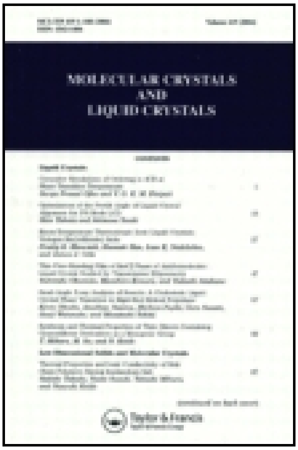

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Orientation and Defects on a Surface of a Thin Film of a Self-assembled Supramolecular Dendrimer

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ORIENTATION AND DEFECTS ON A SURFACE OF A THIN FILM OF A SELF-ASSEMBLED SUPRAMOLECULAR DENDRIMER

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We have investigated the orientation and morphology of a taper shaped supramolecular dendrimer by high resolution transmission electron microscopy (HRTEM). The molecule exhibits hexagonal cylindrical mesophase upon cooling from isotropic melt. Orientation of the cylinders is strongly influenced by surface treatment. Homeotropic alignment of the molecule occurs on carbon substrates, while homogeneous orientation is favored on water substrate. This is an easy way to control orientation of the cylinders, compared to that of block copolymers, leading to a promising material for the nano-sized surface patterning. A variety of defects, which include grain boundaries, elementary edge dislocation and disclinations, have been observed, representing flexible stacking of the molecules.

Keywords: orientation; surface anchoring; supramolecular amphiphilies; TEM

INTRODUCTION

The molecular ordering of most nanostructured molecules depends on the degree of microphase-separation under proper conditions, turn into liquid crystalline mesophases such as lamellar, cylinder, sphere on the basis of range and strength of interaction, and shape of the molecules [1–2]. Among the liquid crystalline mesophases, there has been much interest in cylindrical structure because of their potential applications in nano-fabrications, opto-electronics and biomaterials [3]. In such applications, it is essential

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to control orientation of the highly ordered cylinders. In particular, the self-assembled molecules with homeotropic alignment, in which cylinders are perpendicular to the film surfaces, will lead to a good candidate for a nano-sized surface patterning. Although the orientation of cylinders induced by block copolymers is well understood, few studies on surface ordering of supramolecular amphiphilies have been reported in the literatures [4]. In the ordered cylinders of block copolymers, two approaches have been made in order to align the cylinders perpendicular to substrates. A neutral surface treatment under the ordered cylinders of diblock copolymers was used by means of avoiding preferential interaction with the substrates, resulting in aligning the cylinders homeotropically. High electric field was also applied for the ordered cylinders of poly (styrene) – poly (methyl methacrylate) diblock copolymer. Although the cylinders align homeotropically, both methods require an additional surface treatment as well as strong electric fields [5].

In this study, we control the orientation of the hexagonal cylinders containing a taper shaped supramolecular dendrimer by a simple surface treatment. This self-assembling system forms a highly ordered hexagonal cylindrical mesophase on the basis of molecular architecture and interaction, representing regular stacking of the cylinders with high stability. Homeotropic orientation of the mesophases occurs most readily on carbon substrates. For the homogeneously aligned thin film, in which the column axis is parallel to the film surface, isolated edge dislocation, grain boundary and disclination, are observed on water surface. We clearly identify the phase behavior, size, morphology and perfection of hexagonal packing by controlling orientation of the cylinders. We figure out that the texture is greatly influenced by the rigidity of the mesophase.

EXPERIMENTAL

The compound used in this study, 1,2.3-tris[(3,4,5-tris[(4-(n-dodecan-1-yloxy)benzyl)oxy]benzyl)oxy]-benzene, was synthesized from alkylation of propyl gallate with 3,4,5-tris[(4-(n-dodecan-1-yloxy)benzyl)oxy]benzyl alcohol (Fig. 1). Detailed synthetic procedures are described elsewhere [6].

A polarized optical microscope (Leica DMLB) equipped with hot stage (Mettler FP 82) was used to analyze phase textures and determine $T_{\phi h}$ (hexagonal to isotropic transition temperature).

