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Dong Ki Yoon[a]; Young Koan Ko[a]; Hee-Tae Jung[a]
[a] Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science & Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea,

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Surface alignment and control of a dendritic liquid crystal in ultrathin films

DONG KI YOON, YOUNG KOAN KO and HEE-TAE JUNG*

Department of Chemical & Biomolecular Engineering,
Korea Advanced Institute of Science & Technology, 373-1 Guseong-dong,
Yuseong-gu, Daejeon 305-701, Korea

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Surface alignment and control of hexagonal molecular cylinders from an asymmetric supramolecular liquid crystal was established. Transmission electron microscopy images show that the cylinders are strongly affected by the substrate and film thickness. The cylinders align perpendicular to a hydrophobic substrate, while planar alignment takes place on hydrophilic surfaces. Different morphologies are encountered depending on the film thickness. Thick films of such a material exhibit a highly ordered hexagonal structure where the cylinders are oriented either parallel or perpendicular depending on the substrate. For thin films whose thickness is $10\,\mathrm{nm} < t < 20\,\mathrm{nm}$, they spontaneously form holes with straight edges aligned with hexagonal symmetry of the (1 0) orientation of the underlying molecular lattice. Thinner films lead to a liquid-like disordered in-plane structure. Unlike the behaviour of thin films of a typical block copolymer, where the natural period of the block copolymer is manifested through the formation of hole, the hole structures from these types of asymmetric dendrimers can be attributed to the low surface energy planes, revealed by the faceting of discontinuous films.

1. Introduction

Self-assembling materials have been recognized as a powerful means of nanopatterning surfaces, since they self-assemble into regularly ordered features with nano-sized structures [1–3]. Of particular interest are hexagonal cylindrical mesophases, since the elimination of the selective component makes the materials nanoscopic media, with ordered nanometer-sized pores [4–6]. In such applications, it is crucial to control the orientation of the cylinders, as well as other aspects of the morphology, in thin films, ranging from molecular to macroscopic dimensions. The surface ordering of block copolymers on thin films is well understood in terms of surface energy, periodic characteristic length and chemical components of the block copolymer [7, 8]. However, for block copolymers that form hexagonal cylinders, it is very difficult to obtain an orientation normal to the substrate. Recently, we reported that the orientation of a hexagonal cylindrical phase, comprising asymmetric supramolecular materials, could be controlled by surface anchoring [9–11]. Thick films align homeotropically on a hydrophobic substrate, so that homeotropic alignment may be obtained more easily than with copolymers. Here we investigate the ultrathin behaviour and surface morphology of a taper-shaped supramolecular dendrimer by high resolution transmission electron microscopy (TEM). We show, for the first time, that prism-shaped hexagonal pinholes are formed on ultrathin films of the supramolecular dendrimer. This finding will make significant contributions to the development of nanolithography using supramolecules, since a prerequisite for the use of supramolecules is hole-free thin films.

2. Experimental procedure

To investigate the effect of film thickness and surface on the morphology of hexagonal cylinders, an asymmetric dendrimer, figure 1 (*a*), having a tapered molecular architecture was synthesized by the alkylation of propyl gallate with 3,4,5-tris[(4-(*n*-dodecan-1-yloxy)benzyloxy)benzyl alcohol] [12]. The phase behaviour of the compound was determined by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). The thermal transition behaviour was examined on a Dupont 2010 Thermal Analyzer under N_2 flow at a scanning rate of 5°C min^{-1}. The anisotropic optical textures were observed on a polarizing optical microscope (Leica, Model DMLB), equipped with a hot stage (Mettler FP82 HT). The dendrimer exhibits a melting followed by isotropization in the first heating scan. The following cooling and heating scans show a transition to a liquid crystalline phase at 78°C on cooling, and at 86°C on the second heating, figure 1 (*b*). On

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*Author for correspondence; e-mail: heetae@kaist.ac.kr

