Articles

Controlling the Orientation of Micron-Sized Rod-Shaped SiC Particles with Nematic Liquid Crystal Solvents

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The orientational behavior of micron-sized rod-shaped SiC particles in the liquid crystal (LC) solvents E7, *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA), and 4-octyl-4′-cyanobiphenyl (8CB) has been studied. Particles were observed to predominately orient either parallel or perpendicular to the nematic director, with an equilibrium orientation depending on their surface chemistry and choice of LC solvent. In two cases, a bimodal distribution of particle orientations was found, with a minority population of particles adopting an orientation orthogonal to the majority one. Longer particles were slightly better oriented than shorter ones. No temperature dependence on particle orientation was observed up to the clearing point. Successive deposition of particles onto a solid substrate with different equilibrium orientations controlled through choice of the LC was shown to be effective for producing films with alternating particle arrangement between layers. Taken together these findings demonstrate that liquid crystals can provide a versatile means for solution-phase assembly of ordered films comprised of micron- and submicron-sized rod-shaped building blocks.

Introduction

The behavior of small solid particles imbedded in a nematic liquid crystal (LC) can be very different from that in an analogous suspension in an isotropic fluid.[1] LC anchoring at the particle surfaces combines with the anisotropic elastic properties of the LC medium to produce distortions in the local director field around particles, giving rise to new interparticle forces and new particle ordering behaviors which are completely unique to organized fluid media.[2] For example, nonspherical particles much larger than the size of a single LC molecule tend to adopt a preferred orientation when imbedded in a nematic LC.[3] Their orientation can be controlled through the application of an external alignment field or similar influence, affording a means for organizing small particles in solution and cast as films onto solid surfaces.[4] LC-mediated interactions between nearby particles can be either attractive or repulsive, and generally are direction dependent. Such interactions have been exploited to prepare unusual cellular solids,[5] and pearl-necklace-shaped particle chains.[1a,b] Because these phenomena are associated with molecular ordering in the fluid, any influence which is able to control the alignment of the LC can also be used to control the alignment of a particle or aggregate of interacting particles suspended in it, affording what is potentially a very versatile means for solution-phase assembly of ordered films, materials, and devices constructed from micron- and submimcron-sized building blocks.

This paper seeks to extend recent developments for the use of LC solvents to control alignment of elongated particles in solution and in films deposited on solid supports through exploration of the effects of different nematic solvents and particle surface treatments on orientation. The findings reported here inform LC-based strategies for the preparation of ordered films of objects such as single- and multiwalled carbon nanotubes, semiconductor and metallic nanowires, and related rod-shaped particles.[4] Through experiments involving needle-shaped micron-sized particles of SiC we show that the equilibrium orientation depends on the particle's surface chemistry as well as the choice of LC, and that by combining different surface treatments or LC solvents it is possible to control rod orientation and to form structures such as films with alternating particle orientation in successive layers.

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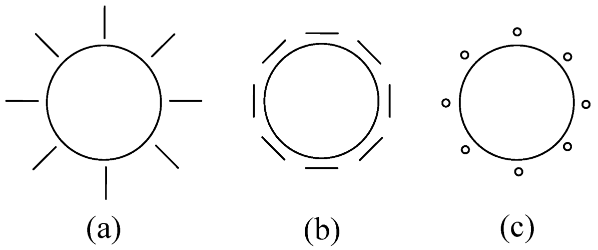

Figure 1. The equilibrium orientation of a rod suspended in a nematic LC depends on its size and on the type and strength of anchoring at the rod surface. Three anchoring orientations are illustrated with the rod viewed end-on: (a) radial or homeotropic anchoring, (b) tangential anchoring, and (c) axial anchoring. Configuration (c) always results in rods orienting parallel to the director, but the first two can lead to parallel or perpendicular orientation, depending on the particle's size and the elastic constants of the LC.

