Electro-induced orientational ordering of anisotropic pigment nanoparticles

Robert J. Greasy1, Robert M. Richardson1, Susanne Klein2, David Cherns1, Michael R. Thomas3, Claire Pizzey4, Nick Terrill4 and Cyrille Rochas5

1HH Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK
2HP Laboratories, Long Down Avenue, Stoke Gifford, Bristol BS34 8QZ, UK
3Bristol Centre for Functional Nanomaterials, Centre for NSQI, University of Bristol, Tyndall Avenue, Bristol BS8 1FD, UK
4Diamond Light Source Ltd, Diamond House, Harwell Science and Innovation Campus, Didcot Oxfordshire OX11 ODE, UK
5CERMAV-CNRS, BP 53, Grenoble Cedex 9 38041, France

The response of anisotropic pigment particle suspensions to externally applied electric fields has been explored for possible application in reflective display technologies. Three different types of pigment particle were suspended in dodecane, using a polymeric stabilizer, and showed Schlieren textures between crossed polarizers at high concentrations (greater than 25–30 wt%), indicating the formation of colloidal nematic phases. Orientational order parameters were determined by X-ray scattering, and the influence of polydispersity on the values is discussed. X-ray scattering measurements also demonstrated a change in the structure factor consistent with the onset of a colloidal nematic phase. In addition, the pigment particles were dispersed into various liquid crystal hosts at low concentrations (less than 5 wt%) with and without the presence of mesogenic mimic stabilizers. However, the influence of these stabilizers on orientational ordering could not be confirmed. The electro-induced ordering determined via scattering was related to the electro-optical response of each suspension using a simple model. The particles in nematic hosts not only showed a high degree of orientational ordering at lower electric field strengths, but also showed a reduction in...
stability. Although these systems have shown strong orientational ordering, the optical response has been limited by the intrinsic shape of the pigment particles and the distribution of the transition dipoles moments within them. Nevertheless, the feasibility of developing materials for display applications has been demonstrated.

1. Introduction

Nematic liquid crystals comprising small elongated molecules have been the basis for many current highly successful display technologies. However, they do have some limitations. Displays based on director rotation in transparent materials (e.g. twisted nematics) require polarizers and colour filters that absorb a significant fraction of the light. This necessitates the use of backlighting and shortens battery life in mobile devices. Reflective displays based on the absorbance of light by guest dye molecules could improve on this [1]. However, there are several constraints to the use of dissolved dyes. For instance, they tend to exhibit low contrast because the orientational order parameter of the dye molecules within the nematic host is low. Their interaction with the nematic host can also lead to increased viscosity or a reduction in the nematic temperature range. Suspensions of pigment particles have therefore been investigated as candidate materials for future display applications. They represent a promising class of particles because it is possible for anisometric nanoparticles to exhibit much higher orientational order parameters than small molecules, and the effect of the suspended particles on the isotropic–nematic transition temperature is minimal [2]. There are also many lightfast pigments with high extinction coefficients. In principle, an ideal system would consist of rod-shaped particles with transition dipoles for visible light absorbance lying parallel to rod axes. A particle with the long axes aligned parallel to the light’s direction of travel would have no absorbance, but there would be strong absorbance if the axes were oriented randomly or perpendicular to the light’s direction.

Rod- or disc-shaped nanoparticles in dilute suspension can be oriented when in isotropic solvents [3–5]. The orienting effect of an applied electric field on individual particles is dependent on the difference in dielectric permittivity between the particles and the solvent, in addition to their aspect ratio [6]. A result of this is that, in many cases, the degree of orientational ordering tends to be weak unless impractically high fields are used. However, there are two possible ways to improve the field response. The particles can be incorporated into an isotropic solvent at sufficient concentration to form a nematic [7–9] where the director can then be oriented by a modest field. Alternatively, the particles can be suspended in a molecular nematic host where an applied field will then orient the host director and, if the anchoring conditions are suitable, the particles will follow [10]. There are many conditions that should be satisfied if this simple concept is to be developed into a working system. Initially, the transition dipole must lie parallel or perpendicular to an axis of the nanoparticles so they must be single crystals rather than amorphous. The largest dimensions of the nanoparticles should also be kept below approximately 300 nm to keep scattered light at an acceptable level [11]. The density difference between the particles and the solvent should be small to assist the production of colloidal suspensions. Aggregation must be minimized by the choice of solvent to reduce the van der Waals attraction and by coating the particles with a steric stabilizer. For the nematic dispersion media, there is the additional destabilizing effect that arises from the elastic distortion of the director around the particles [12,13]. The choice of stabilizer may also contribute to the director anchoring at the surface that determines how the particles are oriented with respect to the director of a molecular nematic host.

In this work, three insoluble, platelet-shaped pigment particles have been investigated using different combinations of stabilizers and solvents, including both isotropic and nematic hosts. They have been selected because, in a concentrated suspension, they have shown nematic characteristics, rather than developed *ab initio* to fulfil the conditions outlined earlier. However, the principle aim of this work was to characterize the electro-optic properties and understand
their origins at the nanoscale level. This can then inform the development of better materials. Several experimental methods have been used to elucidate the properties of the pigment suspensions, but absorption spectroscopy and X-ray scattering have predominated. In §2, the background to the electro-optic response is reviewed. It is followed in §3 by an outline of the X-ray methods that have been used to determine the orientational order of the particles. The next three sections report the details of the materials used, the electro-optic results and the X-ray investigation of the underlying structure.

