

recorded both in a Guiner–Hägg camera and a Stoe diffractometer. The refinement was made using the General Structure Analysis System (GSAS) and 109 reflections for  $d \geq 1.46 \text{ \AA}$ , giving a Bragg factor of  $R(I) = 5.3 \%$  and a structure factor of  $R(F) = 16.9 \%$  [18]. The Lotgering orientation factor

$$f = \frac{(p-p_0)}{(1-p_0)} \quad (1)$$

with

$$p = \frac{\sum I_{00l}}{\sum I_{hkl}} \quad (2)$$

and  $p_0$  for a random-orientation powder pattern was calculated using intensities for 120 reflections at  $2\theta \leq 69.5^\circ$ . The preferred orientation ( $O_{ph}$ ) in the refinement was modeled by the March–Dollase function [19]

$$O_{ph} = \left( R_0^2 \cos^2 A + \frac{\sin^2 A}{R_0} \right)^{-3/2} \quad (3)$$

where  $A$  is the angle between the preferred orientation axis (001) and the reflection vector. The refined value for  $R_0$  was 0.102(17).

The temperature dependence of the dielectric constants was measured at different frequencies using an Agilent 4284A LCR meter. The piezoelectric constant ( $d_{33}$ ) was measured by a quasi-static  $d_{33}$  meter (ZJ-3B, CAS). The ferroelectric-polarization hysteresis loops were measured by a ferroelectric hysteresis measurement tester (NPL, UK). The thermal-depoling experiments were conducted by annealing the poled samples for 2 h up to  $700^\circ\text{C}$ , then measuring  $d_{33}$  at room temperature after cooling.

The domain structures were investigated with piezoresponse force microscopy (PFM), where the interaction between an electrically biased tip (alternating current (AC) voltage  $U = U_0 \sin(\omega t)$ ) and the polarization within a ferroelectric sample due to the local inverse piezoelectric effect is monitored [20,21]. The system consists of a self-built head, a central control unit (CCU), a scanning probe microscopy (SPM) module from Park Scientific Instruments (Sunnyvale, CA), a lock-in amplifier (SR530) from Stanford Research Systems, and a frequency generator (33120A) from Hewlett–Packard. The sensitivity of the lock-in was in the mV range, and the time constant was 1 ms. The coated cantilever (NSC12/Cr–Au/50, Silicon-MDT, Russia) had a typical force constant of  $14 \text{ N m}^{-1}$  and a resonant frequency of 315 kHz. The experiments were done at ambient conditions and room temperature. The applied AC voltage was  $U = 10 \text{ V}$  and the frequency was 8 kHz. The scan frequency was typically 1 Hz.

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## Optically Anisotropic Colloids of Controllable Shape\*\*

By Alberto Fernández-Nieves,\* Galder Cristobal,\* Veneranda Garcés-Chávez, Gabriel C. Spalding, Kishan Dholakia, and David A. Weitz

Monodisperse colloidal dispersions are model systems consisting of identical solid objects dispersed in a liquid solution; these can be charged or neutral, and can have different shapes.<sup>[1]</sup> In analogy to atomic or molecular systems, colloidal dispersions can crystallize into liquid-crystal phases if they possess enough geometric anisotropy, and at high enough volume fractions they can crystallize into a solid phase.<sup>[2]</sup> These similarities have been exploited, for example, to access the initial crystallization stages of nucleation and growth processes<sup>[3]</sup> and to evaluate the importance of particle excursions from their equilibrium position.<sup>[4]</sup> In these and similar studies,