Somewhat surprisingly, the preferred orientation of a rod-shaped object much larger than the size of a LC molecule, when imbedded in a LC medium, is not necessarily one in which the long axis of the rod is parallel to the nematic director. For example, 0.5-μm long single-crystal Fe_2O_3 rods dispersed in the nematic *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA) tend to orient perpendicular to the director.[3] In contrast, single- and multiwalled carbon nanotubes, which are of a similar size and shape, were recently found to orient parallel to the director in several nematic solvents.[4] These results show that orientation is not determined by particle shape alone, and calculations based on continuum elastic theory confirm the equilibrium orientation of rods in nematic LCs is affected by several factors in addition to geometry.[6-8] One of these is the anchoring orientation of LC molecules at the surface of the rod, which can be broadly defined as radial, tangential, or axial, as illustrated in Figure 1. LC molecules tend to adsorb with preferred orientations at interfaces, a phenomenon known as *anchoring*. When anchoring is axial, rods always prefer to orient parallel to the nematic director independent of any other details of the system because this leaves the director field surrounding the particle essentially undisturbed. For other anchoring conditions, the director field in the neighborhood of the particle is forced to distort from uniformity to follow the particle's curved surface. This distortion gradually decays moving away from the particle, after which the director is approximately uniformly aligned. The elastic energy cost is $E_{\text{elastic}} \approx LK$, where L is the particle length and K is the mean Frank elastic constant of the LC. To balance the elastic and anchoring forces, LC molecules at the surface of the particle are also forced to point in a somewhat different direction from their preferred anchoring orientation, giving rise to an additional surface energy $E_{\text{surf}} \approx RLW$, where R is the particle radius and W is the anchoring energy, a measure of the anisotropy in the surface tension at the LC–particle interface.

The preferred orientation of a particle reflects a balance between these two energies which depends on its size, the anchoring orientation, and the elastic properties of the LC solvent. The outcome is conveniently summarized by the dimensionless parameter originally introduced by Burylov and Raikher, $\omega = WR/K$.[7] In one limiting case, $\omega \gg 1$, first considered more than 30 years ago in the pioneering work by Brochard and de Gennes, the energy balance is predicted to favor a particle orientation parallel to that of the bulk director far from the particle.[6] In the other limiting case, $\omega \ll 1$, this balance is predicted to favor perpendicular alignment.[7,8] Particles with axial anchoring are an exception to this rule, as they always prefer parallel orientation. Considering typical anchoring energies ($W \sim 10^{-6} - 10^{-5}$ J m^{-2}) and LC elastic moduli ($K \sim 10^{-11}$ N) one finds the division between the two limiting regimes occurs for particles of radius $R \sim 10^{-6} - 10^{-5}$ m. The particles studied in the present work fall just in this intermediate size range, so one may therefore anticipate that relatively small changes in system parameters will have a pronounced effect on equilibrium particle orientation.

Existing theoretical treatments of rod-shaped particles in nematics restrict their calculations to just two cases: parallel and perpendicular alignment. Indeed, due to the reduced symmetry of the director field arising with intermediate particle orientations, only these two orthogonal cases are analytically tractable. On the basis of general arguments however, Burylov and Raikher predicted there should normally be a single minimum energy orientation corresponding to one case or the other.[8] Andrienko and co-workers reached a similar conclusion through Monte Carlo and molecular dynamics simulations of a rod-shaped particle in a nematic fluid.[9] They also found that, at least for the case of $\omega \ll 1$ and radial anchoring, where perpendicular alignment is preferred, particle alignment parallel to the director is not even metastable due to symmetry breaking in the director field which results in a net torque tending toward perpendicular alignment at all other orientations.

In this work, micron-sized SiC particles were studied in several nematic solvents. Either perpendicular or parallel orientation was observed, with alignment depending on the LC and particle surface treatment, and in two cases minority populations of both orientations occurred simultaneously. The radii of these particles was in the range predicted by theory to be transitionary between perpendicular and parallel alignment ($\omega \sim 1$), making their preferred orientation with respect to the global director very sensitive to the properties of the LC and anchoring conditions.

Experimental Section

SiC is a wide band gap semiconductor with properties that have made it a candidate for applications in high-speed, high-temperature, and high-frequency electronics.[10] We chose to use it in this study because of its availability in the form of elongated particles with uniform shape and high chemical and crystallographic purity, because its surface chemistry can be readily tailored using well-established methods, and because it is representative of a broad class of inorganic microparticles.