2. Orientational order and optical absorbance

The absorbance of a suspension of pigment particles depends on \( \langle \cos^2 \delta \rangle \), the mean-squared value of the cosine of the angle, \( \delta \), between the transition dipole moment of the absorbance and the electric vector of the light. This can be calculated for different geometries, and two examples are considered here. It is assumed that the particles are cylindrical or disc-like in shape, and that in suspension, they form a uniaxial phase whose orientational order parameter is denoted as \( S \). A useful intermediate quantity is \( \bar{P} \), defined as

\[
\bar{P} = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle,
\]

where \( \theta \) is the angle between the particle symmetry axis and the (un-polarized) light’s direction of travel and the brackets indicate an ensemble average. \( \bar{P} \) is determined by the particles’ orientational order parameter, \( S \), and the orientation of the director with respect to the light direction. For homeotropic alignment, when the director is oriented along the light direction, \( \bar{P} = S \), and for planar alignment when the director is oriented perpendicular to the light direction, \( \bar{P} = -S/2 \) (details in the electronic supplementary material). The relationship between \( \bar{P} \) and \( \langle \cos^2 \delta \rangle \) depends on the orientation of the transition dipole within the particle, and these calculations are also detailed in the electronic supplementary material, section S1.

For a rod-shaped particle with a transition dipole along its long axis, the absorbance \( A \) is given by

\[
A = 3A_0 \langle \cos^2 \delta \rangle = A_0 (1 - \bar{P}_2), \tag{2.1}
\]

where \( A_0 \) is the absorbance of an isotropic suspension of the same concentration.

The device field response is defined as the ratio of the absorbance between two different states. Some different states of the director are illustrated in figure 1a. A simple device could change the director from randomly oriented to homeotropic by the application of a field where its device field response (i.e. the absorbance with field applied divided by the initial absorbance) would be

\[
D_1 = \frac{A_H}{A_0} = 1 - \frac{S}{1}. \tag{2.2}
\]

A second possible device could switch the director from perpendicular to parallel to the light’s direction of travel. This could be achieved by application of an electric field parallel to the light, switching the director from planar to homeotropic, as shown in figure 1a. Its device field response would be

\[
D_2 = \frac{A_H}{A_P} = \frac{2 - 2S}{2 + S}. \tag{2.3}
\]

For a system of rods, the material order parameter can approach unity and the corresponding device field response approaches zero, as shown in table 1.

For a disc-shaped particle with a transition dipole at any orientation within its plane, the absorbance \( A \) is given by

\[
A = 3A_0 \langle \cos^2 \delta \rangle = A_0 \left( \frac{\bar{P}_2}{2} + 1 \right), \tag{2.4}
\]

where \( \bar{P}_2 \) is defined for the disc normals (figure 1b). The device field response of a random to homeotropic device is

\[
D_3 = \frac{A_H}{A_0} = \frac{2 + S}{2}, \tag{2.5}
\]
Figure 1. Illustration of the distribution of (a) long rod axes or (b) thin disc normals in three director configurations for transmitted light indicated by the arrows. For the rods, the order parameter $S \sim 1$, so the axes tend to be parallel to the director, $n$. For the discs, the order parameter $S \sim -\frac{1}{2}$, so the normals tend to be perpendicular to the director. The homeotropic state could be achieved by application of a horizontal field to the random or planar configurations. (Online version in colour.)

Table 1. Theoretical values for the device field response for suspensions of rods and discs.

<table>
<thead>
<tr>
<th>Order parameter of particles, $S$</th>
<th>Rods with a transition dipole along the long rod axis</th>
<th>Discs with a transition dipole in plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_1 = \frac{A_H}{A_0}$</td>
<td>$D_2 = \frac{A_H}{A_p}$</td>
<td>$D_3 = \frac{A_H}{A_0}$</td>
</tr>
<tr>
<td>$D_4 = \frac{A_H}{A_p}$</td>
<td></td>
<td>$D_5 = \frac{A_H}{A_p}$</td>
</tr>
<tr>
<td>1.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.9</td>
<td>0.1</td>
<td>0.07</td>
</tr>
<tr>
<td>$-0.45$</td>
<td></td>
<td>0.78</td>
</tr>
<tr>
<td>$-0.5$</td>
<td></td>
<td>0.75</td>
</tr>
</tbody>
</table>

and for a planar to homeotropic device, it is

$$D_4 = \frac{A_H}{A_p} = \frac{4 + 2S}{4 - S}.$$ (2.6)
For a discotic system, the particles’ orientational order parameter, $S$, is typically between $-1/2$ and 0 because the axes tend to be perpendicular to the director, and the corresponding device field responses are given in table 1. For the full derivation of the device field response for both the rods and platelets, see the electronic supplementary material, section S1.

It can be seen that the theoretical device field response for the rod case is very different from one, and does suggest that a high-contrast display could be made based on the reorientation of nanorods with a transition dipole along their axes. The disc case, with the transition dipole effectively distributed about the short axis, is unlikely to be of use for a display, but is useful to test the link between orientational order and optical properties.

3. X-ray scattering background

X-ray scattering methods have been used throughout this work to characterize the suspensions. Small-angle X-ray scattering is a well-established technique for determining the size, shape and state of aggregation of nanoparticles in suspensions [14–16]. For this work, it has also been used to measure the orientational order of the nanoparticles and their response to an applied electric field. Similar work has been previously carried out for gibbsite platelets in magnetic fields [17,18].

The method records the scattered intensity as a function of the scattering vector, $Q$. The aligning field is perpendicular to the X-ray beam, with the X-ray intensity recorded on a two-dimensional detector, as shown in figure 2. This effectively records a slice through reciprocal space.

(a) Scattering from discs

A dilute suspension of perfectly aligned discs would correspond to a rod in reciprocal space, and this appears as a streak parallel to the short axes of the discs, as shown in figure 3a. For a dilute, monodisperse suspension of particles, the variation of intensity with $Q$ is given by

$$I(Q) = \frac{N_p}{V} \Delta \rho^2 V_p^2 P(Q),$$

where $P(Q)$ is known as the particle form factor. The overall intensity is determined by the number of particles per unit volume, $N_p/V$, the scattering length density contrast, $\Delta \rho$, and the particle volume, $V_p$. The particle form factor determines the $Q$ dependence of the scattering. For discs, the form factor is given by

$$P(Q) = P(Q_{\parallel}, Q_{\perp}) = \left( \frac{2_1(Q_{\perp} R)}{Q_{\perp} R} \right)^2 \left( \frac{\sin(Q_{\parallel} T/2)}{Q_{\parallel} T/2} \right)^2,$$
Figure 3. Particle form factor for aligned disc-shaped nanoparticles of thickness 5 nm and radius 50 nm with their director horizontal: (a) perfect order with $S = 1$, (b) $S = 0.5$, (c) $S = -0.50$. (Online version in colour.)

