

# Elastic properties of hexagonal columnar mesophase self-organized from amphiphilic supramolecular columns

Hee-Tae Jung<sup>a)</sup> and Sang Ouk Kim

*Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejeon 305-701, Korea*

S. D. Hudson

*Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, and Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8544*

V. Percec

*Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323*

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By direct imaging, we evaluate the relative stiffness of a hexagonal columnar mesophase induced by the self-organization of amphiphilic columnar supramolecules, both quantitatively and qualitatively, based on examination of the planar texture, and of defects contained therein. Quantitative measurement was performed by an analysis of distortions around edge dislocations. The elastic anisotropy varies significantly with the degree of molecular association. The columnar supramolecule containing rigid tapered molecules is stiffer than weakly associated self-assembled macromolecules by an order, resulting in different stability of the mesophase. In addition, defect characteristics are examined to further understand these supramolecular assemblies and their elastic properties. Highly resolved  $+1/2$  disclinations have been observed in the flexible columnar supramolecules. © 2002 American Institute of Physics. [DOI: 10.1063/1.1432449]

Nano-structured materials are potentially of great technological interest for the development of opto-electronics, nano-fabrication, and bio-technology. For example, synthetic nanostructured columnar supramolecules have become a subject of considerable interest because they organize themselves into nano-scale structures that achieve special properties as membrane, catalysis<sup>1</sup> and electro-optic materials, including photoconductive materials<sup>2,3</sup> with superior charge mobility. Formation of the nanostructure is based on self-assembly from their components.<sup>4-7</sup>

As with all other types of materials, elasticity is one of the key parameters that determine physical properties. Despite its significance in the field of opto-electronics and biology, there have been few studies on the elasticity of synthetic supramolecules. Thus, little information is available concerning the relationship between elasticity, chemical structure and morphology of columnar supramolecules. Different applications call for different properties. For example, supramolecules containing stiff columns may be able to produce defect-free systems, which are essential for certain nanofabrication techniques, including some types of lithography. Instead, flexible columns may be useful for membrane applications. The stiffness of columns may also correlate with the stability of the columnar phase. Thus, indirect information of stiffness, and its relationship to chemical structure, has been estimated from transition temperatures.<sup>8,9</sup> Elasticity of vesicle bilayers, nematic, lamellae (smectic A) and columnar liquid crystals has been studied theoretically and experimentally.

For example, the elastic modulus of highly swollen lamellar liquid crystals ( $L_\alpha$ ),<sup>10</sup> sponge phases ( $L_3$ )<sup>11</sup> and amphiphilic polymer-lyotropic lamellar systems<sup>12</sup> can be determined by diffraction from the amplitude of thermal fluctuations. Moreover, transmission electron microscopy (TEM) methods have been employed to measure elastic anisotropy of nematic liquid crystals by disclination images,<sup>13</sup> elastic anisotropy of a rigid rod polymer by dislocation images<sup>14</sup> and uni-lamellar vesicle bilayers by an analysis of the size distribution of the vesicles through cryo-TEM.<sup>15</sup>

In this letter, we determine the relative stiffness of hexagonal columns formed from synthetic supramolecules using high-resolution electron microscopy and image analysis of the distortions around edge dislocations. The morphology and stability of the columns of various chemical structures are compared.

In this study, we used two taper-shaped supramolecules having a crown ether at one end which forms the center of the column and three fluorinated tails at the other (Fig. 1). Detailed synthetic procedures are described elsewhere.<sup>4,16</sup> The columnar phases of the semi-fluorinated compounds are reported to be quite stable, perhaps because of the dramatic increase in the self-assembly process via microsegregation of the perfluorinated and perhydrogenated parts of the tapered groups due to the fluorophobic effect.<sup>4,16-18</sup> X-ray diffraction (XRD), electron diffraction (ED) and polarized optical textures (not shown here) found that the materials form a hexagonal columnar mesophase ( $\Phi_h$ ). On cooling ( $10^\circ\text{C}/\text{min}$ ) from isotropic phase, compound **1** exhibits only a hexagonal columnar mesophase ( $\Phi_h$ ). However, in addition to the  $\Phi_h$  phase, compound **2** also forms a crystalline phase at lower temperature.