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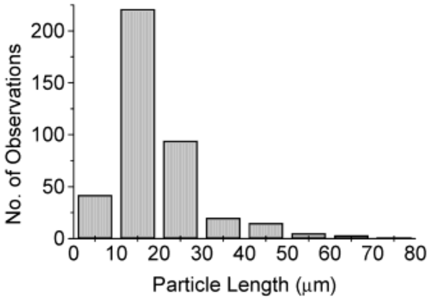

Figure 2. SiC particles varied in length from 7 to 75 μm, with a mean length of 19 ± 10 μm. The aspect ratio for all particles was ∼200:1, independent of size. The histogram shows the distribution of particle lengths based on 400 observations.

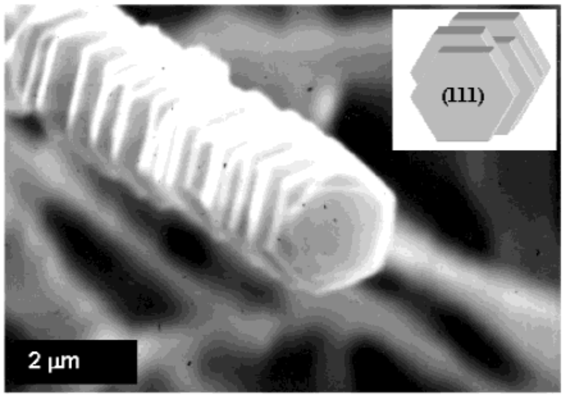

Figure 3. Scanning electron micrograph of one SiC particle. The inset is a schematic representation of a cross section perpendicular to the long particle axis showing the (111) orientation of the hexagonal platelets.

SiC particles measuring 10−100 μm in length and 0.2−2 μm in diameter were purchased as a polydisperse powder consisting mostly of rod-shaped needles with a small amount of larger and irregularly shaped particles (99% SiC, Alfa Aesar). The particles were shape-purified through a series of fractionation steps involving repeated agitation, partial settling, and decanting of aqueous suspensions. Particles in the final purified fraction varied in size (mean length $= 19 \pm 10$ μm, see Figure 2), but their aspect ratio was fairly constant at ∼200:1. Figure 3 presents a scanning electron microscope (SEM) image of one representative particle. Most (>90%) were hexagonal in cross-section, faceted along their length, and had flat ends, similar to the one shown in the figure. Powder X-ray diffraction measurements showed they were almost exclusively of the β-crystalline form. From the hexagonal cross section we deduce the long axis of the particle is normal to the (111) plane.

Some samples were prepared using SiC particles whose surfaces had been functionalized with a self-assembled monolayer (SAM) of octadecyltrichlorosilane ($Cl_3Si(CH_2)_{17}CH_3$, OTS).[11] Surfaces treated with OTS induce homeotropic anchoring in the LCs used in this work.[12,13] The functionalization procedure involved first hydrolyzing SiC in a mixture of concentrated H_2SO_4 (95−97%, J. T. Baker Inc.) and H_2O_2 (30−32%, Jones Hamilton Co.) in a ratio of approximately 3:1 by volume for 90 min at 80 °C. *CAUTION: this solution reacts violently with organics!* After hydrolysis, the particles were allowed to settle to the bottom of the reaction vessel and the liquid was decanted. The material was rinsed 3× with high-purity filtered water (18 MΩ) followed by drying in an oven at 110 °C for at least 24 h. Particles were then dispersed via ultrasonication in a solution of about 2% OTS (Aldrich Inc.) in bicyclohexyl (Eastman Organic Chemicals Inc.) and bath sonicated for 90 min. Excess solvent was decanted and the particles were washed with acetone followed by mixed hexanes. The resulting material was oven dried at 70 °C and stored in a vacuum desiccator.