Figure 4. Showing the angles $\alpha$ and $\beta$ used to define the orientation of a nanoparticle and the angle, $\phi$, used to define the direction of the scattering vector, $Q$, which remains in the $yz$ plane. (Online version in colour.)

where the components of $Q$ parallel and perpendicular to the cylindrical axis of the disc are $Q_{//} = Q \cos \psi$ and $Q_{\perp} = Q \sin \psi$, $\psi$ being the angle between the particle axis and $Q$. The $Q$ dependence perpendicular to the cylindrical axis is determined by the particle radius, $R$, in the Bessel function, and the $Q$ dependence parallel to the axis is determined by the particle thickness, $T$, in the sine-squared term [19]. Equally, this expressions hold for rod-shaped particles. It is often useful to use a Guinier approximation [20] for the scattering at low $Q$,

$$P(Q) = P(Q_{//}, Q_{\perp}) = \exp \left(-\frac{(Q_{\perp}R)^2}{4} - \frac{(Q_{//}T)^2}{12}\right).$$

(3.3)

This emphasizes the fact that the scattering is most intense for $Q_{\perp} < 2/R$ and $Q_{//} < \sqrt{12}/T$. This is seen directly in figure 3a, which was calculated from the evaluation of equation (3.2), which shows the form factor for disc-shaped nanoparticles that have their short axis parallel to the horizontal. The inverse where the platelets have the opposite orientation ($S = -1/2$) with the short dimensions vertical is shown in figure 3c. A useful guide is that the particle-form scattering will be most extended in $Q_{//}$ in the direction where the smallest particle dimension tends to lie.

If the particles are not perfectly aligned, but have a distribution of orientations, then the scattering becomes smeared out, tending to isotropic as the distribution becomes more uniform, as shown in figure 3b. This has been calculated by averaging $P(Q)$ over a distribution of orientations. The distribution of the particle orientations is defined in terms of the azimuthal and polar angles $(\alpha, \beta)$ of the particle axis relative to the horizontal (z) as shown in figure 4.
The distribution, \( f_0(\beta) \), has been assumed to be uniaxial (independent of \( \alpha \)),
\[
f_0(\beta) = Z^{-1} \exp(m \cos^2 \beta),
\]
(3.4)
where \( Z \) is a normalization constant, and the order parameter is determined by the orientational potential parameter, \( m \),
\[
S = \int_0^{\pi/2} f_0(\beta) \left( \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right) \sin \beta \, d\beta = \int_0^{\pi/2} \exp(m \cos^2 \beta) \left( \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right) \sin \beta \, d\beta.
\]
(3.5)
The intensity is then
\[
I(Q_x, Q_y) = \frac{Np}{V} \Delta \rho^2 V_P^2 \int f_0(\beta) P(Q//, Q\perp) \sin \beta \, d\beta \, d\alpha,
\]
(3.6)
where \( Q_x = Q \cos \phi \) and \( Q_y = Q \cos \phi \) and \( \phi \) is the angle between the \( Q \) vector and the horizontal \( (z) \) axis. The components of \( Q \) parallel and perpendicular to the particle axis are evaluated using the angle, \( \psi \), where
\[
\cos \psi = \sin \alpha \sin \beta + \cos \alpha \cos \beta \sin \phi,
\]
(3.7)
so \( Q// = Q \cos \psi \) and \( Q\perp = Q \sin \psi \). In isotropic suspensions, the orientational distribution function is a constant, and the scattering becomes isotropic. If the solution is dilute so that inter-particle interference effects are negligible, then the scattering can be used to determine particle size and shape. In the limit of low \( Q \), the scattering follows the Guinier law that may be used to determine their size in a model-free way. However, in this work, sufficiently, low \( Q \) was not attained; so the particle dimensions were determined by fitting equation (3.6) with \( f_0 = 1/(4\pi) \) and varying \( T \) and \( R \).

For a non-dilute suspension, it is necessary to account for inter-particle interference by introducing another factor into equation (3.1), the inter-particle structure factor, \( S(Q) \) [21]. For dilute suspensions, \( S(Q) \rightarrow 1 \). For suspensions with no local or long-range anisotropy, this factor can be related directly to the pair distribution of the particles [22]. For anisotropic suspensions, the relationship is more complex, even if they are unaligned, but a peak at a scattering vector value, \( Q_P \), would indicate the onset of short-range translational order with a tendency for particles to be separated by \( 2\pi/Q_P \),
\[
I(Q) = \frac{Np}{V} \Delta \rho^2 V_P^2 P(Q)S(Q).
\]
(3.8)
It can be seen that the structure factor can be determined experimentally by division of \( I(Q) \) by \( P(Q) \), which can be estimated from a dilute suspension where \( S(Q) \approx 1 \).

(b) Determining the orientational order parameter from particle-form scattering

The degree to which the scattering from the form of the particles in a suspension is smeared into an isotropic pattern can be used to determine the orientational order parameter. For large thin discs, perfectly aligned, the scattering would be very tightly confined to the \( Q_z \) axis, as shown in figure 3a. Any distribution of orientations would show as a smearing towards isotropic. The azimuthal distribution of intensity around a circle can be used to calculate an order parameter for the scattering,
\[
\bar{P}_{2,S} = \int_0^\pi f(\phi) \left( \frac{3}{2} \cos^2 \phi - \frac{1}{2} \right) \sin \phi \, d\phi,
\]
(3.9)
where \( f(\phi) \) is the normalized distribution of intensity around the circle. Because the distribution of intensity results directly from the distribution of platelet normals, the scattering order parameter is the same as the order parameter of the platelets,
\[
S = \bar{P}_{2,S}(\text{discs}).
\]
(3.10)
This is a special case of a more general relationship between the scattering order parameter and the order parameter of the particles for uniaxial systems [23]. The factor required is the \( \bar{P}_2 \) of the...
particle form factor at the $Q$ value of the circle used to calculate $\bar{P}_{2,S}$,

$$\bar{P}_{2,\text{FORM}}(Q, \phi) = \frac{\int_0^\pi (2J_1(QR \sin \phi)/QR \sin \phi)^2(\sin(QT \cos \phi/2)/QT \cos \phi/2)^2(\frac{3}{2} \cos^2 \phi - \frac{1}{2}) \sin \phi d\phi}{\int_0^\pi (2J_1(QR \sin \phi)/QR \sin \phi)^2(\sin(QT \cos \phi/2)/QT \cos \phi/2)^2 \sin \phi d\phi}. \quad (3.11)$$