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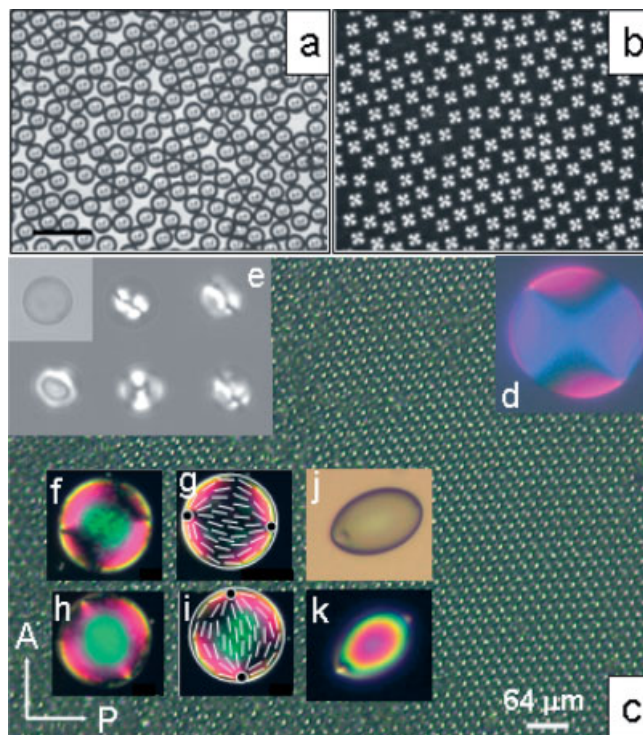
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sample monodispersity is crucial, as a wide size distribution would preclude formation of the crystalline phases.

From another perspective, optically anisotropic colloids are receiving growing interest due to the possibility of manipulation with an external laser. These have been used to prove the orbital and spin angular momentum of light<sup>[5]</sup> and have encountered application as optical switches<sup>[6]</sup> and scattering polarizers.<sup>[7]</sup> In these applications, the colloidal dispersion need not be monodisperse, since typically single particles are trapped for further use.

In this work, we engineer monodisperse birefringent colloids of different shapes. The main idea of the process resides in starting with a liquid-crystal emulsion whose orientational order can be frozen by photopolymerizing the drops. Deformation of the drops before locking in the ordering allows different colloidal shapes to be explored. We employ polarized optical microscopy and optical tweezing to demonstrate both the optical and the geometric anisotropies of these particles. In optical-tweezing systems, this offers a promising mechanism for a range of microfluidic applications.

We used a recently reported method that uses steady-state droplet break-off in a co-flowing stream<sup>[8]</sup> to create monodisperse emulsions of liquid-crystal (LC, 5-cyanobiphenyl, Merck) drops in water. The resulting drops are on the micrometer scale with a polydispersity below 3 %. This technique involves extrusion of liquid-crystal material through a thin capillary, typically having an inner diameter of a few micrometers, immersed in a co-flowing external liquid. A droplet is formed at the end of the capillary as the material is extruded, and its size is controlled by the competition between viscous drag, which tends to pull off the drop from the capillary, and surface tension, which opposes this pull. When drops reach a critical size, the viscous drag exceeds surface tension and break-off occurs. The minimal droplet size is determined by the diameter of the capillary and is therefore limited to a diameter of a few micrometers. Surfactants or amphiphilic polymers can be dissolved in the continuous aqueous phase in order to stabilize droplets against coalescence. In this work we have used either a solution of sodium dodecyl sulfate (SDS) at approximately twice its critical micellar concentration ( $\sim 16$  mM) or a 1 wt.-% solution of  $\sim 20\,000$  g mol<sup>-1</sup> poly(vinyl alcohol) (PVA). Apart from preventing coalescence, the stabilizer has an important role in determining the resulting liquid-crystal configuration within the drop since it determines the molecular anchoring of the LC molecules on the surface.<sup>[9]</sup> SDS yields homeotropic alignment of the liquid crystal at the surface, resulting in radial drops having a point hedgehog disclination at the drop center, while PVA imposes tangential anchoring that results in a bipolar configuration having two point defects, referred to as boojums, at the surface. These director-field configurations are well documented in the literature<sup>[10]</sup> and can be confirmed by polarization microscopy studies. Figures 1a,b show photomicrographs of a typical liquid-crystal emulsion in bright-field mode and under crossed polarizers, respectively. The drops are radial nematics, as shown in the polarization-microscopy image, with characteristic cross-like