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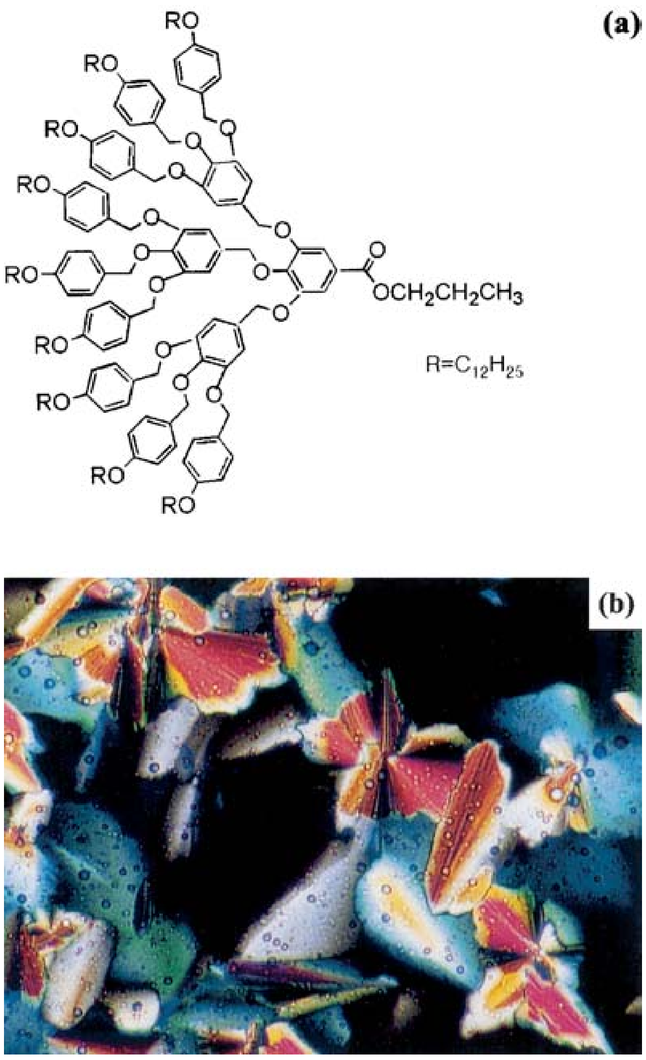

Figure 1. (*a*) Molecular structure of the dendritic liquid crystal; (*b*) POM texture of the compound upon cooling from the isotropic melt, showing a texture with fan-shaped domains. The cooling rate is 5°C min^{-1}.

cooling the isotropic liquid, a low degree of supercooling was seen, followed by transition to a liquid crystalline phase. Optical texture, XRD and TEM support the assignments of isotropization and a hexagonal columnar mesophase for this material.

Syncrotron X-ray diffraction and reflectivity measurement was conducted with a wavelength of 1.54 Å at the 3C2 XRD beamline in Pohang Accelator Laboratory (PAL), consisting of a 2 GeV LINAC accelerator, storage ring, Si (1 1 1) double crystal monochromator, ion chambers, and one-dimensional position-sensitive detector with 2048 pixels. A small amount of sample was sealed with imide films, and the sample was heated above the isotropic melt temperature and then cooled to a specified temperature. The thermal history of the samples was kept the same as for those in the DSC experiment. The temperature was controlled with an accuracy of $\pm 1°C$ in the experimental temperature range.

Thin films for TEM and X-ray reflectivity studies were prepared by casting from solution onto distilled water, held at a temperature at which the columnar phase is stable, and retrieved on carbon-coated copper grids. The sample film thickness was controlled by the solution concentration. The ultrathin films were cast from solution onto freshly clean glass substrates to measure film thicknesses by X-ray reflectivity (Rigaku, D/max-rc, 12 kw).

Different substrates were used to control the molecular orientation of the mesophase. For planar alignment of the columnar materials, thin films suitable for TEM examination were cast from solution onto distilled water, and were carefully recovered on the carbon-supported Cu grids [9]. Identical alignment results were obtained whether methylene chloride, chloroform, toluene or THF were used as the solvent. Homeotropically aligned columnar specimens were obtained by heat-treating thin films that had been prepared by either of these two methods and were supported on highly uniform (100 Å thick) vacuum-evaporated carbon films. These supported films were heated to the isotropic phase and cooled at a rate of 5°C min^{-1} to a temperature well below $T_{\Phi h}$, before final quenching to room temperature. This melting and cooling procedure was used to generate homeotropically aligned films. These films were examined at 120 kV using a Philips CM-20 TEM. Electron diffraction (ED) and bright field phase contrast TEM micrographs were obtained (by low dose procedures) before and after sample staining with RuO_4 vapours (solutions of 0.5 wt % aqueous RuO_4). Electron images were recorded on SO-163 plates at appropriate under-focus conditions to obtain lattice images [13].