<sup>a)</sup>Corresponding author: Assistant Professor, Organic Opto-Electronic Materials Laboratory, Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejeon 305-701, Korea; electronic mail: heetae@kaist.ac.kr; Tel: +82-42-869-3931, Fax: +82-42-869-3910.

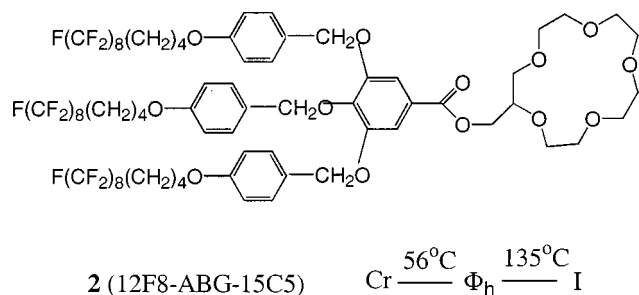
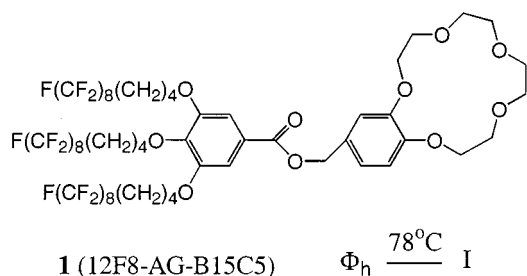


FIG. 1. The chemical structure of the tapered molecules **1** and **2**, and phase transition temperatures of their columnar hexagonal phase.

We obtained planar columns (homogeneous alignment) on a water surface, so that the column axis is parallel to the film surface. Our previous experimental result shows that homeotropic orientation of the mesophases occurs most readily on carbon substrates, while planar alignment is favored a water surface.<sup>9</sup> Columns have more chemical affinity for water than other surfaces that we studied.<sup>18</sup> TEM images show that there is a high degree of perfection in the packing of cylinders in the fluorinated materials (Fig. 2). However, the planar morphology of compound **1** is much different from that of compound **2**. Columns of compound **1** are shown to be curved. In contrast, those of compound **2** are straight. Similar morphologies are observed in other supramolecules. For instance, an amphiphilic glucamine derivative, which contains hydroxy groups of the carbohydrate head group and two aliphatic chains (dodecyloxy) grafted to the benzamine group,<sup>19</sup> forms straight columns, while an asymmetric dendrimeric compound, 1,2,3-tris[3,4,5-tris[4-(n-dodecan-1-yloxy) benzyl] oxy] benzyl] oxy]–benzene,<sup>20</sup> shows a flexible morphology. This morphological difference is indirect evidence of differences in stability of the hexagonal columnar mesophase, consistent with differential scanning calorimetry (DSC) and optical microscopy (OM) results. Specifically, the stiffer compound also has a higher transition temperature to the isotropic phase (135 °C, rather than 78 °C). This difference is remarkable, in view of the chemical similarity of compounds **1** and **2**. It has to be noted that the morphological results are obtained from many different TEM images.

Quantitative measurements of the relative stiffness of the columns were obtained from the distortion around edge dislocations [e.g., Fig. 3(a)]. As shown schematically in Fig. 3(b), the columns adjacent to the dislocation are slightly bent and tilted with respect to the central column. Each structure is distinguished by a characteristic length,  $\lambda$ , which is proportional to the square of the length,  $L$ , of the bent segment

