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A partially crosslinked bicontinuous cubic phase exhibiting a temperature range of more than 100 $^\circ C \dagger$

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A new methodology of partial crosslinking is presented for stabilizing the bicontinuous cubic phase without losing its dynamic nature. It was applied to a mixture of 1,2-bis[4'-(9''-decenyloxy)benzoyl]hydrazine with a bi-functional linker, remarkably stabilizing the phase in comparison with the neat compound having no C==C bond at the end of the alkyl tail.

Liquid crystals (LCs) are one of the soft materials having selforganized structures in dynamic state.¹ Utilization of those self-organized dynamic structures is a promising approach for nano-structured functional materials.² The LCs utilized so far are one-dimensionally ordered smectic phases or two-dimensionally ordered hexagonal phases, but recently, bi-continuous cubic (Cub_{bi}) LCs have attracted more attention.^{3–7}

One of the features of Cub_{bi} LCs is their three-dimensional periodic structures with local liquid-like mobility preserved. Several applications have been proposed for the Cub_{bi} LCs such as nano-porous templates, 5a,b catalytic bases, 3 separation membranes,^{5c,d} three-dimensional (ionic/electronic) conductors^{5e-i} and so on. In those cases, stabilization of the Cub_{bi} LC structures is crucial, but at present the structures are formed usually in narrow ranges and at relatively high temperatures in thermotropic systems. From this viewpoint, the in situ photopolymerization of LC molecules with polymerizable moieties has been recognized as a useful approach, and in fact, the preservation of lyotropic Cub_{bi} LC structures was already reported by Gin and his coworkers.^{5c,d,f} In thermotropic systems, however, there is another difficulty encountered because the balance of size and shape of nanosegregated parts within the molecule is so delicate that the introduction of conventional polymerizable moieties such as acrylate groups into LC molecules often destabilizes the original Cub_{bi} LC structures. Recently, Kato and co-workers have synthesized fan-shaped molecules having three long aliphatic tails, into two of which 1,3-diene end groups are incorporated, and successfully preserved the thermotropic Cub_{bi} LC structures in a solid polymer film.5h



Fig. 1 Molecular structures of BABH-10 and compound 1.

Our research group has established the phase diagram of a series of rod-like molecules, 1,2-bis(4'-alkyloxybenzoyl)hydrazines [denoted as BABH-n, where n is the number of carbon atoms in the alkyl tail].⁶ In contrast with the simplicity of the molecular structure, the diagram is complicated; in addition to a layered smectic C (SmC) phase region, regions of two types of Cub_{bi} LC phases with symmetries Ia3d and Im3m are seen, the formation of which are dependent upon the chain length *n* and temperature.^{6*c*-*f*} In chemistry of Cub_{bi} LC phases, the majority of molecules exhibiting those phases documented so far is rod-like,^{4a} although Kato's success was accomplished for fan-shaped molecules. Considering the quite high sensitivity of thermotropic Cub_{bi} LC structures to the molecular structure as mentioned above, preservation of thermotropic Cub_{bi} LC structures is still a challenging subject to be continued. Thus, we have in this communication introduced at the end of the alkyl tails of BABH-10 not a 1,3-diene as utilized by Kato but a C=C bond, as shown in Fig. 1. Although it is known that the reactivity of the C = Cbond for photopolymerization is quite low, we have found that UV irradiation of the mixture of this compound with a diacrylate monomer and a photoinitiator profoundly stabilizes the Ia3d-Cubbi LC structure in a remarkable wide temperature range of more than 100 °C.

1,2-Bis[4'-(9''-decenyloxy)benzoyl]hydrazine (1) was synthesized in two steps. The first step is Williamson etherification of ethyl 4-hydroxybenzoic acid and 10-bromo-1-decene, to produce 4-(9'-decenyloxy)benzoic acid (2). The second step is transformation of 2 into the acid chloride, followed by a reaction with hydrazine monohydrate to give the final product 1. The crude product was recrystallized, dried under vacuum, and the purity was checked by TLC, ¹H and ¹³C NMR, and elemental analysis. Characterization data are included in ESI.†