3. Results and Discussion

The synchrotron XRD pattern shows narrow reflections at small angles but broad bands centred at 4.8 Å (figure 2). The small angle peak at $2\theta \sim 2.1°$ (42 Å) starts to appear around 86°C, which corresponds to the transition temperature. This indicates that the molecules are arranged in periodic structures, but that the structure at the atomic level is disordered. The relative positions of small angle scattering peaks of the compound are 1, $\sqrt{3}$, 2, corresponding to hexagonal packing. The hexagonal packing is retained, but the lattice dimension is reduced as the temperature increases, perhaps due to shrinkage at higher temperatures.

To elucidate the effect of the surface and film thickness on surface ordering, TEM observation was made, to observe directly the structural and morphological changes as a function of film thickness. All thickness measurements cited in this communication were made by X-ray reflectivity. Figure 3 shows TEM micrographs and electron

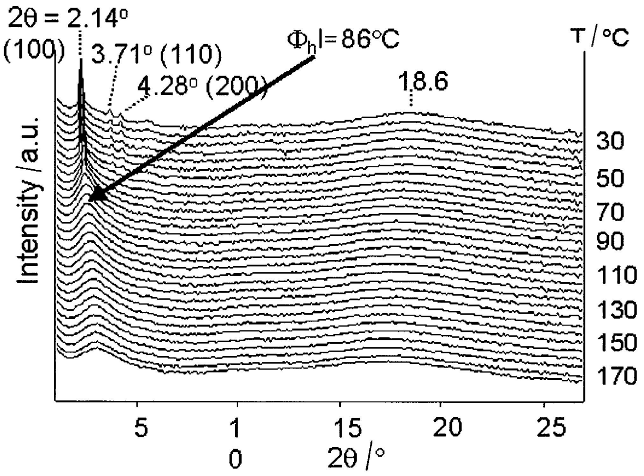

Figure 2. Synchrotron XRD pattern of the supramolecular dendrimer upon cooling from the isotropic melt at a rate of 5°C min^{-1}. The arrow indicates the phase transition (86°C) from isotropic to hexagonal cylindrical mesophase.

diffraction pictures of the material for a 30 nm thick film. Similar images were observed in all specimens for thicknesses above ~20 nm. However, the reorganization of the molecules strongly depends on the nature of the substrate.

Various substrates, including water, glycerin, mica, salt, clean glass, glass coated with a fluorinated coupling agent and polycrystalline Pd, were used to produce different surface-induced orientations. Homeotropically aligned films in which the column axis is perpendicular to the film surface were mostly achieved on hydrophobic substrates, whilst a homogeneous orientation was obtained on hydrophilic surfaces such as distilled water. The images show that there is a high degree of perfection in the cylinder packing, in which ordered cylindrical moieties are packed on a hexagonal lattice. Ruthenium tetraoxide (RuO_4), which was used as staining agent, attacks the centre of the column, appearing dark because RuO_4 is sensitive to the aromatic and the ester portions. Hence, bright and dark spots correspond to the outside and centre of the columns, respectively. The planar texture prepared from solution casting on distilled water at Φ_h is shown in figure 3 (*b*).

A much thinner specimen was cast onto a carbon surface to determine whether the film thickness was of significance. When thinner films (~10 μm < t < 20 nm) on a carbon substrate are cooled from the isotropic phase, the homeotropic orientation is again obtained (figure 4). Comparing films of thickness 10 μm < t < 20 nm with a relatively thick film (⩾20 nm), figure 3 (*a*), no changes of symmetry and dimension are detected by ED or imaging. However, the cylindrical film is perforated. The edges of the holes are sharp and parallel to the (1 0) plane, so that the holes are hexagonal in shape. The lengths of the edges are irregular, and holes of different sizes and shapes are observed in the TEM micrograph; the average radius of holes is measured to be approximately ~25 nm from many different TEM images, see histogram in figure 4 (*b*). The large shape anisotropy of the holes is consistent with the fact that the (1 0) direction is preferred to all others.