**Figure 1.** a) Photomicrograph of a monodisperse emulsion consisting of  $d = (30 \pm 1)$   $\mu\text{m}$  radial nematic liquid-crystal drops in bright-field mode. b) Cross-polarized image of the same emulsion as in (a) showing the characteristic appearance expected for the drops. The scale bar in these images corresponds to 100  $\mu\text{m}$ . c) Bright-field image of a three-dimensional crystal consisting of bipolar nematic liquid-crystal drops and d) single bipolar nematic liquid-crystal drop shown between cross-polarizers. After sedimentation of the emulsion, crystallization occurs spontaneously, reflecting the monodispersity of the sample. e) Bright-field image (upper left) and cross-polarized photomicrographs of a polymerized liquid crystal colloidal sphere ( $d \sim 5$   $\mu\text{m}$ ) experiencing Brownian motion. The observed textures reflect the bipolar character of the colloid; the photopolymerization process does not disrupt the initial liquid-crystal configuration. f–i) Solid birefringent oblate ellipsoid obtained by stretching the original polymerizable liquid crystal (PLC) bipolar drop in two perpendicular directions by equal amounts. The axis joining the two surface disclinations resides in the image plane, and is rotated with respect to the incident light polarization. The approximate director-field configuration and the two boojums within the particle inferred from the images are shown in (g,i). The color change from the center towards the edge indicates that the ellipsoid thickness varies from  $\sim 5$   $\mu\text{m}$  to  $\sim 2$   $\mu\text{m}$ . The in-plane length of the object equals 30  $\mu\text{m}$ , and the analyzer (A) and polarizer (P) axis directions are indicated. j) Bright-field and k) cross-polarized photomicrographs of a prolate ellipsoid obtained by stretching the original PLC bipolar drop in a single direction. The shape and anisotropy of the object are evident. Its major axis is 20  $\mu\text{m}$ .

appearances. The sample is clearly monodisperse with only slight deviations from the mean size,  $d = (30 \pm 1)$   $\mu\text{m}$ . This high level of monodispersity becomes further apparent through the observation of three-dimensional (3D) crystals that spontaneously form after particle sedimentation in the containing vial (Fig. 1c). In this case, the drops have a diameter of  $(16.0 \pm 0.6)$   $\mu\text{m}$  and are bipolar, as can be seen between crossed polarizers as shown in Figure 1d. This image is taken from a di-

lute emulsion sitting over a glass slide with a coverslip on top that slightly squishes the drops, forcing the polar axis joining the two surface defects to lie within the plane of the image. The observed texture reflects the molecular ordering within the drop and precisely matches what is expected for a bipolar configuration.<sup>[11]</sup> The short-range steric repulsion induced by the presence of PVA at the drop surface prevents coalescence and ensures a long life for the formed structures.

Solid birefringent particles are obtained by emulsifying a UV-reactive liquid-crystal monomer (RMM14, Merck) mixed with a photoinitiator at 10 wt.-% (Darocur 159, CIBA Inc.) in aqueous solution.<sup>[6]</sup> To avoid freezing of the RMM14, it is normally necessary to maintain the temperature of the experimental setup above 40 °C during the emulsification process. In addition, extremely high pressures (~2000 kPa) are needed to extrude these viscous mixtures through micrometer-sized tips. To overcome these difficulties, we dissolved the RMM14 photoinitiator mixture in chloroform to reduce the fluid viscosity, allowing room-temperature to be used, since under these conditions the mixture remains in the isotropic liquid phase. Once the monodisperse emulsion was obtained, chloroform evaporated through the aqueous continuous phase, leaving the rest of the components within the drop. This could be verified by checking the anisotropic character of the drops after chloroform evaporation, which did indeed appear birefringent under crossed polarizers. The chloroform evaporation through the aqueous phase occurred slowly over ~12 h and is possibly related to the small but non-zero solubility of the chloroform in the continuous water phase. In addition, fine control of the drop size could be achieved by selecting the amount of chloroform in the dispersed mixture. The final LC droplet size can be estimated in a very naive way as  $R_{LC} = R/(1 + \chi)^{1/3}$ , where  $R$  is the initial chloroform/LC mixture droplet radius and  $\chi$  is the chloroform volume ratio in the dispersed-phase mixture. An initial 1:1000 mixture of LC to photoinitiator and chloroform yielded a reduction by a factor of 10 in the droplet size after evaporation of the chloroform.