The correction is made by division,

$$S = \frac{\bar{P}_{2,S}(Q)}{\bar{P}_{2,\text{FORM}}(Q, R, T)}. \quad (3.12)$$

For thin discs, $R \to \infty$ and $T \to 0$, $\bar{P}_{2,\text{FORM}}$ tends to a value of one, so the simple formulae given in equation (3.10) is recovered.

(c) Determining the orientational order parameter from Bragg scattering

If the particles have an internal crystalline structure, then the lattice planes may also be used to determine the orientational order parameter. The case where the lattice planes are at a general angle to the particle axis has been considered extensively in fibre diffraction [24]. Here, only one case is considered. If the lattice planes are perpendicular to the platelet normal axis, then the corresponding Bragg peak will occur when the scattering vector is parallel to the particle axis (i.e. $Q_\perp = 0$). In an aligned sample, the distribution of the Bragg peak around a circle will be the same as the orientational distribution of the particle axes. As for particle-form scattering from thin discs, the particle order parameter can be calculated from the distribution of Bragg intensity using equation (3.9).

(d) The influence of polydispersity on order parameter determination

The value of the orientational order parameter may be deduced from the particle-form scattering in addition to any Bragg scattering. In principle, these values would be the same for a perfectly monodisperse suspension. However, polydispersity of particle size can lead to a discrepancy between the experimental values because larger particles are expected to be better ordered with respect to the director, and the different experimental methods have different sensitivities to particle size.

To explore this effect, a polydisperse suspension of discs is considered. The discs all have the same aspect ratio, but have a distribution of thicknesses ($T$), and the larger particles are assumed to be better aligned with the director. This assumption is justifiable if the orientational part of the inter-particle interaction potential is greater for larger particles. The orientation distribution becomes a function of disc thickness,

$$f_0(\beta, T) = Z^{-1} \exp(m(T) \cos^2 \beta) \text{ with } m(T) = \frac{\bar{m}T}{T}. \quad (3.13)$$

The particle form scattering can then be evaluated using equation (3.6), but for simplicity, it is assumed that all the radii are large enough for the scattering to be confined to the $Q_\parallel$ axis, and that the Guinier approximation (equation (3.3)) has been used for the form factor. This gives the following distribution of intensity from the particle-form scattering (see the electronic supplementary material, section S2 for full derivation):

$$I_F(Q, \phi) \propto \int f_T(T) V_P(T)f_0(\phi, T)T \exp \left(\frac{-2(QT)^2}{12}\right) dT, \quad (3.14)$$

where $f_T(T)$ is the distribution of particle thicknesses.

It can be seen that at small $Q$ (i.e. $Q \ll 1/T$), the larger particles will contribute more to the average, but at high $Q$ (i.e. $Q \gg 1/T$), they contribute very little. Thus, an order parameter derived from a ring at high $Q$ will tend to be closer to zero, as illustrated in figure 5.
Figure 5. Showing the orientational order parameter calculated from the form and Bragg scattering from platelet particles with the same mean strength of the orientational potential (i.e. \( \bar{m} = -2 \)) but different polydispersity. They have Gaussian distributions of thickness, with a mean thickness of 10 nm and standard deviations of 1% or 20%. It can be seen that the analysis of the form scattering from the 20% sample would give a \( Q \)-dependent value for order parameter that could be much closer to zero than that deduced from the Bragg peak. The analysis of the Bragg scattering from the 20% sample gives a more negative value than the 1% because the larger, more ordered particles contribute more weight to the scattering. (Online version in colour.)

For a Bragg peak, the intensity is simply dependent on the particle volume. Other factors such as the crystal structure factor are constant, so the azimuthal dependence becomes

\[
I_B(Q, \varphi) \propto \int f_T(T) V_P(T) f_\theta(\phi, T) dT. \tag{3.15}
\]

Thus, the azimuthal intensity distribution of a Bragg peak and the orientational order parameter value derived from it are not influenced by the \( Q \) value.

The order parameter deduced from absorbance changes in a device field response measurement will also be an average over values for different size particles. As for the Bragg peak, the average is simply weighted by particle volume. So it is expected that the absorbance and the Bragg peak values of the orientation order parameter should agree in principle, but the values deduced from particle-form scattering may be closer to zero and \( Q \)-dependent if the dispersion is polydisperse.

4. Pigment particle suspensions

Three types of pigment particle supplied by Clariant (Frankfurt) have been studied. The details are summarized in table 2. The particles have the form of thin platelets whose dimensions (length, \( L \), and width, \( W \)) have been determined from transmission electron microscopy images. The thickness has been estimated using the Scherrer broadening of their Bragg peaks. The mean thickness (\( \bar{T} \)) and polydispersity (\( p \)) have been estimated by fitting the Bragg peak profile with the form expected from a distribution of the crystal thicknesses,

\[
I(Q//) \propto \int f_T(T, \bar{T}, p) \left( \frac{\sin Q//\bar{T}/2}{Q//\bar{T}/2} \right)^2 dT, \tag{4.1}
\]

where \( f_T(T, \bar{T}, p) \) has been taken to be the Shultz distribution.

During the pigment manufacturing process, it is known that the growth of the particles is arrested by the addition of resins or surfactants such as abietic acid for Permanent Rubine. However, they are commercial products, and there is limited information available on their
Table 2. Pigments investigated giving the trade name, colour index [25], molecular structure, dimensions (polydispersity) and transmission electron microscope images.