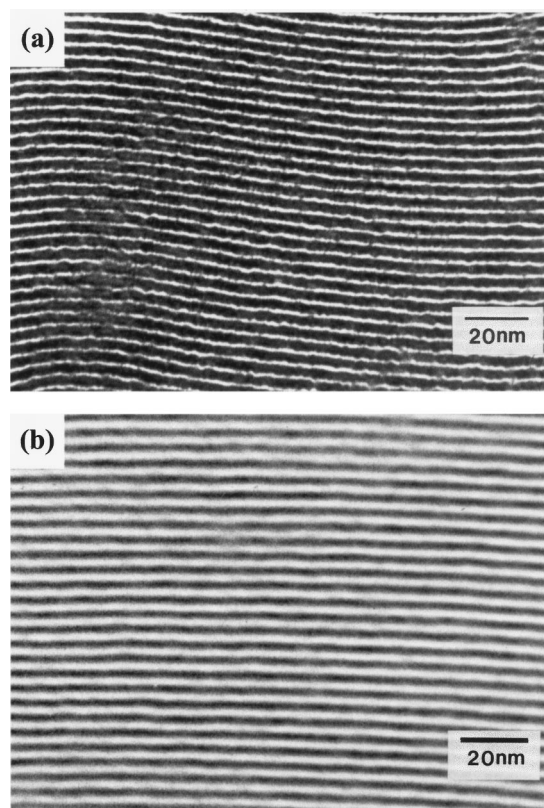


FIG. 2. TEM micrograph and ED of (a) compound **1** and (b) compound **2** of solution cast on distilled water at  $T_{ph}(\sim 50^\circ\text{C})$  showing planar textures of columnar hexagonal mesophase.

of a column divided by its distance,  $z$ , from the central column, i.e.,  $\lambda \sim L^2/z$  and therefore, estimates the column stiffness. Specifically, the angle of inclination ( $\theta$ ) of the columns is expressed as function of  $x$  (column axis),  $z$  (the distance from the dislocation along the Burger's vector, i.e., perpen-

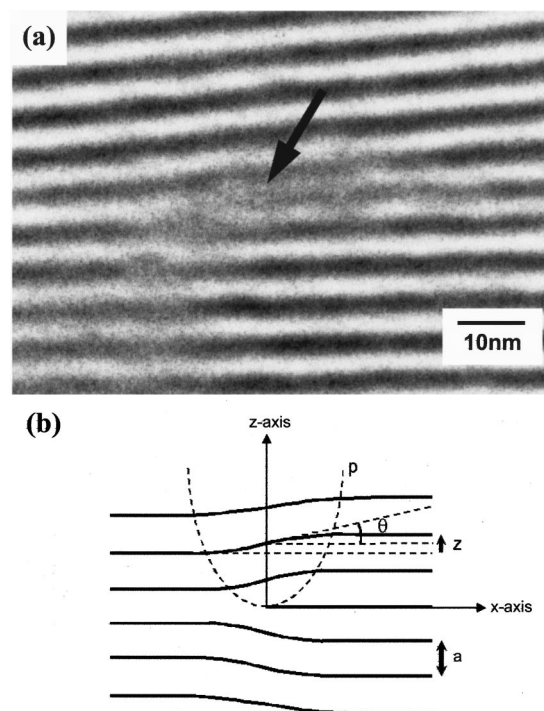


FIG. 3. (a) TEM micrograph (b) and its corresponding schematics showing an edge dislocations in a well-aligned specimen of compound **2**.

