Double gyroid structures made of asymmetric dimers

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ABSTRACT

Gyroid cubic phases are interesting for both scientists and engineers due to possible applications in electronic devices. New series of dimeric molecules, despite their flexible molecular structure, can display double gyroid cubic phase with Ia3d symmetry and lattice parameter corresponding to double molecular length. The cubic phase is structurally related to columnar phase and both phases often coexist in the same temperature window. Apparently, for studied compounds stronger molecular asymmetry promotes cubic structure. Interestingly, for the examined compounds the transition between two isotropic liquids was observed.

Introduction

In the last few years, self-organised three-dimensional (3D) thermotropic liquid crystalline materials have been extensively studied due to their unusual network structures,[1–11] which can be very useful for applications requiring easy molecular accessibility and fast molecular transport.[5] For example, the thermotropic cubic bicontinuous phases (Cubbi) can be attractive for potential alignment-free 3D π-electronic semiconductors, [11–14] ion transportation and stimulus-responsive...
materials.[15] The cubic bicontinous phases, despite short-range positional correlations of neighbouring molecules, exhibit large-scale 3D periodic structure, due to the nanosegregation mechanism.[1–5] Initially, the 3D liquid crystalline phases were found as a lyotropic state of matter, common among water solutions of lipids and surfactants,[6,7] such phases are also frequently observed for di-block copolymers,[8] however only rarely they are formed by thermotropic mesogens.[1–5] They can be classified as: micellar type – where supramolecular nano-spherical micelles are arranged into a cubic lattice with Im3m or Pn3m symmetries;[9,10] or channel type – made by congruent network of channels filled with chemically incompatible parts of molecules. For typical mesogenic molecules the interwoven channels are filled with aromatic parts of molecules, disconnected by regions occupied with molten alkyl chains.[5,11] Depending on the arrangement of channels in space a few different types of phases were recognised: a double gyroid cubic structure with the Ia3d [5] or Pn3m [16] symmetry, tri-continuous cubic phase with the Im3m symmetry,[17] a single gyroid cubic structure with the I4132 symmetry [2,4] and a multicontinuous type Pm3m structure [18]; the most frequently observed was the Ia3d cubic phase.[19–22] The ability to exhibit 3D liquid crystalline phases depends strongly on the molecular architecture. They were observed for polycatenar, sanidic, polyhydroxy and dendritic molecules.[1,2] For some systems the cubic phase can be induced by specific intermolecular interactions: strong hydrogen bonding [23,24] or ionic interactions.[14,25] Herein we describe a new class of compounds able to form 3D liquid crystalline phases with cubic symmetry – bimesogenic molecules built of two different rigid cores connected by flexible spacer (Figure 1). Dimeric molecules, in which two rigid mesogenic units are connected via flexible spacers,[26] have additional degree of freedom due to the flexibility and parity of the alkyl chain linking two mesogenic cores. It is known that such flexibility leads to special structures, for example twist bend nematics,[27–30] modulated smectics [31,32] and broken-layer type columnar phases.[33,34] There is also limited number of reports about cubic phases formed by symmetric dimeric molecules with long internal spacer.[35,36]

Results and discussion

Molecules of studied dimers L1–L4 (Figure 1) are built of two rigid parts connected by flexible chain of different lengths (n = 5, 10 or 16 carbon atoms). One of the rigid units, the same for all compounds, contains trans-stilbene moiety connected by ester bond to biphenyl group. The core is terminated by three decyloxy chains attached to the stilbene group. The second rigid part is made of benzoate unit having one or two terminal decyloxy chains. Final compounds were obtained via synthetic route presented on Figure 1. The methyl 3,4,5-trihydroxybenzoate was reacted with 1-bromododecane via Williamson reaction in the presence of potassium carbonate and potassium iodide. Next the methyl 3,4,5-tridecyloxybenzoate (1) was reduced to the alcohol (2) with lithium aluminium hydride and subsequently oxidised into aldehyde (3) with activated manganese (IV) oxide. The aldehyde (3) reacted with phosphonium salt via modified Wittig reaction in slightly alkaline conditions. The trans-stilbene derivative (4) was initially converted to sodium salt, next into acid chloride derivative (5) and finally connected with biphenol group via esterification reaction at the presence of diisopropyl azodicarboxylate (DIAD). Ester derivative (6) was attached to the four types of alcohol derivatives (9) via Mitsunobu reaction for achieving a final product L. Alcohol derivatives (9) were obtained from proper methyl hydroxybenzoate via Williamson reaction with decyloxy bromide, subsequently hydrolysed, then transformed into acid chloride (8) and finally connected with appropriate diol (n = 5, 10, 16) via esterification reaction in the presence of DIAD.

All studied compounds exhibit liquid crystalline phases, however the type of the phase and its thermal stability varied significantly (Table 1).