We used a water–PVA solution to make polymerizable liquid crystal (PLC) droplets. After chloroform evaporation, the typical droplet size ranged from 2 µm to 30 µm, and the polydispersity was below 10 %. The resultant emulsion was then exposed to UV radiation to lock in the liquid-crystal order. Prior to UV exposure, the solution was heated to a temperature of 60 °C to enhance the nematic liquid-crystalline order within the drops. The emulsion was then exposed at a distance of ~10 cm from a 5 mW cm<sup>-2</sup> UV lamp (Schleicher and Schuell,  $\lambda = 365$  nm) for ten minutes and at a constant temperature of 60 °C. Several attempts at lower polymerization temperatures gave undesirable PLC droplets with multiple oriented domains within the drop. Temperature turned out to be a key parameter in the engineering of bipolar solid particles. Figure 1e shows a typical PLC colloid undergoing Brownian motion. The upper-left image is taken in bright-field mode and shows the spherical shape of the particle after photopolymerization. All other photomicrographs are snapshots corresponding to different orientations of the particle polar axis

with respect to the incident-light direction as reflected by the various observed textures. As can be seen, the spheres are anisotropic and retain the original liquid-crystal order.

Bipolar colloids of anisotropic geometry can also be obtained. We did so by stretching thin films of a PLC emulsion prior to photopolymerization. A few milliliters of solution were deposited on a plastic substrate and a uniform film of 500 µm in height was obtained by spreading the solution with a 25 gauge cylinder. Before spreading, the PVA content of the continuous phase was increased to give higher mechanical strength to the films and to ensure higher deformation without rupture. After slow water evaporation, the films were peeled off and placed in a stretching rig. The resultant films contained monodisperse PLC droplets embedded in a PVA-polymer matrix. The films were mechanically stretched at 120 °C under high humidity conditions. Stretch factors as high as 12 with respect to their original size could be achieved.<sup>[7]</sup> The geometrically anisotropic objects were then UV-polymerized. With this procedure, we obtained optically anisotropic solid prolate or oblate ellipsoids, depending on the stretching directions. As a final step, the polymerized structures were again dispersed in water by dissolving the PVA film. Figures 1f–k illustrate two examples of solidified bipolar oblate and prolate ellipsoids. The colors can be understood by considering the uniaxial character of the nematic liquid crystal prior to UV exposure. When linearly polarized light travels through a uniaxial medium, it usually becomes elliptically polarized after traversing the sample; therefore, the second polarizer transmits some of the incident light. This results in interference colors when white light is used to illuminate the sample. The resulting interference color depends on the sample thickness  $d$  and birefringence  $\Delta n$  through the induced path difference  $\Delta n \times d$ , and is catalogued in the Michel–Levy chart.<sup>[12]</sup> By observing the color sequence of the oblate ellipsoids in Figures 1f–i and taking  $\Delta n = 0.14$  for the PLC,<sup>[13]</sup> we deduce that the disk thickness varies from 5 µm to 2 µm as we move from the central region towards the edge. The variation takes place as indicated by the color change. By rotating the sample relative to the crossed polarizers and observing the resultant textures, we found similar patterns to that of a bipolar object with its axis perpendicular to the field of view.<sup>[11]</sup> Therefore, the polar axis lies in the image plane and adopts the bipolar structure depicted in Figures 1g,i. This could have been anticipated, since the two boojums in the original PLC object will try to maximize their separation so as to minimize the system free-energy density.<sup>[14]</sup> They will thus be located within the image plane in the case of the objects considered here. For uniaxial stretching, the boojums are along the major axis of the ellipsoid, as shown in Figures 1j,k. In this case, we show both bright-field and cross-polarized microscopy images, allowing precise determination of the shape and optical anisotropy of the particle.

Such optically anisotropic solid objects can find important applications in the emerging microfluidic domain as microstirrers or valves. To date, one of the most interesting approaches to mixers, pumps, and valves have been obtained with non-in-

vative pressure actuators designed by the Quake group.<sup>[15]</sup> This approach is successful only in poly(dimethylsiloxane)-based devices and cannot be used in “solid” devices such as glass or Teflon.<sup>[16]</sup> The materials presented in this work scale down to the micrometer dimension, unlike conventional laboratory benchtop stirrers. To show their potential for microfluidic applications, we used optical tweezers consisting of circularly polarized light and demonstrated that the PLC colloidal spheres indeed follow the electric field ( $E$ -field) direction of the beam (Figs. 2a–c). A  $(2.0 \pm 0.2)$   $\mu\text{m}$  diameter PLC colloidal sphere was trapped in three dimensions near the bottom wall of a sample cell by a laser beam consisting of anticlock-