The sample for electron microscopy examination was prepared by casting from solutions onto distilled water at held a temperature, at which the cylindrical phase stable. For homeotropic specimens, a 2 wt% toluene solution of the sample was spread on distilled water, and retrieved on copper grid. The thin film samples on the amorphous carbon coated

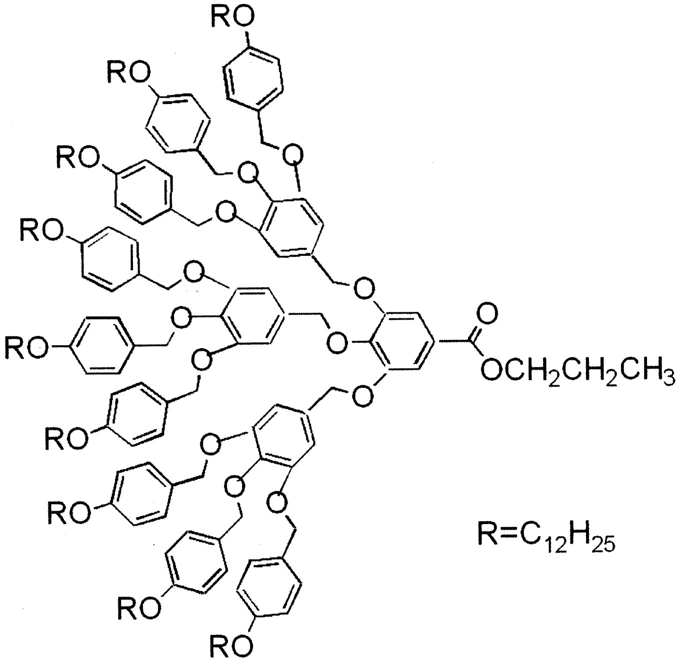

FIGURE 1 Chemical structure of a taper-shaped dendrimer used in this study.

substrates were cooled from isotropic phase (90°C) to $T_{\Phi h}$ (50°C) at a rate of 0.1°C/min, and quenched to room temperature. Homogeneous alignment was obtained by spreading the sample on water substrate [7]. In order to improve mass thickness contrast and radiation-sensitivity, the thin films were slightly exposed to RuO_4 vapor (solutions of ~0.2 wt% aqueous RuO_4) and examined at 120 kV using a Philips CM-20 TEM. The bright field phase contrast TEM micrographs were obtained by low dose procedures [8,9].

RESULTS AND DISCUSSION

Based on the polarized optical texture, the material exhibited a fan-shaped domains, which is one of the characteristic textures of columnar mesophase (Fig. 2). The fan-shaped texture was formed a few degree below the $T_{\phi h}$, which is effect of the high viscosity and birefringence [10].

Further identification of the hexagonal cylindrical mesophase was obtained by high-resolution TEM. Figure 3 shows an end-view micrograph

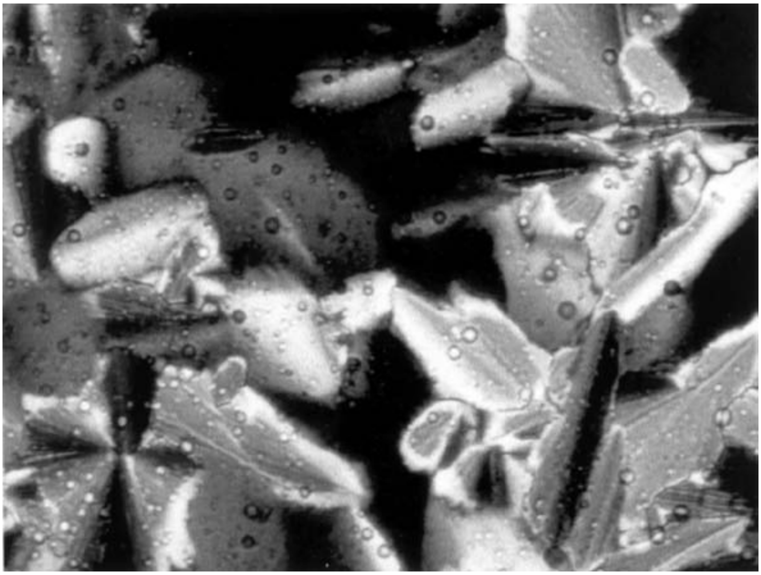

FIGURE 2 Polarized optical microscopy texture of the hexagonal mesophase of the compound.