<table>
<thead>
<tr>
<th>Pigment Name</th>
<th>Molecular Structure</th>
<th>Dimension in nm and Polydispersity (s.d. as a percentage)</th>
<th>Transmission Electron Microscope Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanent Rubine L4B01 (Calcium 4B toner, CI)</td>
<td><img src="image" alt="Permanent Rubine L4B01" /></td>
<td>$L = 180$ (45%), $W = 64$ (35%), $T = 11.5$ (69%)</td>
<td><img src="image" alt="Image of Permanent Rubine L4B01" /></td>
</tr>
<tr>
<td>Pigment Red 57:1</td>
<td><img src="image" alt="Pigment Red 57:1" /></td>
<td></td>
<td><img src="image" alt="Image of Pigment Red 57:1" /></td>
</tr>
<tr>
<td>Novoperm Carmine HF3C, CI Pigment Red 176</td>
<td><img src="image" alt="Novoperm Carmine HF3C, CI Pigment Red 176" /></td>
<td>$L = 322$ (50%), $D = 63$ (34%), $T = 17.3$ (64%)</td>
<td><img src="image" alt="Image of Novoperm Carmine HF3C, CI Pigment Red 176" /></td>
</tr>
<tr>
<td>Graphtol Carmine HF4C, CI Pigment Red 185</td>
<td><img src="image" alt="Graphtol Carmine HF4C, CI Pigment Red 185" /></td>
<td>$L = 330$ (52%), $D = 66$ (37%), $T = 10.8$ (64%)</td>
<td><img src="image" alt="Image of Graphtol Carmine HF4C, CI Pigment Red 185" /></td>
</tr>
</tbody>
</table>
Figure 6. The 30 wt% suspension of Novoperm Carmine observed under an optical microscope with: (a) crossed polarizers and (b) one polarizer. Scale bars, 50 µm. (Online version in colour.)

manufacturing process [26,27]. The first surface and structural characterization of pigment red 57 : 1 was described by McKay [28–30], and recently the crystal structure has been reported in detail [31].

Suspensions of both Permanent Rubine and Novoperm Carmine have been previously examined in dodecane under applied electric fields as described in Eremin et al. [32] and Greasty et al. [33]. The suspensions in dodecane (Sigma-Aldrich) were prepared by milling the pigment particles with the stabilizer and solvent using a planetary bead mill (Fritsch Pulverisette 7 premium line) with 0.5 mm yttria-stabilized zirconia beads in zirconia lined pots at 600 r.p.m. for 30 min. This was repeated three times, with appropriate cooling cycles to prevent over-heating inside the pots. The polymeric stabilizer, Solsperse 11200 (Lubrizol, Brussels, Belgium), which is 50 wt% active was used as received. The polymer is a polyethyleneimine with poly(carbonyl-C_{3−6}-alkyleneoxy) side chains as disclosed in US patent no. 4645611 [34]. This stabilizer was pre-dissolved in the suspension medium at 29 wt% of the particle weight, before the addition of the particles. The particle suspensions were milled at 30 wt%, and a dilution series was prepared from these stock solutions. The choice of 29 wt% of stabilizer to particle was made based on the variation of hydrodynamic radius of the particles with stabilizer wt%. This was determined using a Malvern Nano Zetasizer on dilute (1 × 10^{-5} wt%) suspensions that had been sonicated for 30 min to break up any flocs.

Suspensions of the three different pigments all showed Schlieren textures at high particle concentrations when observed between crossed polarizers (figure 6a). The onsets of Schlieren patterns were at 25 wt% for Permanent Rubine and Novoperm Carmine, but at 30 wt% for Graphtol Carmine. Because the particles are dichroic, Schlieren textures can be observed with just one polarizer (figure 6b).

Pigment particles were also prepared for transfer into nematic hosts. A range of short-chain molecules were chosen to mimic the nematic host molecules and explore the influence of the stabilizer–nematic interaction. Three examples are 4-n-pentylbiphenyl-4′-carboxylic acid (ST474), trans-4-(4-n-pentylcyclohexyl) benzoic acid (ST2762) purchased from Synthone Chemicals GmbH & Co. KG and P-xylene-2-sulfonic acid (PX2SA) purchased from Sigma-Aldrich. They all have molecular structure with some similar features to the liquid crystal hosts but with the cyano head group exchanged for an acid head group such as a carboxylic acid. For a liquid crystalline host, the preparation procedure was different. The stabilizer was dissolved in 50/50 wt% benzyl alcohol/toluene solvent mixture at 9 wt% to particle. The pigments were dispersed in the same solvent mixture but in a separate vial. The dissolved stabilizer was added to the particles and sonicated. The particles were centrifuged out and washed several times in ethanol before being re-dispersed in cyclohexane and then transferred into the liquid crystal host; the cyclohexane evaporated off, leaving particle concentrations of 0.5–5 wt%. These nematic suspensions were sonicated for 1 h before testing. This procedure was chosen to avoid the issue of the solubility of the mesogenic stabilizers in solution. The amount of stabilizer remaining on the particle surface after this transfer process was not determined experimentally because of the similarities between the stabilizer, nematic solvent and pigment particles. However, as a control, unmodified particles
were added directly to the nematic hosts, again followed by sonication for 1 h. Differences in response were observed, suggesting the stabilizer has absorbed to some extent.

Three liquid crystal hosts were purchased and used as received. The first one is 5CB (Synthon), which consists of a single component of 4-cyano-4′-pentylbiphenyl. The second host is E7 (Synthon), which consists of four components: 50 per cent 4-cyano-4′-n-pentylbiphenyl (5CB), 25 per cent 4-cyano-4′-n-heptyl-biphenyl (7CB), 16 per cent 4-cyano-4′-n-octyloxy-biphenyl (8OCB) and 8 per cent 4-cyano-4′-n-pentyl-p-terphenyl (5CT). The third host, ZLI2293, was a proprietary mixture from Merck Chemicals, although it is thought that one component may be trans-4-(4′-n-pentylcyclohexyl)benzonitrile [35].

