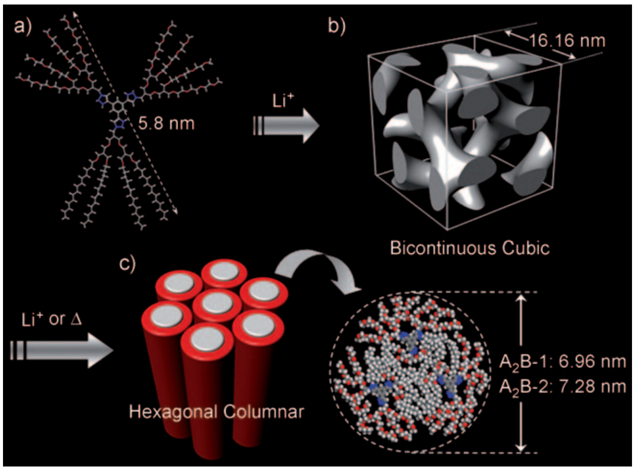

Figure 2. Schematic illustrations of a) the molecular model of A_2B, b) the bicontinuous cubic structure of A_2B-1, and c) the hexagonal columnar structure with the bilayered cross-section of A_2B-1 and A_2B-2. For reasons of clarity, the red hydrophilic matrix is not shown in (b), and lithium salts are omitted in the columnar cross-section in (c). The gray and red colors in (c) represent the hydrophobic and -philic parts, respectively.

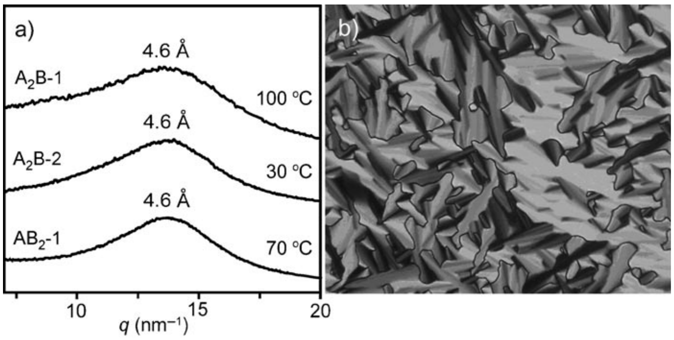

Figure 3. a) WAXS spectra in the Col$_{hex}$ of A_2B-1, A_2B-2, and AB_2-1, and b) the optical texture of AB_2-1.

Contrary to A_2B, the majority of AB_2 is the hydrophobic dendron block. Therefore, we expected a certain phase-inverted morphology consisting of hydrophobic matrix and hydrophilic cores, in contrast to the ionic samples of A_2B. We chose $[Li^+]/[EO]$s to be 0.2 and 0.4 for AB_2-1 and AB_2-2, respectively. In the melt, both samples showed LC phases, which persisted up to 160 °C and 197 °C for AB_2-1 and AB_2-2, respectively.

From the POM observations, sample AB_2-1 with $[Li^+]/[EO]=0.2$ showed a birefringent fanlike texture taken at 140 °C, which is typically found in the columnar LC phase of discotic liquid crystals (Figure 3b).[14] This texture suggests that the aromatic discs form an anisotropic stacking, from which our block codendrimers share the self-assembling character of discotic LCs. Consistent with the POM results, the SAXS data of AB_2-1 at 70 °C displayed a Col$_{hex}$ pattern where three reflections with q-spacing ratios of $1{:}\sqrt{3}{:}\sqrt{4}$ (Figure 1c). From the (100) plane, the intercolumnar distance was estimated to be 6.48 nm. The comparison of this intercolumnar distance with the AB_2 stretched molecular length of 5.80 nm,[15] suggests a bilayered packing in the columnar cross-section, as proposed for the ion-doped A_2B samples (Figure 4a). Taking into account the wedgelike molecular structure (i.e., the higher grafting density of tetradecyl chains in AB_2) and the hydrophilic volume fraction ($f=0.47$) of AB_2-1, however, the configuration of hydrophilic and -phobic parts must be inverted in comparison with the bilayered Col$_{hex}$ of the ion-doped A_2B samples. By using the 4.6 Å thick column stratum from Figure 3a and the relevant densities, the number of AB_2 per column cross-section was calculated to be approximately 2.4.