For two homologue compounds, L1 and L2, having single terminal chain at the phenyl ring and the internal spacer of 5 and 10 methylene groups, respectively, the cubic phase was formed on heating, between crystalline phase and isotropic liquid. Observed under crossed polarisers the cubic phase appeared as dark areas with sharp boundaries growing over the crystallites, lack of the optical birefringence is consistent with cubic symmetry of the phase. The x-ray diffraction (XRD) pattern, registered in the cubic phase contained a number of sharp, incommensurate reflections in the small-angle range. The ratio between first two peak positions in the reciprocal space being close to $\sqrt{6} : \sqrt{8}$ indicated the Ia3d symmetry of the phase, such lattice assignment was confirmed by fitting the whole pattern to chosen symmetry (Figure 2(a)). The crystallographic unit size, a, only weakly depends on temperature, it varies in range 114–116 Å for L1 and 118–120 Å for L2; in both cases the lattice parameter decreases on heating. The lattice parameter corresponds roughly to double molecular length. Assuming average density of the cubic phase to be 1 g/cm$^3$, the number of molecules
filling the unit cell can be estimated as 550–600. The size of crystallographic unit cell suggests that cubic phase is made of channels formed by non-intercalated molecules, while the interface between the regions filled with mesogenic cores and alkyl chains is curved to accumulate large number of tails per single mesogenic core. The wide-angle XRD pattern confirmed short-range positional correlations between neighbouring molecules, evidenced by broad diffraction signal centred at ~4.5 Å (Figure S1 in Supplementary Material). In the temperature range above the cubic phase, an isotropic liquid with pronounced density fluctuations is observed, fluctuations manifest in x-ray diffractograms as strong, diffused, low-angle signal, corresponding to ~4.5 Å (Figure S2 in Supplementary Material). Further heating of the sample causes a transition into another isotropic liquid. The transition is

Figure 1. Synthesis of the final compounds L.

Table 1. Phase transition temperatures (in °C) and enthalpy changes (in parentheses, J/g) determined by differential scanning calorimetry (DSC) on heating runs for studied compounds.

| n  | R   | Phase sequence                                                                 |
|----|-----|-------------------------------------------------------------------------------|
| L1 | 5 H  | Cry1 63.7 (7.8) Cry2 87.1 (46.6) Cub (Col) \(^a\) 116.9 (3.8) Iso \(^b\) 122.5 (3) |
| L2 | 10 H | Cry1 64.5 (46.8) Cry2 74.7 (11.5) Cub (Col) \(^a\) 83.0 (1.2) Iso \(^b\)          |
| L3 | 10 C  | Cry 78.8 (7.4) Col 81.8 (81.8) Iso                                             |
| L4 | 16 H | Cry [70.4 Col] 78.7 (65.6) Iso                                                 |

Notes: \(^a\)Co-existence of Col and cubic phases on cooling from isotropic liquid has been detected by microscopic observations for L1 and L2 compounds. \(^b\)Transition between two isotropic liquids was poorly resolved on heating runs, see Figure S3 in Supplementary Material.
marked by the change of the intensity of the low-angle diffraction signal, its position do not change. The transition between two isotropic liquids could be also detected in calorimetric experiments (Figure S3 in Supplementary Material). Microscopic observations performed on cooling the sample revealed formation of additional liquid crystalline phase between isotropic liquid and cubic phase; based on the optical texture the phase could be identified as columnar hexagonal one (Figure 2(b)). However, this assignment could not be confirmed by XRD experiments due to metastable character of the phase: even at constant temperature it quickly transforms into cubic structure.

The longest homologue L4, with 16 methylene units in the internal spacer, exhibits much weaker mesogenic properties than shorter analogues. It melts directly to isotropic liquid, however on quick cooling the birefringent texture characteristic to columnar phases was observed together with growing solid crystals (Figure S4 in Supplementary Material). Coexistence of crystalline and liquid crystalline phases prevents the identification of the columnar phase.

Compound L3, which differs from L2 by additional terminal chain at the phenyl ring, does not form cubic mesophase. Instead, on cooling the columnar phase is formed, with the optical texture (Figure 3(a)) characteristic to rectangular rather than hexagonal type phase. However, the XRD pattern clearly showed the sixfold symmetry (Figure 3(b)) evidencing the hexagonal packing of the columns. Molecular positions within the columns are correlated over short distance only (disordered type phase).

From the lattice parameter, \(a = 53\, \text{Å}\), assuming the density \(1\, \text{g/cm}^3\), it can be deduced that the average cross section of the column is made of 3–4 molecules. It should be also noticed that apart from the signals resulting from the hexagonal array of columns, additional sharp reflection, related to periodicity \(d = 28.8\, \text{Å},\)

![Figure 2](image1.png)  
*Figure 2.* (a) Experimental (black) and simulated (red) small-angle XRD patterns for the cubic phase of L1 compound; for the simulation the la3d structure with lattice parameter \(a = 115.6\, \text{Å}\) was assumed, in the simulation peak positions were determined by the lattice symmetry and the unit cell parameter, while their intensities were freely fitting parameters; (b) optical texture of the Colh phase formed by L1 compound on cooling the isotropic liquid. The black areas are the domains of cubic phase growing from columnar phase.

![Figure 3](image2.png)  
*Figure 3.* (a) Optical texture of columnar phase formed by L3 compound, (b) 2D small-angle XRD pattern of columnar phase of L3 compound, sixfold symmetry of the pattern reflects hexagonal lattice of columns. Note the presence of a diffraction signal, which is not related to hexagonal columnar structure.
has been detected in the XRD pattern (Figure 3(b)). Such a signal is typically ascribed to some helical arrangement of molecules along the column.[37,38] The helical structure might be due to the twist of adjacent mesogens along the column, caused by compensation of different volumes of the aliphatic ends of the molecule.

Conclusions

With our work we have proved that dimeric mesogenic molecules can exhibit double gyroid cubic phase, despite their flexible molecular structure. We also found important structural parameters which decide whether cubic or columnar phase is formed. It seems that stronger molecular asymmetry, that is large difference in number of terminal alkyl chains at both ends of molecules, promotes cubic structure. Above the cubic phase the isotropic liquid exhibiting very strong density fluctuations was found; similar phenomenon has been lately observed for other mesogens forming 3D structures.[39,40] Most probably, the isotropic liquid with strong fluctuations is a sponge [41] phase or cubosome [42] type phase. By opening access to a new class of materials forming double gyroid structures our findings may be beneficial for alignment-free and solution-processable electronic devices.

Disclosure statement

No potential conflict of interest was reported by the authors.

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