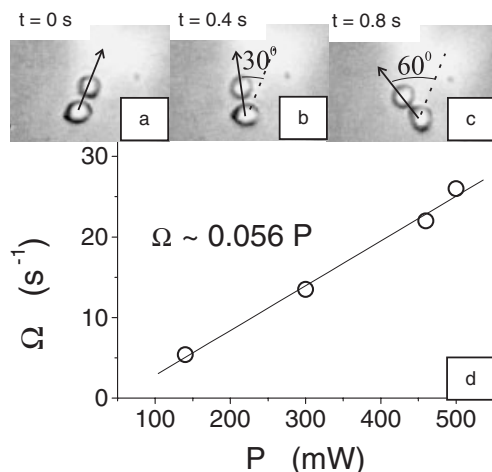
shown that microrheology using rotating particles is a key requirement for the future.<sup>[19]</sup>

We have shown how to engineer monodisperse colloidal suspensions consisting of birefringent particles with various shapes. The method relies in obtaining a monodisperse liquid-crystal emulsion that is photopolymerized to yield the desired colloids; moreover, we have shown that their shape can be tuned by mechanically deforming the drops prior to polymerization. Optical microscopy and optical tweezing demonstrate that the particles indeed can be made optically and geometrically anisotropic. Electro-optic switches and microfluidic stirrers and valves can be constructed from these novel colloids.

## Experimental

We used a standard optical-tweezers setup. A continuous-wave Nd:YVO<sub>4</sub> laser beam (1070 nm, 15 W maximum power) was incident on the back of a microscope objective (100 $\times$ ; numerical aperture NA=0.4) which tightly focused the beam into a sample chamber containing polymerizable liquid-crystal colloids dispersed in a water solution. The sample was also illuminated by white light. The size of the focused beam was smaller than the particles, which were trapped in three dimensions and underwent rotation due to the change in the polarization state of the light passing through them due to conservation of angular momentum. The position of the beam in the sample was changed by motion of a mirror which was conjugate to the back of the microscope objective. The cell sample was placed on an  $x$ - $y$ - $z$  translator to move the spheres. A second objective placed underneath the sample imaged the particles onto a charge-coupled device (CCD). By sending part of the output beam that passed through this objective to a linear polarizer and detector (photodiode), the rotation rate of the trapped object was accurately measured [20]. In this work, we measured the rotation of the dragged particle by a sequence of frames captured on videotape. This measurement was adequate due to the relatively slow rotation rate.

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**Figure 2.** a–c) Three frames taken from a video recorder when a liquid-crystal sphere (bottom) is trapped by a circularly polarized Gaussian beam and forced to rotate. A second LC sphere (top) was dragged by the liquid allowing the particle rotation to be easily followed. d) Frequency of rotation  $\Omega$  versus input laser power  $P$  showing a linear relation given by  $\Omega/P = (0.056 \pm 0.003) \text{ s}^{-1} \text{ mW}^{-1}$ .

wise circularly polarized light. The particle followed the rotation direction of the  $E$ -field and, as shown in the sequence of frames, dragged a second sphere sitting on top of it, allowing the rotation to be precisely followed. We measured this rotation as a function of the input beam power  $P$  (Fig. 2d) and obtained a clear linear dependence with the particle-rotation frequency  $\Omega$ . This linear behavior arises from the balance between the torque exerted by the  $E$ -field on the particle, which is linear in  $P$ , and the viscous torque, which increases with  $\Omega$  in laminar flow (the Reynolds numbers in our experiments are always below  $\sim 5 \times 10^{-4}$ ). By knowing the dielectric anisotropy and response time of the PLC colloidal sphere to the field, one can use these particles as micrometer-scale Zimm rheometers to measure the viscosity of the surrounding media, as has been recently demonstrated using calcium carbonate particles<sup>[17]</sup> and wax microdisks.<sup>[18]</sup> Also, the polymeric nature of our particles, coupled with the external laser manipulation, allows this approach not only to be used in polar fluids but also in nonpolar solvents, extending its versatility. Notably, recent work on rotation using birefringence has