SiC particles were ultrasonically dispersed in the LCs E7 (EM Industries Inc.),[14] 4-octyl-4′-cyanobiphenyl (8CB, EM Industries Inc.),[15] and N-(4-methoxybenzylidene)-4-butylaniline (MBBA) (Aldrich Inc.).[16] Suspensions had to be used directly, as particles gradually settled out over time. To study their orientation in the LC a droplet of freshly prepared dilute particle suspension was sandwiched between two rubbed glass microscope slides separated by 450-μm thick spacers, which was larger than the longest particles. Initially the LC was disordered, but over a period of about an hour defects gradually diminished despite the large thickness of the cell, leaving a highly ordered planar LC slab as determined with polarizing optical microscopy. At the end of this period most particles had settled to the lower glass surface. The particles did not strongly adhere to the glass interface; if the LC was made to flow slightly by mechanical agitation, the particles moved as well. Thus, we believe their orientation reflected the ordering state of the LC at the time their orientations were measured because they remained at all times free to rotate, even though some may have settled to the lower glass surface before the bulk LC had fully annealed. This picture was confirmed by observing the orientation of a smaller number of particles that had not yet settled out using very thick cells (3−5 mm thick), which were found to be oriented in the same way as those at the LC-glass interface. With E7 and MBBA cells were filled and assembled at room temperature. Samples involving 8CB were prepared and studied in a 40 °C oven, at which temperature 8CB is in the nematic phase. After well-aligned films had formed, particles that had settled to the lower glass surface were photographed with a digital camera mounted to an optical microscope (an example image is shown as the inset of Figure 4b). At least 100 particles were photographed for each sample preparation.

Suspensions were prepared with particle concentrations well below the dilute limit (volume fraction of SiC less than 10^{-4}), where entropic ordering due to excluded volume packing effects is negligible. In addition, only isolated particles separated from their neighbors by 50 μm or more were included in the reported alignment statistics. This separation is greater than the distance over which the nematic distortions are expected to extend, so that LC-mediated interparticle interactions are unlikely to be significant. We note that in films cast from such dilute solutions the particles appeared to settle into random positions on the substrate, indicating a lack of long-range attractive or repulsive interactions. The one exception, which was observed only among particles that had not yet settled out of solution in very thick cells, was that a small minority tended to accumulate in a head-to-tail arrangement at disclination lines. There were few such defects in the fully annealed cells, however, and these regions were excluded from the reported statistics. Thus, in the following we assume that rod−rod interactions did not play a significant role in particle alignment.

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[15] Transition temperatures C → SmA (21.5 °C), SmA → N (33.5 °C), N → I (40.5 °C) (Product Information sheet, BDH Inc., 1986), elastic constants at 40 °C, $K_{11} = 6.3$ pN, $K_{22} = 2.8$ pN, $K_{33} = 6.4$ pN (Madhusudana, N. V.; Pratibha, R. *Mol. Cryst. Liq. Cryst.* **1982**, *89*, 249−257).

[16] Transition temperatures C → N (22 °C), N → I (48 °C) (Sorai, M.; Nakamura, T.; Seki, S. *Pramana Suppl.* **1975**, *1*, 503), elastic constants at 23 °C, $K_{11} = 6.95$ pN, $K_{22} = 4.4$ pN, $K_{33} = 8.99$ pN (de Jeu, W. H.; Claassen, W. A. P.; Spruijt, A. M. J. *Mol. Cryst. Liq Cryst.* **1976**, *37*, 269).

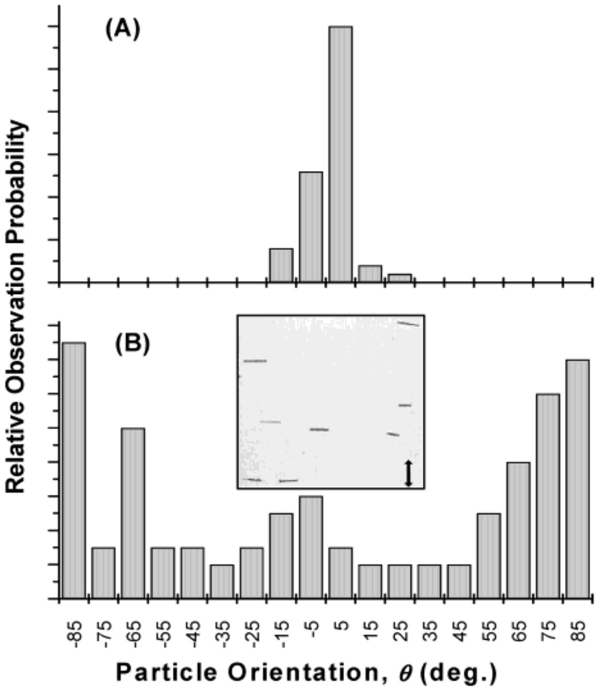

Figure 4. Histograms showing the orientations of SiC particles settled from uniformly aligned E7. The orientation of the nematic director was parallel to $\theta = 0$ in both cases. (a) As-received particles (100 observations), (b) particles functionalized with an OTS SAM (153 observations). The inset in part (b) is a typical optical micrograph (140 × 140 μm) used to measure particle alignment statistics, where small line-shaped features are SiC particles and the black arrow shows the director orientation.

