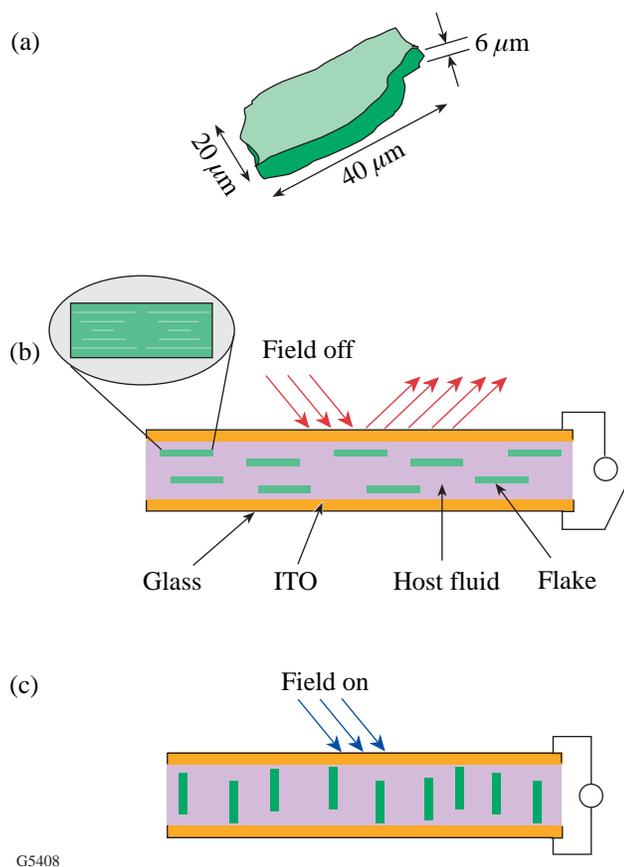

Electric-Field-Induced Motion of Polymer Cholesteric Liquid Crystal Flakes in a Moderately Conductive Fluid

Polymer cholesteric liquid crystals (pCLC's) are commonly limited to passive applications as thin films reflecting a specific wavelength and polarization of light due to their inherent selective reflection properties. Some pCLC's in the state above their glass transition temperature can be used for active applications, but due to their high viscosity, switching times are long compared to low-molar-mass liquid crystals with a similar structural composition. New possibilities for pCLC applications emerged in 1994 when Faris proposed fracturing pCLC films with Grandjean texture (the helical axis of the molecular structure is normal to the film surface) into tiny particles called "flakes."¹ Initial research on pCLC flakes, performed by Korenic *et al.*, focused on cyclic polysiloxanes² exhibiting selective reflection in the visible. The flaking process was refined, and passive optical effects were studied. By characterizing the selective reflection effect for both films and flakes, Korenic showed that bulk properties were preserved. Colorimetry of pCLC flakes in various drying binders (e.g., glues and adhesives) leads to the development of new paint and pigment concepts for potential applications in both the decorative arts and document security.^{3,4} Optimization of the vivid selective reflection effect for passive applications was found to depend on particle concentration, the use of a restricted particle size range (e.g., ~90 to 180 μm), and immersion in a drying binder with comparable refractive index (~1.6).

The use of an electric field to control the motion of particles has been investigated for decades. The prospect of electrophoretic image displays⁵ replacing cathode ray tubes was very realistic in the early 1970s until liquid crystal displays took the lead in development. Particle displays remained a novelty until recent advances involving particle encapsulation and the novel concept of a mechanically flexible display that emerged from work with polymer-dispersed liquid crystal technology in the 1980s.⁶ An electrophoretic display based on the encapsulation of hundreds of micron-sized charged particles that migrate back and forth inside a 50- to 200- μm capsule is being developed by E-Ink[®].⁷ A second leading particle display technology, Gyricon[®],⁸ relies on individually encapsulated bichromal, 25- to 200- μm spheres with oppositely charged hemispheres

that rotate with the application of a suitable electric field. Response times for these technologies, currently ~200 to 300 ms, are judged to be sufficient for applications such as electronic books, commercial advertising signs, or personal data assistants (PDA's). Achieving color with these technologies is complex and requires the addition of color filters or the development of multichromal spheres,⁹ respectively. A new concept that involves ~10- μm birefringent polymer nematic liquid crystal spheres¹⁰ may also have applications in particle display technology. These spheres were shown to reorient within 100 to 200 μs in an electric field due to the negative dielectric anisotropy of the polymer nematic material. Crossed polarizers would be necessary to observe optical effects.