5. Electro-optical response

The cells used to measure absorbance were anti-parallel planar aligned cells and were either purchased (Instec, USA and E.H.C., Japan) or handmade. The cells constructed were made from two glass substrates that had been sputtered with a transparent conducting layer of indium tin oxide (ITO), which allowed the application of the applied electric field perpendicular to the substrate surface. Each cell was first spun coated with an insulating layer of 20 wt% Su8 2010 resin (Microchem), which was fully cured before alignment layers were added by spin coating a polyimide (SE-130, Nissan Chem. Ind.) solution onto the ITO side of the substrates, then baking at 180°C for 1 h. The polyimide layer was then rubbed in the preferred direction, giving a 2° tilt angle. The cells were then assembled and glued in anti-parallel geometry using UV-curable epoxy glue with appropriate spacers ranging from 5 to 50 µm thick.

For each pigment, optical micrographs of the cells were recorded with different fields, and frequencies applied with varying combinations of polarizer and analyser. For the suspensions in dodecane, these appeared reasonably homogeneous with no field or with a high-frequency field (greater than or equal to 1 kHz; figure 7a,b), but heterogeneous patterns were induced when lower frequencies were applied. This is demonstrated in figure 7c for Permanent Rubine, which shows the presence of induced phase separation. Similar observations of suspensions in nematic hosts clearly showed the presence of aggregates and that the suspensions were not homogeneous with or without the pre-treatment with stabilizer. This demonstrates that the steric nature of the stabilizers was ineffective in preventing aggregation or the coverage was insufficient in the nematic host. The degree of aggregation became greater after the application of a field, suggesting that the field-induced flow of the liquid crystal during switching enhanced aggregation, as shown in figure 7e.
Figure 8. (a) The visible absorption spectrum for a 5 wt% suspension of Permanent Rubine with and without the application of a field at 1 kHz. (b) The normalized integrated absorbance as a function of applied electric field. (Online version in colour.)

However, the presence of aggregates and the occurrence of electro-induced aggregation were less pronounced for the Novoperm Carmine and the Graphtol Carmine particles in the nematic host (see the electronic supplementary material, section S3). Electro-optic effects were measured using an integrating sphere set-up that was used to determine the absorbance of light through suspension filled cells as a function of applied field. An integrating sphere was used to ensure any forward scattered light was detected. Figure 8a shows the decrease in the absorbance for Permanent Rubine in dodecane when it was ‘switched’ by the application of a field of amplitude 2 V µm⁻¹ and frequency of 1 kHz. Figure 8b shows the integrated absorbance as a function of increasing applied field in increments of 0.5 V µm⁻¹ for varying frequency. The alternating field was applied for 1 s prior to a measurement, it was then removed for a further second before increasing the amplitude and repeating the absorbance measurement. The absorbance has been normalized to the absorbance intensity with zero field applied. The observed switching was found to be reproducible over multiple field switching sweeps (greater than or equal to 1 kHz) in dodecane.

It can be seen that the effect of the field is gradual and has not saturated, suggesting that the orientational order parameter has changed, but has not reached its minimum value. The 9 per cent drop in the absorbance at 2 V µm⁻¹ suggests the transition dipole is, on average, becoming more parallel to the applied field. At lower frequencies (0.1 kHz), the absorbance begins to plateau, this can be explained by the onset of electro-hydrodynamic convection-inducing phase separation, as observed in figure 7c.

A smaller decrease in absorbance (3%) was found for Novoperm Carmine (figure 9a) in dodecane compared with Permanent Rubine at 1 kHz. Graphtol Carmine showed a similar drop in absorbance (9%) comparable to that of Permanent Rubine at 1 kHz and above (figure 9b). At low frequencies (0.1 kHz), there is a strong decrease in absorbance for both pigments. This decrease can again be explained by electro-hydrodynamic convection.

On their first switch, the suspensions in nematic hosts showed a much sharper transition at a lower field, remaining constant after 0.3 V µm⁻¹, with the absorbance dropping by 20–30%. This suggests a higher degree of alignment parallel to the electric field component of the incident light than in dodecane (figure 10a). There is also a greater reduction in absorbance with the stabilizer pre-treatment compared with without, and this was consistent for all three liquid crystal hosts. This may be due to different anchoring of the host director on the particles or due to
**Figure 9.** The visible normalized integrated absorbance spectrum as a function of applied electric field for: (a) 10 wt% suspension of Novoperm Carmine and (b) 5 wt% suspension of Graphtol Carmine in dodecane. (Online version in colour.)

**Figure 10.** The 0.5 wt% Permanent Rubine in SCB. (a) Normalized integrated absorbance as a function of the applied electric field at 1 kHz with and without stabilizer. (b) Absorbance as a function of applied electric field for multiple switches with stabilizer ST474. (Online version in colour.)

better dispersion of the particles. However, repeated switching causes an irreversible drop of absorbance, possibly because of induced defect binding [36,37] causing aggregation, as shown in figure 7e.

In the nematic hosts, Graphtol Carmine demonstrates a sharper transition than in dodecane (figure 11). The drop in absorbance is of similar magnitude to that of Permanent Rubine in nematic hosts, but the switch is not as sharp.

In contrast, in the nematic hosts, Novoperm Carmine shows an increase in absorbance with the application of the applied field (figure 12a), suggesting the transition dipole is becoming less parallel to the applied field. The particles without stabilizer pre-treatment were reasonably
Figure 11. The absorbance of 1 wt% Graphtol Carmine in liquid crystal with and without stabilizer as a function of applied electric field at 1 kHz. (Online version in colour.)

Figure 12. (a) The absorbance of 1 wt% Novoperm Carmine in liquid crystal with and without stabilizer as a function of the applied electric field at 1 kHz. (b) Absorbance as a function of applied electric field at 1 kHz for multiple switches without stabilizer. (Online version in colour.)

stable in the 5CB host, and the suspensions of Novoperm Carmine show only a small change in behaviour after repeated switching sweeps, suggesting this pigment has some degree of stability in the nematic host with and without stabilizer (figure 12b). A similar degree of stability was also observed for Graphtol Carmine in the nematic host.