Some samples, where specifically mentioned below, were prepared in an electromagnet to aid in alignment of the LC. These samples involved polycarbonate etch-track membrane substrates (Millipore Nuclepore, 200-nm diameter pore size), to which a droplet of suspension was applied and drawn through with a mild vacuum, leaving particles lying flat on the surface.

Results

Figure 4 shows histograms of particle orientations from dispersions in E7 using (a) unfunctionalized particles, and (b) particles functionalized with an OTS SAM. In both cases, the direction of surface rubbing, and hence the LC director, were parallel to the angle defined as $\theta = 0°$. The histograms were fairly strongly peaked, reflecting the anistropic nature of the particle–LC interaction. They were also symmetric with respect to the orientation of the director, as expected from the uniaxial symmetry of the rods and nematic fluid. Unfunctionalized particles oriented parallel to the director, whereas those with an OTS coating were generally perpendicular. Histograms from samples in MBBA and nematic 8CB are shown in Figures 5 and 6, respectively. The results found with MBBA were similar to those found with E7, but in 8CB both functionalized and unfunctionalized particles preferred perpendicular orientation. Control samples were prepared using rubbed glass cells, unfunctionalized SiC, and the isotropic (non-liquid crystalline) solvent phenyloctane. These films showed a random distribution (see Table 1), demonstrating that alignment was caused by an orientational effect of the LC, and not by surface grooves or flow effects.

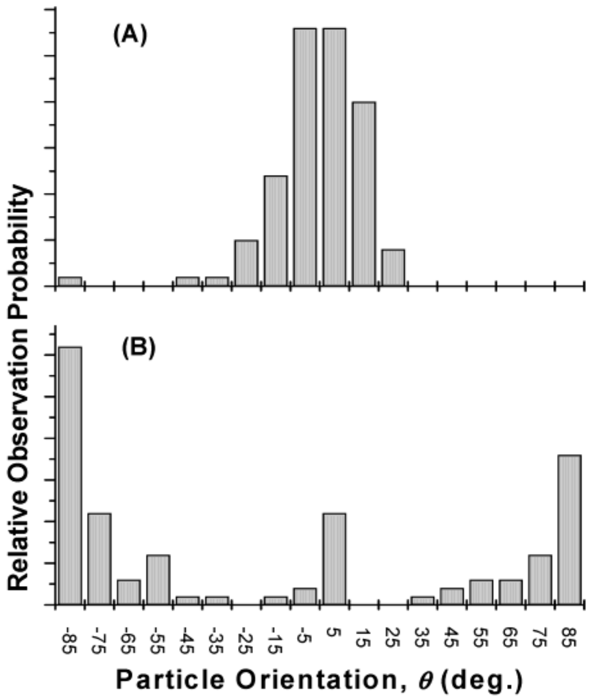

Figure 5. Histograms showing the orientations of SiC particles settled from uniformly aligned MBBA. The orientation of the nematic director was parallel to $\theta = 0$ in both cases. (a) As-received particles. (100 observations), (b) particles functionalized with an OTS SAM (100 observations).