Here we report an extension of the pCLC flake technology from entirely passive optical applications to an investigation of motion in an electric field.^{11,12} Commercial polycyclosiloxane flakes,¹³ typically 6 μm thick, with an arbitrary shape and a selective reflection peak at $\lambda_0 = 520$ nm (green) were sieved and dried² to obtain batches with sizes between 20 and 50 μm [Fig. 90.32(a)]. The pCLC flakes were suspended in propylene carbonate (PC) (Aldrich, 99.7% HPLC grade), a host fluid that is transparent, chemically compatible with the pCLC material, of a comparable density, and has a non-negligible conductivity of $\sim 5 \times 10^{-6}$ siemens/cm (Table 90.IV). Test cells were constructed using pairs of 25 \times 25 \times 3-mm indium tin oxide (ITO)-coated glass substrates.¹⁴ A mixture of 41 \pm 3- μm -diam soda lime glass spheres (Duke Scientific Corp.) dispersed in a UV-curing epoxy (Masterbond UV 15-7TK1A) was applied in four corners of one substrate to set the cell gap. Cells were then filled by capillary action and sealed with epoxy (Devcon 5-Min[®]). Basic observations were made using a polarizing microscope (Leitz Orthoplan). A digital camera (Panasonic Digital 5100) with a timer was used to record flake motion with a time resolution of 100 ms. Data on flake motion occurring on a sub-second timescale was obtained by detecting the light reflected from the rotating flake surface using a photomultiplier tube (PMT) (Hamamatsu R905) coupled to the microscope ocular by means of a fiber optic mounted in a precision fiber coupler (Newport Corp.). The PMT signal was displayed



on one channel of an oscilloscope (HP 54520A) and directly compared with the field applied to the cell displayed on the second channel. A function generator (Stanford Research Systems DS345) provided the sinusoidal driving voltage for ac fields. Flake motion was observed as a function of the waveform's magnitude and frequency. Rotational behavior was easily detected under near-normal illumination through a 10× objective (N.A. = 0.2). Brightly reflecting flakes lying in the plane defined by the substrates [Fig. 90.32(b)] darkened substantially after reorienting [Fig. 90.32(c)].

Experiments concentrated on investigating ac sine wave-driven devices. Using the polarizing microscope and the digital camera to track flake motion, we found that pCLC flakes responded to electric fields by rotating approximately

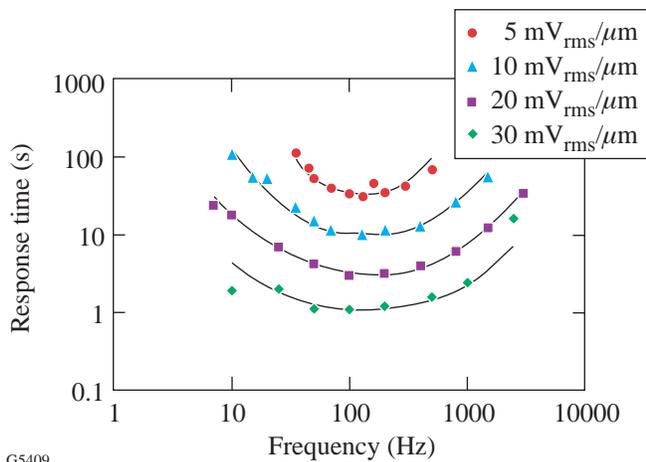
Figure 90.32

Dimensions of a typical irregularly shaped pCLC flake are depicted in (a). Flakes lie approximately parallel to cell substrates when no electric field is applied (b) and appear green due to selective reflection caused by the helical molecular structure of cholesteric liquid crystals, as depicted by the enlarged flake. Flakes reorient with one long axis parallel to the applied field (c). They appear dark since light is no longer reflected off their flat surfaces.

Table 90.IV: Properties of CLC520 flakes and host fluid.