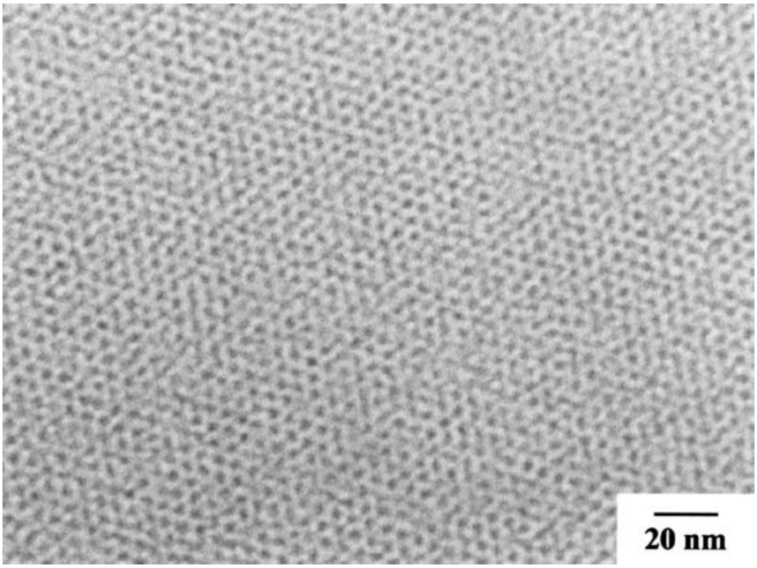

FIGURE 3 TEM micrograph of a highly packed end view of the hexagonal cylindrical mesophase.

of the material, which can be clearly identified as hexagonal cylinders. Various substrates were used to control the cylinders. Homeotropic alignment where the columns are aligned normal to the surface was obtained in most hydrophobic surfaces; while homogeneous texture the columns lie parallel with the interface was achieved in polar substrates such as water. There is a high degree of perfection in the packing of cylinder in which ordered cylindrical moieties are packed on hexagonal lattice showing six-fold symmetry. The cylinder cores appear dark, since the RuO_4 vapor preferentially stains aromatic and ether portions of the molecules [7]. Thus the aromatics and ether form the core of the cylinders, which is consistent with the expected molecular shape. Surface properties of substrate have been proved to be important factor to control orientation of liquid crystalline material. The carbon substrate is relatively flat on the scale of the cylinder diameter, and it may not interact strongly with either the core or the tails. Because homeotropic alignment on carbon surface may require serious distortion of the tails, they must stretch to reach the surface between neighboring surface cylinders. Homeotropic alignment of cylinders on carbon substrates has been found for all thermotropic cylindrical mesophases that we have been examined thus far. As in other self-assembling materials, the grain boundary of the homeotropically aligned specimen was observed on the substrate (Fig. 4). It consists of successive edge dislocation in the boundary of two grains, indicated by arrow marked beside the figure. The dislocation line vector is normal to the Burgers' vector b, which is normal to dirctor of the cylinders [11].

In contrast, homogeneous alignment was obtained by casting the material on a water surface (Fig. 5). The columns align to parallel to the water surface. This orientation can be described by the structure of the surface layer in contact with the water substrate. As in the surfactant self-assembly, the hydrophobic tails must orient away from the water, and the more hydrophilic core is in contact with the water. Additional characteristics of the structure of this layer depend on the tapered shape of the molecules and the strength of intermolecular interactions [12–15]. Further studies are in progress to gain the insight of molecular association at free surface. During electron irradiation, the lifetime of sharp reflections in the planar texture is lower than that of the homeotropic texture, indicating the strength of the molecular association along the cylinder axis is stronger than the interaction between cylinders. Careful inspection shows that the cylinders are curved, representing that the molecules of two adjacent stacks may not be exactly in register, leading to abundant defects of the system.

Figure 6 shows portions of typical transmission electron micrographs of homogeneous texture in the thin film of the hexagonal cylinders. Grains of cylinderical microdomains consist of regions of uniform molecular orientation bounded by disclocations. The average length of the cylinders is