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## A Zone-Casting Technique for Device Fabrication of Field-Effect Transistors Based on Discotic Hexa-*peri*-hexabenzocoronene\*

By Wojciech Pisula, Anoop Menon, Michael Stepputat, Ingo Lieberwirth, Ute Kolb, Adam Tracz, Henning Sirringhaus, Tadeusz Pakula, and Klaus Müllen\*

Organic semiconductors have attracted considerable interest over the last decade due to an immense improvement in the performance of electronic devices based on these materials. This attention has mainly been focused on conjugated polymers and oligomers, as well as small molecules which can be utilized as active layers in devices such as field-effect transistors (FETs),<sup>[1,2]</sup> photovoltaic cells,<sup>[3]</sup> and light-emitting diodes.<sup>[4]</sup> An interesting group of materials with potential application as organic semiconductors in electronic devices are columnar discotics.<sup>[5,6]</sup> These mesogens consist of an aromatic

core, which can be chemically modified by peripheral substitution (e.g., with alkyl chains), and self-assemble into one-dimensional (1D) columnar superstructures that then arrange in a two-dimensional (2D) lattice. The overlapping of the  $\pi$  orbitals of adjacent molecules within the columns ensures 1D intracolumnar charge-carrier transport. Another essential requirement for undisturbed 1D charge migration along the columns is a high degree of long-range order in the active layer which is deposited between the electrodes.<sup>[7]</sup> Local defects at domain boundaries in unoriented layers can trap charge carriers and significantly decrease the device performance.

Thus, the development of appropriate processing techniques became an essential challenge for the fabrication of unperturbed long-range-oriented organic semiconductors. This close relationship between supramolecular structure and electronic properties has been investigated impressively for planar metallophthalocyanine (Pc) and metalloporphyrin derivatives, in which the charge-carrier mobility of the holes depends strongly on the processing technique.<sup>[8–11]</sup> For vacuum-deposited thin layers of phthalocyanine, the mobility varied from  $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for nickel Pc<sup>[8]</sup> to  $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for copper Pc.<sup>[9,10]</sup> Other processing techniques, such as solution deposition onto substrates with a friction-oriented poly(tetrafluoroethylene) (PTFE) layer<sup>[12]</sup> and the Langmuir–Blodgett (LB) method, require chemical substitution of Pc, which results in decreased mobility in comparison to samples prepared by vacuum deposition.<sup>[13]</sup>

The history of discotic liquid-crystalline hexa-*peri*-hexabenzocoronene (HBC) derivatives as semiconductors is significantly shorter than that of phthalocyanines. Nevertheless, HBC derivatives have been successfully exploited in photovoltaic devices and field-effect transistors.<sup>[14]</sup> FETs were prepared by solution casting on substrates with the pre-oriented PTFE layer, resulting in uniaxial columnar order with an edge-on arrangement of the molecules.<sup>[15]</sup> The high supramolecular orientation was confirmed by field-effect anisotropy: the charge-carrier mobilities along the columns were significantly higher than in the perpendicular direction.<sup>[16]</sup> The high anisotropy of the charge-carrier mobility was demonstrated by flash-photolysis time-resolved microwave conductivity measurements.<sup>[17]</sup> The LB technique<sup>[18]</sup> and zone crystallization<sup>[19]</sup> have also been reported as efficient methods to obtain layers based on HBC derivatives, which are highly ordered over a long range.

Recently, we reported a novel orientation technique involving the zone-casting of dodecyl-substituted HBC (HBC-C<sub>12</sub>, Fig. 1a,b) from solution directly onto a desired support.<sup>[20]</sup> Atomic force microscopy (AFM) studies revealed long-range order of the columnar structures uniaxially aligned in the casting direction. Due to the high order and unique molecular arrangement between the two phases, these layers also showed interesting optical properties.<sup>[21]</sup> The optical anisotropy of the HBC-C<sub>12</sub> layers was switched reversibly between two considerably different values: a negligibly low level in the crystalline phase at low temperatures, and a high level in the mesophase at higher temperatures.

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