Property at 20°C	Wacker polysiloxanes CLC520	Propylene Carbonate ^(d)
Index of refraction @ 589 nm	1.573* (Ref. 4)	1.422 ^(c)
Dielectric permittivity @ 1 kHz	~ 3 ^(a)	69 ^(d)
dc conductivity (S/cm)	–	~ 5 × 10 ⁻⁶
Dynamic viscosity (Pa·s)	Solid	2.9 × 10 ⁻³ ^(c)
Density (g/cm ³)	~1.1 ^(b)	1.189 ^(c)
All materials were used as received without further processing.		
* Average index of refraction.		
^(a) Measured with an impedance meter (253 Electro Scientific Instruments)		
^(b) Measured by a water displacement technique		
^(c) Sigma-Aldrich-Fluka Catalog (2000)		
^(d) High Purity Solvent Guide, Baxter Diagnostics Inc., Burdick & Jackson Division (1990)		

90° about one axis, typically the longest one [Fig. 90.32(c)]. Flake motion was seen in electric fields as low as $5 \text{ mV}_{\text{rms}}/\mu\text{m}$ ($0.21 \text{ V}_{\text{rms}}$) within a specific frequency bandwidth defined as the range where the flake response time increased by a factor of 3 from the fastest response detected. In a typical set of data for one flake (shown in Fig. 90.33) the flake's fastest response at $5 \text{ mV}_{\text{rms}}/\mu\text{m}$ required 47 s at 130 Hz. The frequency bandwidth extended from 45 Hz to 500 Hz for this very low magnitude field. As the magnitude of the driving field increased to $30 \text{ mV}_{\text{rms}}/\mu\text{m}$, the frequency range for motion broadened to extend from approximately 25 Hz to 1000 Hz. This sixfold increase in voltage greatly reduced the reorientation time for the flake to less than 1 s. Many other flakes were seen to behave in a similar manner.



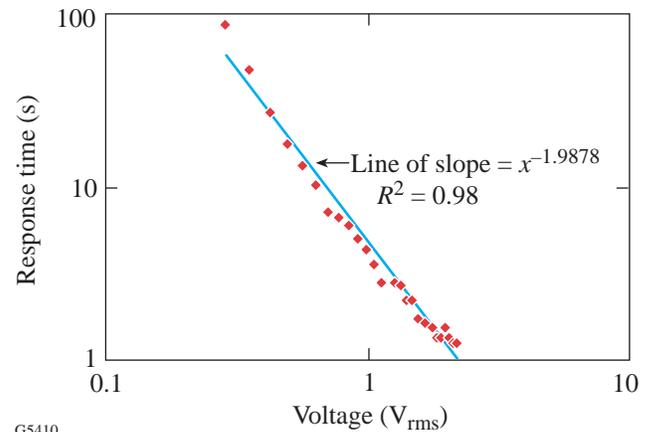
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Figure 90.33

The characteristic time response of a representative pCLC flake as a function of frequency at specific electric field values. Lines are drawn to guide the eye. Similar behavior was observed for dozens of flakes.

The reorientation times of flakes in the field of view imaged onto the digital camera ($2 \text{ mm} \times 1 \text{ mm}$) were examined as a function of incremental voltage increases of a 50-Hz electric field. Attention was directed to two types of flakes: (1) “small” flakes with the largest dimension of the order of $25 \mu\text{m}$ (typically square or triangular) and (2) “large” flakes with a 35- to $50\text{-}\mu\text{m}$ dimension that tended to be rectangular. The small flake's response curve in Fig. 90.34 shows an inverse quadratic dependence on the field ($R^2 \approx 0.98$); however, for fields larger than approximately $30 \text{ mV}_{\text{rms}}/\mu\text{m}$ ($1.3 \text{ V}_{\text{rms}}$) the large flakes consistently reoriented more quickly than the small flakes. Inertial terms are small enough to be neglected in this system, so it is possible that at higher voltages these flakes carried a

proportionally larger induced dipole moment due to their size and (typically) rectangular shape, thereby causing these flakes to reorient more quickly than smaller flakes.



G5410

Figure 90.34

The average response time of several flakes has an inverse quadratic dependence on the applied voltage. The standard deviation of 10% is of the order of the size of the data points.