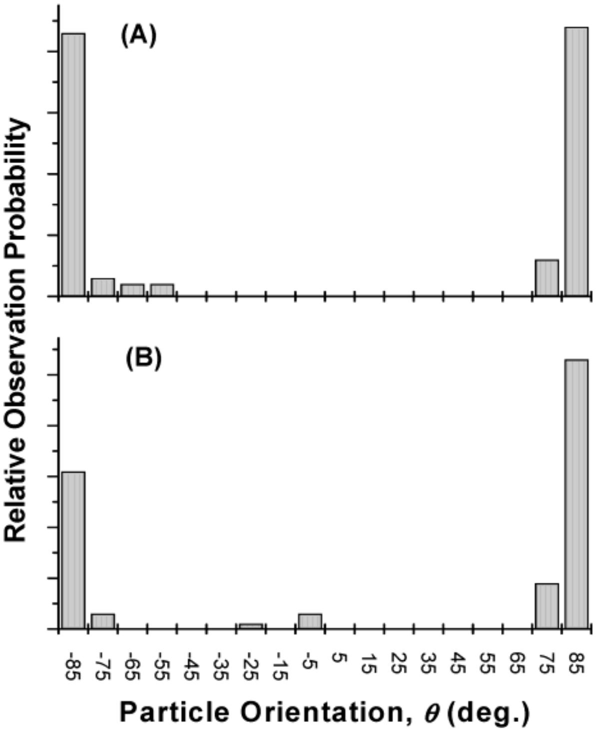

Figure 6. Histograms showing the orientations of SiC particles settled from uniformly aligned 8CB at 40 °C. The orientation of the nematic director was parallel to $\theta = 0$ in both cases. (a) As-received particles (100 observations), (b) particles functionalized with an OTS SAM (100 observations).

The overall order in these samples can be summarized through the two-dimensional orientational order parameter $s = <2\cos^2\phi - 1>$, where ϕ is the angle between the long axis of a particle and the average orientation of all particles, and the brackets denote an average over

Table 1. Summary of Results

LC	functionalized	orientation	S	no. obsd
phenyloctane[a]	no	random	0.04	138
E7	no	parallel	0.97	100
E7	yes	perpendicular	−0.41	153
MBBA	no	parallel	0.88	100
MBBA	yes	perpendicular	−0.45	100
8CB	no	perpendicular	−0.90	100
8CB	yes	perpendicular	−0.87	100

[a] Phenyloctane, a nonliquid crystalline solvent, was used to prepare control samples.

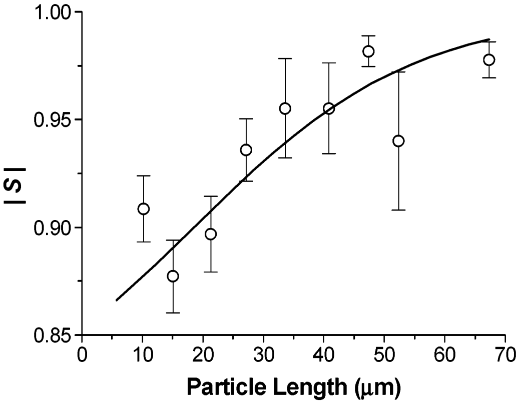

Figure 7. Orientational order was slightly greater among long particles as seen in this plot of the average unsigned order parameter against particle length. The figure combines data on 400 unfunctionalized particles in E7, 8CB, and MBBA, and functionalized particles in 8CB. The line is a guide to the eye.

all observations. The order parameter varies between −1 and 1, with large absolute values representing higher order. The sign of s is positive if particles tend to align parallel to the average orientation and negative if they tend to orient perpendicular to it. Findings from all sample preparations are summarized in Table 1.

The relationship between particle size and degree of orientational order was also investigated, and these results are presented in Figure 7. The figure combines data on 400 unfunctionalized particles in E7, 8CB, and MBBA, and functionalized particles in 8CB. The order parameters for most particles were close to ±1.0 in all systems, with the longest particles showing higher order. The orientational energy, and hence degree of order, is expected to increase with particle length, but the small observed correlation in this case is probably a result of the fact that longer particles encountered a larger number of LC microdomains, averaging over the effect of micron-scale variations in director orientation caused by imperfect alignment by the rubbed glass walls.