6. The structure of pigment particle suspensions

(a) Internal particle structure of Permanent Rubine

The orientation of the Bragg planes within the particles of Permanent Rubine has been confirmed directly by transmission electron microscopy. Bright field images were obtained using a Philips
The structure of the particles is readily damaged by the electron beam and therefore, to obtain images of the fringes, the sample area of interest must not be exposed to the beam for more than a few seconds. To avoid beam damage, an image was brought into focus prior to moving the sample to an area of interest and taking an image. Figure 13 shows the lattice planes (corresponding to $Q = 0.35 \text{ Å}^{-1}$) are parallel to the faces of the platelets and will provide information on directional ordering of the platelet normals.

(b) Internal structure of Novoperm and Graphtol Carmine

In these cases, images showing the planes were not achieved. However, it was possible to record electron diffraction from single particles, as shown in figure 14a for Novoperm Carmine. The scattering vector for these Bragg peaks is $Q = 1.28 \text{ Å}^{-1}$, and by comparing with figure 14b, they must be produced by lattice planes perpendicular to the platelets’ long dimension. X-ray diffraction from a suspension (shown in figure 14c) shows this Bragg peak is parallel to the field. The peak at $Q = 0.28 \text{ Å}^{-1}$ is strongest in a perpendicular direction to the peak at $Q = 1.28 \text{ Å}^{-1}$. It can therefore be concluded that the Bragg peak of 0.28 Å⁻¹ is parallel to one of the shorter dimensions of the platelet. The Scherrer broadening of this peak gives a dimension of 17.3 nm, which indicates that the Bragg peak is parallel to the platelet normal. The Bragg peak at $Q = 0.54 \text{ Å}^{-1}$ also has the same orientation and Scherrer broadening. Both peaks have therefore been used to extract the order parameter of the platelet normals directly.

A similar procedure was used to establish that the 0.75 Å⁻¹ Bragg peak from Graphtol Carmine is parallel to the platelets’ normal, and the thickness was determined through Sherrer broadening and found to be 10.8 nm.

7. Particle dimensions and translational ordering from X-ray scattering

The scattering data from unaligned suspensions of Permanent Rubine in dodecane were processed to subtract both the instrumental and solvent backgrounds. The data were then regrouped to give intensity as a function of $Q$, both on logarithmic scales. The initial slope of the log–log plot was between $-2$ and $-3$, suggesting platelet-shaped particles. Although the slope becomes more negative at higher $Q$, it is not possible to identify a point where it changes to $-4$, suggesting a high degree of polydispersity. The inter-particle structure factor has been estimated
Figure 14. (a) Single particle electron diffraction taken from the same particle as in (b) showing Bragg spots at \( Q = 1.28 \, \text{Å}^{-1} \). (b) Transmission electron micrograph of the single Novoperm Carmine particle used for diffraction. (c) Wide angle X-ray scattering pattern showing the orientation of 1.28 and 0.28 \( \text{Å}^{-1} \) peaks relative to the applied field. (Online version in colour.)

Figure 15. The inter-particle structure factor for Permanent Rubine in dodecane calculated as described in the text. The structure factor has been normalized such that at high \( Q \), \( S(Q) \) tends to 1. (Online version in colour.)

by dividing the intensity from the more concentrated suspensions by that of a 1 wt% suspension, taking account of the different numbers of particles. It was found that even at 5 wt%, \( S(Q) \) was constant and equal to one. Therefore, it is justifiable to interpret the intensity for 5 wt% and less in terms of a dilute system (equations (3.1)–(3.3)) (figure 15).

At higher concentrations (25 wt% and above), a clear peak develops in the structure factor. With increasing concentration, the peak increases in \( Q \), suggesting the onset of short-range translational order, consistent with a nematic phase. The peak corresponds to about 24 nm, which suggests a face-to-face approach of the platelets (11.5 nm thick) and a typical solvent gap of 12.5 nm. A similar procedure has been used to determine the structure factor of Novoperm Carmine and Graphtol Carmine suspensions that were found to be broadly similar to the Permanent Rubine.
The scattering from the 1 wt% suspension of Permanent Rubine in dodecane was fitted by that expected from discs at random orientations by varying the radius and thickness parameters (equations (3.1) and (3.6)). The fit quality was found to be insensitive to the disc radius, but it was assumed to be 100 nm, a thickness of 9.6 nm with a polydispersity of 61 per cent was determined, this supports the value deduced from the Scherrer broadening of the Bragg peak (figure 16).

**Figure 16.** The points are the intensity from 1 wt% suspension of Rubine in dodecane. The fit is for a large disc of thickness 9.6 nm with a polydispersity of 61%, calculated using equation (3.2), averaged over an isotropic distribution. (Online version in colour.)

### 8. Order parameter determination

Samples ranging from 1 to 35 wt% of particle were sonicated for 30 min before being filled into 1.5 mm diameter glass tubes. A monochromatic X-ray beam was incident onto the sample, and scattering patterns were measured on a two-dimensional detector. Insulated brass electrodes were held in place either side of the sample such that a horizontal electric field, ranging in amplitude from 0 to 2.13 V μm$^{-1}$, could be applied perpendicular to the incident beam. The frequency was generally 1 kHz or above to avoid the turbulence-induced aggregation described in §5. The schematic shown in figure 2 demonstrates the applied electric field direction relative to the incident beam and two-dimensional detector.

The X-ray measurements were carried out using two camera lengths at both the European Radiation Synchrotron Facility (Beamline BM02) and the Diamond light Source (I22 Beamline). The short camera length was used to collect Bragg diffraction peaks at wide angles from the internal crystal planes of the particles. The longer camera length was used to collect the particle-form scattering at smaller angles. The diffraction patterns for each technique are initially isotropically distributed because the particles are randomly orientated. As the electric field is applied, the particles orientate and so do the lattice planes, thus the Debye–Scherrer ring from the Bragg peaks and the particle-form scattering become anisotropic.