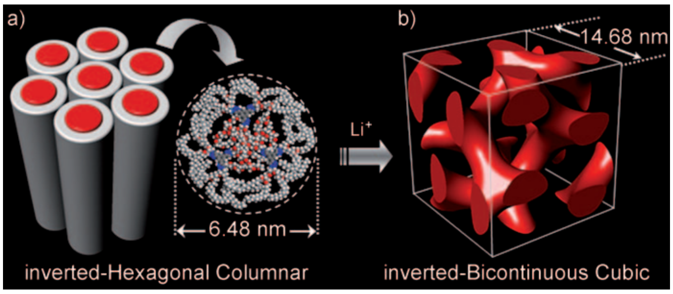

Figure 4. Schematic illustrations of a) the inverted-hexagonal columnar structure (with a bilayered cross-section) of AB_2-1, and b) the inverted-bicontinuous cubic LC structure of AB_2-2. For reasons of clarity, lithium salts are omitted in the columnar cross-section in (a), and the gray hydrophobic region is not shown in (b). The gray and red colors represent the hydrophobic and -philic parts, respectively.

In contrast to AB_2-1, AB_2-2 with $[Li^+]/[EO]=0.4$ was optically isotropic over the entire LC temperatures, indicative of a cubic phase. The SAXS data of AB_2-2 detected at 120 °C displayed a similar reflection pattern to the Cub$_{bi}$ of A_2B-1. It displayed the (211), (220), (321), (400), (420), (332), and (422) planes of a cubic structure with space group $Ia3d$ (Figure 1d). The cubic lattice parameter was estimated to be 14.68 nm. Considering the phase sequence with increasing lithium concentration, this cubic phase can be considered an "inverted" bicontinuous cubic (Cub$_{bi}$) structure. On going from AB_2-1 to AB_2-2 (i.e., increasing f), more added lithium salts expand the minority cylindrical core by which the cubic phase of AB_2-2 must be more continuous than the Col$_{hex}$ of AB_2-1.[16] Accordingly, only the cubic candidate is a $\mathrm{Cub_{bi}}$ consisting of a hydrophobic matrix and hydrophilic cylindrical networks (Figure 4b). Remarkably, the $\mathrm{Cub_{bi}}$ phase of AB_2-2 persisted over a wide temperature range (from 15 to almost 197 °C). This is in marked contrast to linear block copolymers in which bicontinuous cubic networks change into hexagonal cylinders with the addition of ionic species.[17]

As described above, the ion complexation of the discotic block codendrimers showed the induced LC phases with hexagonal columnar and bicontinuous cubic architectures. Notably, to date, cubic LC phases observed from dendrimer architectures have all been revealed to be discrete micellar structures.[1b,18] To the best of our knowledge, the $\mathrm{Cub_{bi}}$ phases of A_2B-1 and AB_2-2 are the first bicontinuous cubic example in LC dendrimers, although only a few dendron–polymer conjugates showed this cubic phase.[19] Furthermore, the $\mathrm{Cub_{bi}}$ is still unusual in discotic LC molecules.[4]

Along with the generation of the unique $\mathrm{Cub_{bi}}$ LC phase, it is worth noting that the local properties in the $\mathrm{Cub_{bi}}$ morphology (i.e., the inversion of hydrophilic and -phobic properties between cylindrical cores and matrix) could be fine-tuned; in other words, we can endow an exterior matrix with either hydrophilic or -phobic character by the simple alteration of the majority dendritic block.

In summary, we prepared two discotic block codendrimers by a stepwise click reaction, and investigated the LC-forming behavior of their ion-doped samples. Thermal and X-ray analyses revealed the generation of the $\mathrm{Col_{hex}}$ and $\mathrm{Cub_{bi}}$ LC phases as well as their phase-inverted homologues, as a function of hydrophilic volume fraction. Interestingly, the $\mathrm{Cub_{bi}}$ phase shown herein could be utilized as a promising platform applicable to organic electronics, such as LC semiconductors or electrolytes, when we consider the 3D connectivity of its cylindrical core domain, including aromatic discs and ions.

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Keywords: click chemistry · dendrimers · liquid crystals · morphologies · self-assembly

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