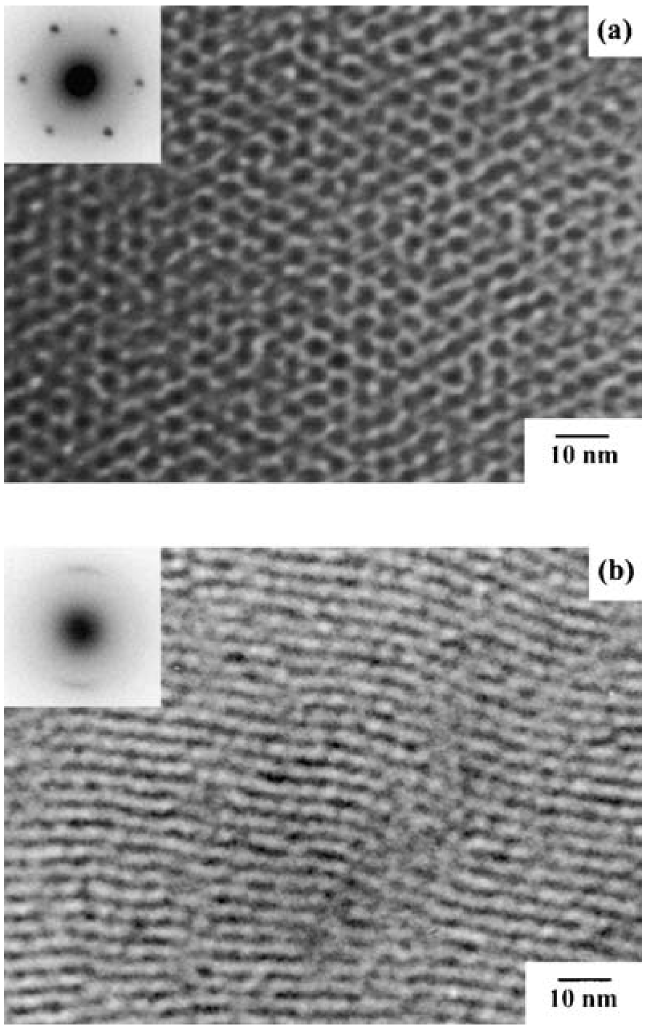

Figure 3. TEM micrograph of (*a*) homeotropically and (*b*) homogeneously aligned hexagonal cylindrical mesophase. The highly ordered structure was obtained for a 30 nm thick film. Insets are electron diffraction patterns obtained from these specimens. The homeotropic orientation occured on evaporated carbon substrates; homogeneous alignment of the molecule was favoured on a water surface.

The film thickness outside the holes was estimated to be fairly uniform on the basis of nearly uniform image contrast. Many such holes occur within a single grain of hexagonal order, so that the hexagonal holes are all oriented in the same direction, as dictated by the surrounding ordered phase. Although most holes are empty, weak hexagonal ordering is also observed in some