Fig. 2 compares the phase behaviors of four systems, which are BABH-10, compound **1**, mixture of **1** with the bi-functional linker and the photo-initiator, and the mixture after photopolymerization at ~140 °C. BABH-10 exhibits two LC phases, an *Ia3d*-Cub_{bi} phase (143.5–153.9 °C) and a SmC

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Fig. 2 Comparison of phase behaviors of BABH-10, compound 1, mixture of 1 with a bi-functional linker and a photo-initiator, and the mixture after photopolymerization at \sim 140 °C.

phase (153.9–166.4 °C) on heating.^{6a,b,e} Compound 1 showed an Ia3d-Cubbi phase (135.2-151.2 °C) but unlike BABH-10, not followed by the formation of the SmC phase at the high temperature side, directly transitioned to the isotropic liquid (see Fig. S1-S3, ESI⁺). This can be explained in terms of change in the average molecular shape previously discussed for BABH-n.^{6e} In the Cub_{bi} phase, it is expected that the alkyl tails are laterally expanded slightly compared to the central molecular core. This is an origin of the Ia3d-Cub_{bi} structure, which is described in terms of the G type of a triply periodic minimal surface (TPMS) framework.³ When going on to the high temperature region, in BABH-10, weakening of the intermolecular hydrogen bonding interactions effectively expands the central core part, putting back the shape into a rod, in favor of a lavered structure of the SmC phase. In the case of compound 1, on the other hand, the presence of C=C bond at the extremity of the alkyl tail would reasonably lead to more lateral expansion than in BABH-10. In fact, the lattice dimension of 1 was a = 6.95 nm at 150.1 °C, based on the X-ray diffraction (XRD) studies, which is by 1.3% shorter than that of BABH-10 (a = 7.04 nm at 150.1 °C).6e This is consistent with the above-mentioned picture, because the larger extent of deformation from a rod-shape would result in a smaller size of the lattice dimension. The infrared spectra (IR) for 1 revealed that the strength of the intermolecular hydrogen bonding varies with temperature but no difference is visible between 1 and BABH-10 (Fig. S4, ESI⁺). Finally, what to note here is that the replacement of ethyl with vinyl (ethenyl) headgroup is quite tiny but actually has a profound effect on the phase behavior of the Cub_{bi} phase-forming molecule. The lowering of the clearing temperature by ~ 10 °C is also consistent with the results of Kelly's extensive work on other LC materials.⁷

For photopolymerization, to compound **1** were added 1,6-hexanediol diacrylate as a bi-functional linker and 2,2dimethoxy-1,2-diphenylethan-1-one as a photo-initiator in a molar ratio of 66.8:24.7:8.5. As shown in Fig. 2, the mixture also showed an *Ia3d*-Cub_{bi} phase, whose temperature range (130.1–146.1 °C) shifted by ~5 °C toward lower temperature owing to the freezing-point depression in comparison with the neat compound **1**. The lattice dimension was a = 6.90 nm at 142.5 °C, based on XRD (Fig. S5 and S6, ESI†), slightly shorter than that of compound **1**. However, one may be a little bit surprised at the preservation of the *Ia3d*-Cub_{bi} phase with a quite similar lattice dimension in the mixture, if recalling both the substantial amount of adducts in the mixture and the usual high sensitivity of Cub_{bi} LC phase formation to the molecular structure. This result, however, can be understood as follows: the Cub_{bi} structures are described by a TPMS dividing the space into two separate sub-spaces. In the case of BABH-10, the TPMS layers with a finite thickness are filled with molten alkyl tails.^{6d} By analogy with lyotropic Cub_{bi} LC systems, Saito and Sorai *et al.*⁸ pointed out that such alkyl tails serve as a solvent (self-solvent), and in the binary mixtures with alkanes, the alkyl tails can dissolve some amount of the second component molecules with low dielectric constant, preserving or inducing Cub_{bi} phases identical with those formed in the corresponding neat compounds.^{8a,c} Therefore, in the present mixture, the coexisting diacrylate monomer and the photo-initiator are also considered such additional components soluble in the TPMS regions.