Using the signal from the PMT to detect light reflected from a single typical flake, we found that the actual time necessary for a flake to rotate was less than the reorientation time measured with the digital camera through the microscope eyepiece (Fig. 90.35). In the presence of a $40\text{-mV}_{\text{rms}}/\mu\text{m}$ ($1.7 \text{ V}_{\text{rms}}$, 100 Hz) field there was a delay time D_t of 420 ms for the flake to initiate movement after the field was first applied. The flake then completed the full reorientation, as determined by its reflectivity shifting from a maximum to a minimum value, with a fall time R_t of 560 ms. The total reorientation time was therefore just under 1 s. (Here we define the reorientation time of a flake as the sum of the D_t and the R_t). We attribute D_t to the time necessary for an insulating pCLC flake to acquire a dipole moment.

The motion of pCLC flakes was not bistable, but this system showed “memory” or hysteresis. Flakes relaxed to their initial position in the plane of the cell several minutes after the driving field was turned off. There was also a gradual, approximately linear increase in response time for suspended flakes in the PC host for over 48 h.

Electrophoresis can be discounted as a possible mechanism because pCLC flakes are not charged initially, but acquire an

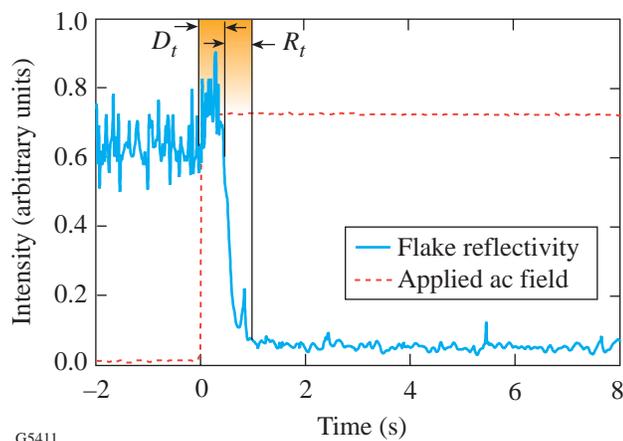


Figure 90.35

Flake motion in a $40\text{-mV}_{\text{rms}}/\mu\text{m}$ ($1.72\text{-V}_{\text{rms}}$) field at 100 Hz was studied with a PMT detecting light reflected from the flake surface. Initially, the flake reflected brightly but little light was detected upon reorientation. The resulting contrast ratio, with no attempt to eliminate light from other flakes and sources of scatter, was approximately 15:1.

induced polarization that is presumed to come from migrating charges. Since the electric fields applied to test cells were uniform to within $\pm 3\%$, dielectrophoresis, which requires an electric field gradient, can also be eliminated as a possible effect contributing to flake motion. The mechanism leading to flake reorientation in host fluids with non-negligible conductivity is most likely the orientational effect described by Jones.¹⁵ This effect is caused by an induced dipole, with a quadratic dependence on the electric field, brought about by the difference in the conductivity and dielectric constant between the flake and the host fluid. The response time for flake motion is determined by solving the equation of motion for the system, which includes the torques due to the induced dipole and the viscous retardation, while the moment of inertia is neglected. Calculations show that the flake response time will have an inverse quadratic dependence on the electric field, as was experimentally observed. A closed-form solution in two dimensions was obtained, and time response calculations corresponded well with the experimental observations in Fig. 90.33. A numerical solution, based on Okagawa's work,¹⁶ was found for flake motion in three dimensions.

Summary

In summary, we have observed the reorientation of pCLC flakes suspended in propylene carbonate, a moderately conductive host fluid. Flakes align with one axis parallel to the electric field. Motion has been observed in applied fields as

low as $5\text{ mV}_{\text{rms}}/\mu\text{m}$. Reorientation time decreased, while the frequency range for motion increased with the applied voltage. We have observed 90° flake rotation in times R_t as short as hundreds of milliseconds. We envision much faster response times in device geometries where the flake rotation is restricted to a few degrees. The response time, which has an inverse quadratic dependence on the applied field, is also dependent upon flake shape and size as well as various material characteristics. Though flake motion is not bistable, it has a memory effect that needs to be explored further. Controlling flake orientation can lead to both commercial and scientific applications. Display applications with the capability for color are envisioned, as well as optical filters, polarizers, and spatial light modulators.

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