Discussion

Let us begin the discussion by considering the anchoring orientation on the particles' surfaces. The situation was complicated by the fact that the particles were not smooth cylinders on a submicron scale, but instead were highly faceted in a rather complex pattern. As is apparent from Figure 2, each was formed of a stack of monocrystalline hexagonal platelets with nearly uniform orientation and thickness, but with slightly differing diameters and transverse positions along the column. The topography seen by the LC along an axis tangential to the particle was therefore smooth and flat, whereas parallel to the long axis it resembled an irregularly grooved surface with square side-walls. The faceted geometry left portions of SiC (111) faces exposed along the entire length of the particles, one of which is labeled in the inset of Figure 3. From SEM images these facets are estimated to comprise 25−50% of the total surface area of the particle, so anchoring on these regions cannot be neglected. As a consequence of this complex geometry, the nematic layer adjacent to the particle is likely to have had irregular variations in the director profile and a high concentration of topological defects in order to accommodate changes in anchoring orientation and surface geometry. With particles somewhat larger than those studied here ($R > 5$ μm) it is often possible to use polarizing optical microscopy to analyze the director configuration in the neighborhood of a particle, and from this to deduce the anchoring orientation.[17] However, the SiC particles were too small to use this technique because defect textures could not be clearly and reproducibly observed, making it impractical to directly establish the anchoring orientation.

Some insight can be gained by considering the director orientation at a small distance d away from a particle's surface, which is greater than the characteristic roughness of its faceted surface but less than the nematic extrapolation length, i.e., 0.1 μm $< d <$ 1 μm. This allows one to neglect the details of the particle's submicron geometry by averaging over the detailed influences of variations in shape and crystallographic orientation, and treat it as a smooth cylinder with an effective anchoring energy and orientation. Then based on the conditions $\omega \gg 1$ ($\ll 1$) for parallel (perpendicular) particle orientation, along with literature values for the elastic constants of MBBA,[16] E7,[14] and 8CB,[15] one can calculate the limiting anchoring energy necessary to produce the observed orientation for the smallest and largest particles.[8] Doing so we find that in those cases where perpendicular alignment was observed, $W < 1 \times 10^{-5}$ Jm^{-2}, and for parallel orientation, $W > 5 \times 10^{-5}$ Jm^{-2}. These fall within the range of anchoring energies commonly found at solid interfaces,[18] and show that in these systems even a relatively small change in W (by a factor of 5 or so) can lead to a change in equilibrium orientation.

The temperature dependence of a particle's orientational energy near the nematic−isotropic transition T_{NI} has been discussed by Anderson et al.[19] They point out that, although both W and K vanish as T_{NI} is approached from below, they do so with different rates: to a first approximation $K \sim S^2$, whereas $W \sim S$, where S is the nematic order parameter. Consequently the ratio $WR/K \sim 1/S$ can become large as the temperature nears T_{NI} and $S \rightarrow 0$. The situation would then correspond to the limit originally considered by Brochard and de Gennes[6] ($\omega \gg 1$), where all anchoring orientations favor parallel alignment. Under such conditions, particles which orient perpendicular to the director deep in the nematic phase would then be expected to rotate into parallel alignment as the temperature is raised. However, whether a change in alignment occurred in practice would depend on the material parameters of the system, because at the N → I transition S jumps discontinuously to zero.

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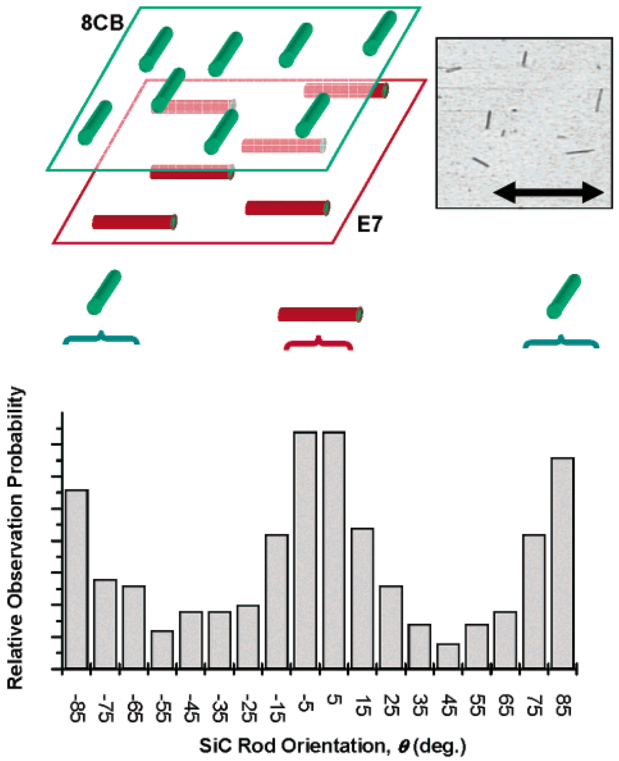