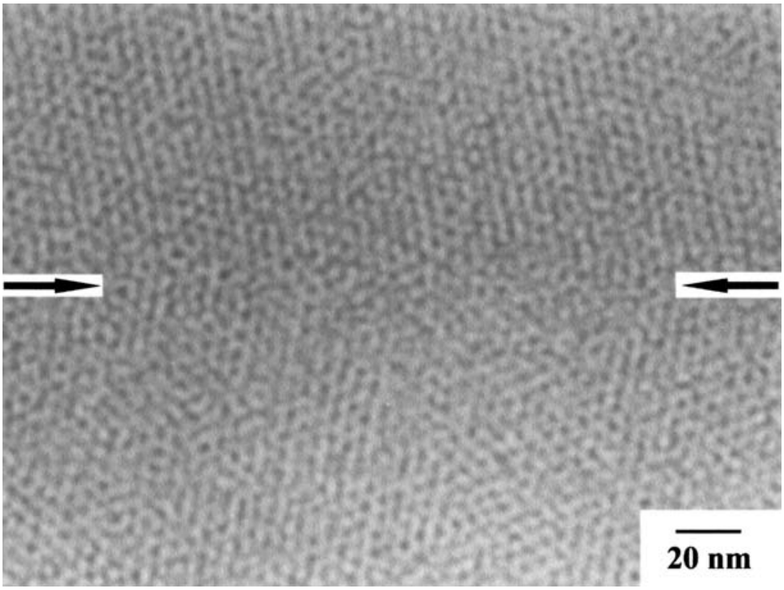

FIGURE 4 TEM micrograph of a high angle grain boundary in the homeotropic texture.

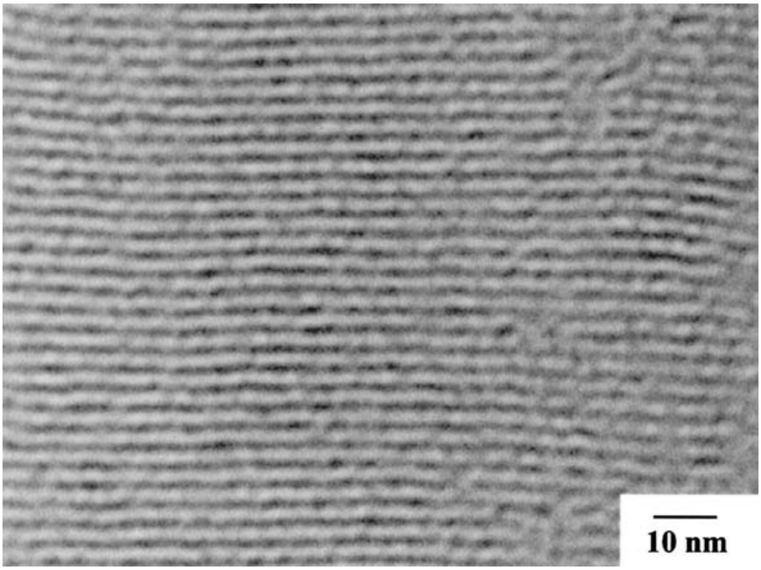

FIGURE 5 TEM micrograph of homogeneously aligned hexagonal cylinders on water surface.

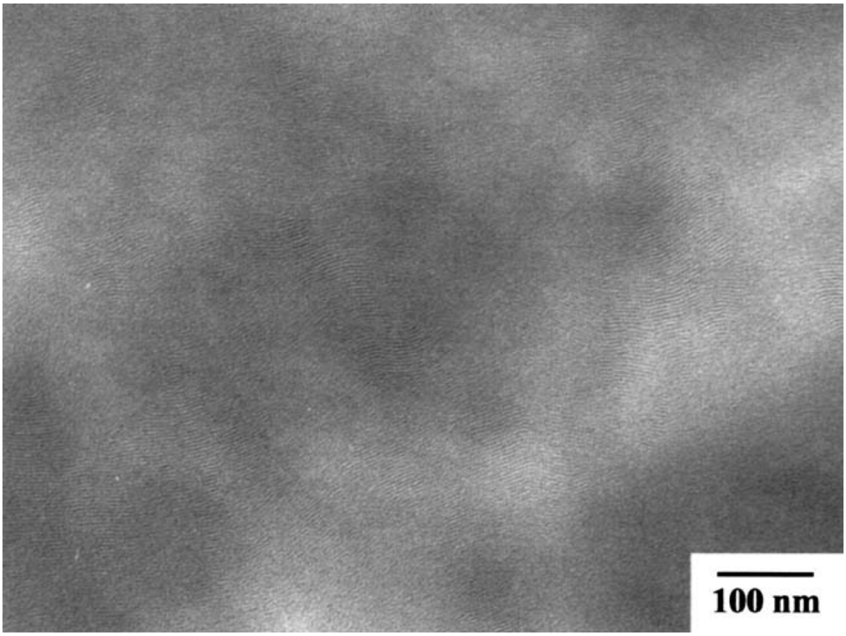

FIGURE 6 TEM micrograph of homogeneously aligned hexagonal cylinders on water surface showing various defects.