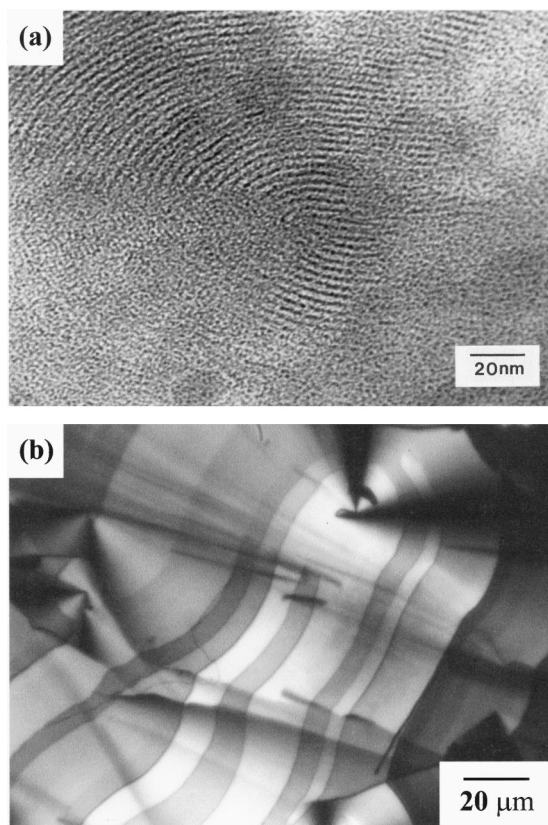


FIG. 4. (a) TEM micrograph showing +1/2 disclination in compound **1**. (b) Polarized optical microscopy texture of columnar hexagonal mesophase of compound **1** formed on cooling from the isotropic phase at a rate of  $\sim 0.1$  °C/min.

dicular to the central column) and the characteristic length ( $\lambda$ ):<sup>21</sup>

$$\frac{1}{4\sqrt{\pi}} \frac{a}{\sqrt{\lambda z}} \exp\left(\frac{-x^2}{4z\lambda}\right), \quad (1)$$

where  $a$  is the undistorted layer thickness, and  $\lambda$  is defined as:

$$\lambda = \sqrt{\frac{k_{33}}{B+D}}, \quad (2)$$

where  $k_{33}$  is the Frank elastic constant for bending of the columns, and  $B$ ,  $D$  are bulk moduli corresponding to column dilation and column shear, respectively. The distortions are confined essentially to parabolas ( $x^2 = 4\lambda z$ ), denoted as  $P$  in Fig. 3(b).

In the plane at  $x = 0$ , the inclination of columns is given by:

$$\theta = \frac{1}{4\sqrt{\pi}} \frac{a}{\sqrt{\lambda z}}. \quad (3)$$

Therefore, the angle of inclination of columns near the dislocation core was measured at  $x = 0$  as a function of  $z$ , and  $\lambda$  was determined by fitting Eq. (3).  $\lambda$  is predicted to be of the order of column diameter (a).<sup>18</sup> In the case of **1**,  $\lambda$  is 16 Å (in rescaled form,  $\lambda/a = 0.35 \pm 0.15$ ;  $a = 45.7$  Å), and in the case of **2**  $\lambda$  is 230 Å (i.e.,  $\lambda/a = 5 \pm 1$ ;  $a = 45.6$  Å). Due to the large diameters of **1** and **2**, their  $\lambda$  values are larger than the only literature data available for a rigid rod polymer, for which  $\lambda = 8$  Å;  $\lambda/a = 0.9a$ . In addition, the rescaled value of  $\lambda$  of **1** is significantly larger than 1.0. This is consistent with

a column based on a rigid core surrounded by a deformable sheath. These data indicate that the rigidity of these supramolecular columns and their interaction can be controlled independently by design.

The stiffness of the columns also influences the density of defects, which were generally rare in **2**, but common in **1**. Indeed, highly bent columns were observed only in compound **1**, at the core of  $+1/2(\pi)$  disclinations [Fig. 4(a)]. Such defects were also observed at much larger length scale by optical microscopy [Fig. 4(b)] in a sample that was cooled from the isotropic at approximately 0.1 °C/min.

Therefore, direct evidence by TEM was used to determine elastic properties of columnar hexagonal mesophases formed by two chemically similar materials. Planar alignment of the columnar phase was obtained by casting the material on a warm water surface. Based on quantitative analysis of dislocation structure and qualitative examination of defect morphology, the columns of **2** are many times stiffer than those of **1**. These results indicate that the molecular association and packing of compound **2** is much greater, consistent with its significantly higher phase transition temperature, despite its chemical similarity to **1**. Apparently, the rigid aromatic groups of **2** cause stronger molecular association in the core and induce substantial rigidity.

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