Figure 8. When layered films were deposited from successive applications of particles in nematic E7 and 8CB, the resultant films exhibited two orientations, reflected in this bimodal distribution (based on 300 observations). Particles in the first layer deposited using E7 oriented parallel to $\theta = 0°$, whereas those in the second layer deposited from 8CB oriented near ±90°. In both applications the LC director was globally aligned by a magnetic field of ~10 kG applied parallel to the arrow in the inset (defined as $\theta = 0$). The photograph shows a region from one sample (130 × 130 μm).

Systems of functionalized and unfunctionalized SiC particles in MBBA and E7 were examined for temperature-dependent changes in ordering near the N → I transition by gradually increasing the temperature in a small oven specially designed to minimize temperature gradients and convection currents. No changes in orientation were observed right up to T_{NI}. Experiments were also performed using functionalized particles in E7 and MBBA with the oven placed in a 10 kG magnetic field directed in the plane of the sample. The particles remained oriented perpendicular to the director and field with no discernible change up to T_{NI}, whereupon they uniformly rotated parallel to the applied field. This showed that LC alignment forces remained strong enough to overcome the action of an external influence tending to rotate the particles away from their preferred orientation in the LC throughout the nematic phase.

Figures 4B and 5B seem to show evidence of two orientational populations, with a majority of particles orienting perpendicular to the director and a much smaller, but significant, minority orienting parallel to it. Bistable orientations are not predicted by existing analytical models, nor are they observed in computer simulations. Those particles orienting parallel to the director in Figures 4B and 5B did not appear to differ in size or shape from the remaining majority of the population adopting perpendicular orientations. Likewise, they were not associated with irregularities on the glass surface, or defects in the nematic fluid. In fact their orientation was the only evident feature differentiating them from those with perpendicular alignment. We can only speculate that this unexpected behavior may be associated in some way with the irregular shapes of the particles, which as discussed above differed significantly from the smooth cylinder geometry considered by theories of particle ordering in nematics.

The results reported above show that nematic LCs can be used to control the orientation of SiC particles, and that modification of anchoring conditions through particle surface functionalization along with the choice of LC can affect orientational distributions. They suggest the potential of combining different LCs or particle surface treatments to assemble small-scale building blocks into more complex orderings. To test this concept, we performed the following demonstration. Using polycarbonate etch-track membrane substrates, films of unfunctionalized SiC particles were cast in two steps. In the first step, particles were deposited from E7, in which they oriented parallel to the nematic director. The LC was drained through the small pores in the membrane by application of a vacuum, leaving behind a film of SiC particles lying flat on the membrane surface. To uniformly orient the LC, a magnetic field of ~10 kG was applied parallel to the plane of the substrate during deposition. Micrographs of the film at this stage showed the SiC particles were uniformly oriented parallel to the LC director and magnetic field. With the magnetic field and sample orientation unchanged, a second droplet of SiC in nematic 8CB was then applied and drawn through the porous membrane, depositing a second particle layer. The resulting layered film contained particles in two orthogonal orientations. A histogram summarizing its alignment properties is presented in Figure 8. The distribution was bimodal, with $\theta = 0$ corresponding to the dominant particle orientation in the first layer and the axis of the magnetic field. Particle orientation in each deposition appeared to be essentially unaffected by the other.

To summarize, the orientational behavior of micron-sized SiC particles in several LCs has been studied. Most particles oriented either parallel or perpendicular to the nematic director, but in two cases a minority bimodal distribution was observed. It was found that a self-assembled monolayer formed on the particles' surfaces could alter their equilibrium orientation, and that different LCs led to different alignment. Longer particles were slightly better oriented than shorter ones. No temperature dependence on rod orientation was observed up to the clearing point. Successive deposition of particles from different LCs with different equilibrium orientations produced a layered film with alternating particle arrangement between layers. This approach may be useful for organizing small particles into crossbar-type structures, or to create more complex layered films, such as helical patterns formed by rotating the alignment field during deposition.

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