The photopolymerization of the mixture was carried out at around 142 °C in the temperature region of the Cub_{bi} LC phase, and as the result of the polymerization, the Cub_{bi} structure was outstandingly stabilized: upon cooling from that region, the structure was almost preserved down to room temperature (Fig. 3b). The photograph taken at 50.0 °C displays a completely black area (Fig. 3a). However, the subsequent heating DSC curve (Fig. S7, ESI⁺) showed a tiny endothermic peak at 120 °C, indicating the presence of a small amount of region recrystallized, which is estimated as $\sim 18\%$ from the evaluation of the enthalpy change. A little bit complicated result is that further heating showed a faint peak at around 152 °C, suggesting a transition to the isotropic liquid, although the XRD result (mentioned below) reveals that the material is still in the Cub_{bi} state. This suggests the presence of some crosslinking inhomogeneity in the mixture.

The preservation of the *Ia3d*-Cub_{bi} structure was also confirmed by XRD as shown in Fig. 4. The radially-averaged pattern at 45.0 °C shows two peaks at 2.19 and 2.52 nm⁻¹ with a shoulder peak at 2.06 nm⁻¹. The reciprocal *d*-spacing ratio of the former two peaks is $\sqrt{6}$: $\sqrt{8}$, which can be indexed to the (211) and (220) reflections of an *Ia3d*-Cub_{bi} lattice with a lattice dimension a = 7.03 nm. The left-sided shoulder is probably attributable to the crystalline state (see Fig. S2 and S5, ESI†). The curve-fitting was applied to the pattern to extract the crystalline peak, and from the peak area the percentage of the crystalline state is evaluated as ~20% (Fig. 4b). At temperatures above 120 °C, the crystalline peak completely disappears, indicating the formation of the *Ia3d*-Cub_{bi} phase in the whole area. The lattice dimension is a = 7.10 nm at 150.0 °C.



Fig. 3 Polarizing optical microphotographs of the mixture of 1/diacrylate/photo-initiator; (a) at 50 °C, where the whole area was irradiated, and (b) at 49.3 °C, on cooling from the Cub_{bi} phase temperature region after polymerization. In (b), unlike in (a), the area includes the region not irradiated in the left side, where the bright image is seen; in the right side, a mosaic texture is barely visible, suggesting partial crystallization.



Fig. 4 (a) XRD patterns of the mixture of **1** with diacrylate and photo-initiator at 45.0, 150.0, 180.1, 200.0, and 215.0 $^{\circ}$ C on the second heating after photopolymerization at around 142 $^{\circ}$ C and subsequent cooling down to room temperature. (b) Fraction of the Cub_{bi} phase evaluated from the XRD pattern as a function of temperature.

The relatively broad peaks clearly come from the crosslinking inhomogeneity mentioned above. Increasing the temperature further increases gradually the fraction of a broad halo at around 2.4 nm⁻¹, attributable to thermal fluctuation of the Cub_{bi} structure. The percentage of the halo increases beyond 160 °C, suggesting partial melting of the Cub_{bi} lattice, which corresponds to the above-mentioned DSC peak. However, very surprisingly, the (211) and (220) reflections of the *Ia3d*-Cub_{bi} lattice still remained at the highest temperature examined (215 °C), although becoming quite weak.

An important point is that this stabilization of the Ia3d-Cub_{bi} LC structure is achieved in the presence of the terminal C=C bond of compound **1**, although it is known that the reactivity of the C=C bond for photopolymerization is quite low. The same type of photopolymerization was performed for the mixture of BABH-10 with the similar molar ratios of diacrylate and photo-initiator, but failed in preserving the Cub_{bi} structure, showing a macrophase-separation (Fig. S8, ESI†). This demonstrates that the terminal C=C bond of compound **1** plays a crucial role in preventing macrophase-separation, although the contribution to the network formation is partial (estimated as ~5%, see ESI†) and the network in the *Ia3d*-type TPMS region is mainly produced from the bi-functional linkers.

In conclusion, in this communication, partial crosslinking of the terminal alkyl tails of compound 1 with bi-functional linkers has enabled the formation of the Cub_{bi} LC phase in a very broad range of temperature of more than 100 °C. This success demonstrates that the concept of partial crosslinking can be a useful methodology when preserving the dynamic nature of the self-organized structure characteristic of LCs.

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