estimated to be a few μm, and the size of the grain is about ten times of that as estimated. Disclinations do not typically occur in isolated pairs, but interact with many neighbors, and regions that are concentrated in one type of defects are common. +1/2 disclination lines and wall defects are most prevalent. As expected, dislocations in splayed and twisted columnar structure were not observed in this system, perhaps because the dislocations geometrically require high free energy [11]. This highly bending texture may be strongly influenced by the material elastic constant arising from different chemistries [16–18]. The absence in the splay distortion would increase the elastic anisotropy near the core. Although the morphological behavior of the hexagonal cylinders seems to be similar to that of block copolymer, direct relations may not be reasonable because the hexagonal cylindrical mesophase is strongly influenced by surface anchoring. As a result, the morphological behaviors should be influenced by molecular structure and sensitive to the hexagonal cylindrical mesophase having larger aromatic group. Further studies about scattering experiments and surface investigation of the supramolecular amphiphilies are expected to establish further morphological identification.

CONCLUSION

Orientation of the hexagonal cylinders containing a taper-shaped supramolecule was controlled by surface anchoring. Unlike the block copolymers, the columns aligned perpendicular to carbon substrate, and it align parallel to the water surface. The curved shape of the homogenous texture indicates that molecular architecture constitutes an important parameter in the morphology of the hexagonal cylindrical mesophase. This plurality of defects associated disclination interactions and grain boundary in both alignment represent flexible nature of this molecule.

REFERENCES

[1] Klug, A. (1983). *Angew. Chem. Int. Ed. Engl.*, *22*, 565.
[2] Tsukruk, V. V. (1997). *Prog. Polym. Sci.*, *22*, 247.
[3] Adam, D., Schuhmacher, P., Simmerer, J., Haussling, L., Siemensmeyer, K., Etzbach, K. H., Ringsdorf, H., & Haarer. D. (1994). *Nature*, *371*, 141.
[4] Yoon, D. K. & Jung, H.-T (2003). *Langmuir*, *19*, 1154.
[5] Thurn-Albrecht, T., Schotter, J., Kästle, G. A., Shibauchi, T., Krush-Elbaum, L., Guarini, K., Emley, N., Black, C. T., Tuominen, M. T., & Russell, T. P. (2000). *Science*, *290*, 2126.
[6] Percec, V., Cho, W.-D., Mosier, P. E., Ungar, G., & Yeardley, D. J. P. (1998). *J. Am. Chem. Soc.*, *120*, 11061.
[7] Hudson, S. D., Jung, H.-T., Percec, V., Cho, W.-D, Johansson, G., Ungar, G., & Balagurusamy, V. S. K. (1997). *Science*, *278*, 449.
[8] Jung, H.-T., Hudson, S. D., & Lenz, R. W. (1998). *Macromolecules*, *31*, 637.
[9] Jung, H.-T., Kim, S. O., Hudson, S. D., & Percec, V. (2002). *Appl. Phys. Lett.*, *80*, 395.
[10] Jung, H.-T., Kim, S. O., Ko, Y. K., Yoon, D. K., Hudson, S. D., Percec, V., Holerca, M. N., Cho, W.-D., & Mosier, P. E. (2002). *Macromolecules*, 35, 3717.
[11] de Gennes P. G. & Prost, J. (1993). *The Physics of Liquid Crystals*, Clarendon Press: Oxford.
[12] Percec, V., Heck, J., Johansson, G., & Tomazos, D. (1994). *Macromol. Symp.*, *77*, 237.
[13] Percec V. & Johansson, G. (1995). *Macromol. Symp.*, *96*, 173.
[14] Johansson, G., Percec, V., Ungar, G., & Zhou, J. P. (1996). *Macromolecules*, *29*, 646.
[15] Percec, V., Cho, W.-D., & Ungar, G. (2000). *J. Am. Chem. Soc.*, *122*, 10273.
[16] Jung, H.-T., Coldren, B., Zasadzinski, J. A., Iampietro, D. J., & Kaler, E. W. (2001). *Proc. Natl. Acad. Sci. USA*, *98*, 1353.
[17] Jung, H.-T., Kim, S. O., Hudson, S. D., & Percec, V. (2002). *Appl. Phys. Lett.*, *80*, 395.
[18] Drummy, L. F., Voigt-Martin, I., & Martin, D. C. (2001). *ibid*, *34*, 7416.