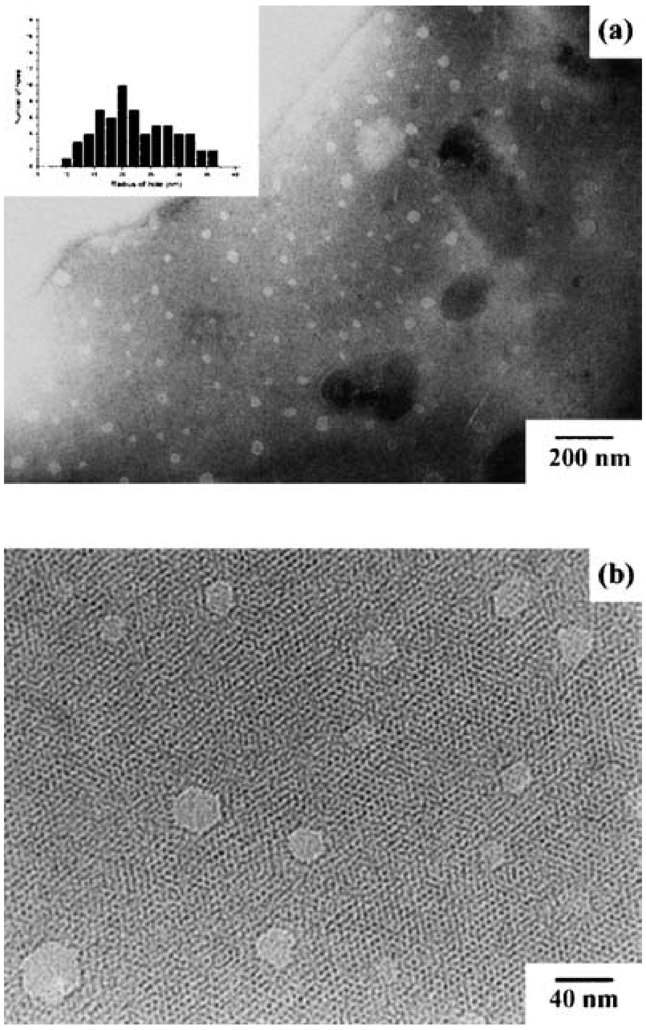

Figure 4. (*a*) TEM micrograph of a homeotropically hexagonal cylindrical mesophase formed in a 15 nm thick film; inset is size distribution histogram of pinholes. (*b*) A higher magnification image of (*a*) showing the hexagonal holes morphology. (*c*) ~ 6 nm.

areas, indicating a remnant thinner film of homeotropic cylinders. This was confirmed through a TEM focus series. Most of the prism-shaped pinhole images were independent of the focus, which indicate truly empty holes. In some holes, the Fresnel fringe contrast around the edge of the prism was different, indicating the interior of the prism shaped region has some number of dendrimer layers in it. The faceted shape of the holes provides information about the relative surface energy of planes that are parallel to the columns, i.e. perpendicular to the sample film. In particular, the lowest energy surface that is parallel to the columns is the (1 0) surface. No holes are observed that have edges of any other orientation, e.g. $(2\,\bar{1})$. Therefore, the interfacial energy of the $(2\,\bar{1})$ plane with air must be at least 15% greater than that for the (1 0) surface.

As reported previously from block copolymer thin films, the formation of holes on the free surface arises from periodic structure [14–16]. In these examples, relative surface energies determine the orientation of lamellae within ultrathin films. If the thickness matches the periodicity of the ordered phase, the free surface of the film is flat. Otherwise, either islands or holes are formed on the surface after annealing. Similar behaviour was observed for the surface morphology of block copolymers with a cylindrical microphase [17]. It was also shown that the orientation of the cylinders also depends on the film thickness. Thus, we may not rule out the possibility that the holes are formed by the periodic structure of the dendrimer. That is, an incomplete thickness may form in a manner identical to, and in register with, the existing periodic cylindrical assemblies, which results in either perfect hole depth or a periodic column within a hole.

However, hole development by periodic structure is unlikely to occur in these types of small supramolecular dendrimer. The thickness of molecules arranged by side by side in a single slice of the columns is too small (~ 5 Å) for them to assemble in such a relatively long periodic fashion, because the molecules are associated by physical molecular interaction instead of strong covalent interaction, such as in amphiphilic polymers. Thus, it is likely that, at a given annealing temperature, there is tendency to create holes and to start thickening to minimize the surface energy plane. In this case the film is very thin and, upon annealing, the cylinders arrange in homeotropic orientations and holes nucleate in order to allow the film to thicken.

Small holes can coalesce into bigger holes by minimizing surface energy. Orientation (1 0) and shape (hexagon) of the hole should be determined by the neighbouring structure. Therefore, a high degree of hexagonal packing determines a hexagonal shaped hole with (1 0) orientation. These holes seem to be evidence for dewetting of the substrate, but it is not clear whether the dewetting occurred while the film was in the isotropic or cylindrical state.

In much thinner films ($t < 10$ nm), the structure is disordered on the substrates, figure 4(*c*), as compared with the close packed chains in thicker films. For such a film thickness, it is suggested that the hydrophilic core is at the water surface, and the hydrophobic alkyl chains are directed perpendicular to the interface [18]. Work continues, to gain further understanding of the self-organization phenomena on the ultrathin flms.

4. Conclusion

We have investigated the evolution of thin films of a tapered dendritic liquid crystal by TEM, XRD, DSC and POM. Syncrotron X-ray diffraction experiments revealed the sequential phase transition through isotropic and a hexagonal cylindrical liquid crystalline phase. The orientation of the cylinders was controlled by surface anchoring. Homeotropic orientation occurs most readily on a hydrophobic substrate, while homogeneous alignment of the amphiphilic molecule is favoured on a water surface. A different morphology was observed on the free surface of ultrathin films. Low surface energy planes are identified through examination of the morphology of ultrathin films, which contain hexagonally-shaped holes on a free surface. The film forms into pinholes (with sharp edges) that have orientations related to an approximately hexagonal symmetry. The predominant direction of the hole edges corresponds to the (1 0) molecular lattice direction. For thicknesses less than 10 nm, the layer structure is unstable.

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