The orientational order parameter of the particles has been determined in two ways. The first uses the Bragg peaks arising from the internal crystal planes that are parallel to the platelet faces. The Bragg intensity has been extracted from the scattering data by defining an array of bins, centred on the Debye–Scherrer ring. The Bragg intensity in each bin is calculated by summation
The extraction of the azimuthal angular variation of the intensity of a Bragg peak from a suspension of 25 wt% Permanent Rubine in dodecane with the accompanying two-dimensional scattering plot, including data bins at: (a) 0 V µm\(^{-1}\) and (b) 2 V µm\(^{-1}\) at 1 kHz. (Online version in colour.)

with a background estimated from similar arrays of bins just inside and outside the Debye–Scherrer ring, as illustrated in figure 17. The distribution of Bragg intensity was then used to determine the orientational order parameter of the Bragg scattering, \(\bar{P}_{2,BS}\), using equation (3.9).

The second approach is to use the particle-form scattering. In this case, the intensity variation around several rings at different \(Q\) values was determined. The background was estimated from a part of the scattering image at high \(Q\) that was free of features. After background subtraction, the orientational order parameter of the particle-form scattering, \(\bar{P}_{2,FS}(Q)\), was calculated using equation (3.9).

(a) Orientational order of pigment particle suspensions in dodecane

Figure 18a,b shows the scattering at two camera lengths from suspensions of Permanent Rubine in dodecane under a horizontal electric field. The particle-form scattering at low \(Q\) indicates that the smallest dimension of the particles (i.e. their thickness) tends to be perpendicular to the field. The Bragg peaks at \(Q = 0.35\) Å\(^{-1}\), corresponding to a layer spacing of 1.8 nm as imaged directly in figure 13, also indicate that the platelet normals tend to be perpendicular to the field. The broadening of the diffraction peak at \(Q = 0.35\) Å\(^{-1}\) has been used to determine the thickness given in table 2. Analogous alignment was observed for both the Novoperm and Graphtol Carmine, using the lattice plane spacings of 0.54 and 0.61 Å\(^{-1}\), respectively. The schematic of figure 18c summarizes the particle orientation qualitatively. The scattering order
Figure 18. Scattering plots of log(intensity) as a function of $Q$ at 2 V $\mu$m$^{-1}$ with a frequency of 1 kHz for 25 wt% Permanent Rubine in dodecane. (a) Bragg peak for Rubine at 0.35 Å$^{-1}$. (b) Particle-form scatter. (c) Schematic of field-induced orientational ordering in dodecane. (Online version in colour.)

Figure 19. Variation of particle-form scattering order parameter with $Q$ for 5 wt% Permanent Rubine in dodecane and the fit to the data using equation (3.14). The best-fit parameters are for platelets of mean thickness 12 nm, with a Gaussian distribution of 37% (s.d. as a percentage) and orientational energy parameter, $\bar{m} = -0.68$. The volume-weighted order parameter that would be indicated by the Bragg peak is overlaid for reference. (Online version in colour.)

parameters, $\bar{P}_{2,FS}$, calculated from the particle-form scattering are strongly $Q$-dependent, as shown in figure 19.

The $Q$ dependence is much greater than expected from the form factor for a typical particle calculated using equation (3.11). The predominant cause is believed to be the polydispersity in particle thickness. The relationship of this polydispersity with the particles’ order parameter is complex for the reasons given in §3d and demonstrated in figure 19, so it has not been used quantitatively. The model fit in figure 19 suggests a $Q$ variation consistent with a 37 per cent polydispersity of thickness. This variation in the particle-form scattering with $Q$ was similar for both Novoperm and Graphtol Carmine.

The scattering order parameter values calculated, $\bar{P}_{2,BS}$, from the Bragg peak are shown in figure 20a. Because these Bragg peaks indicate the platelet normals, $\bar{P}_{2,BS}$ is identical to the particle order parameter (equation (3.10)). At all concentrations, each of the pigments showed a monotonic response to the applied field. Figure 20a shows an example of the order parameter response for each of the suspensions at 10 wt% with applied field. The order parameter in each
case becomes more negative with no threshold field observed. The variation with concentration of the order parameter at 1.5 V µm\(^{-1}\) is plotted in figure 20b for Permanent Rubine and at 2 V µm\(^{-1}\) for Novoperm and Graphtol Carmine. It shows that, initially, the order parameter becomes less negative with increasing concentration up to 20 wt% for Permanent Rubine and Novoperm Carmine. However, at 25 wt%, the order parameter suddenly becomes more negative. This increase at 25 wt% also marks the onset of the observed Schlieren textures and the clear peak in the structure factor, suggesting the formation of the nematic phase. However, the order parameter returns towards zero at higher concentrations, which may be the result of the increase in viscosity for the more concentrated suspensions. This is supported by the observation that the 35 wt% sample of Permanent Rubine was initially flow aligned during the filling of the capillary and showed the smallest response to the applied field. In addition, the high viscosity of the Novoperm Carmine suspensions at 30 wt% and above prevented them being filled into the 1.5 mm sample cells. In a similar manner, Graphtol Carmine suspensions show an increase in order parameter with increasing concentration up to 25 wt%, above which there is a sharp decrease in order parameter. This is again consistent with the observed onset of Schlieren textures at 30 wt% by optical microscopy.

(i) Orientational order of pigment particles in the liquid crystal host

In the nematic host, both Permanent Rubine and Graphtol Carmine show strong orientational ordering, again, with their platelet normals aligning perpendicular to the applied field, as shown by the example in figure 21 of Permanent Rubine with ST474 in 5CB. Figure 21b shows the particle-form scattering becoming strongly anisotropic perpendicular to the applied field direction. Examining the Bragg peak at \(Q = 0.35 \text{ Å}^{-1}\) also indicates a high degree of ordering, giving rise to two sharp maxima suggestive of near perfect orientational ordering. Figure 21a also shows additional peaks at 0.26 Å\(^{-1}\) owing to the 2.4 nm end-to-end distance of the 5CB dimer. This confirms that the nematic host director is horizontal, parallel to the applied field as expected. Figure 21c shows a schematic demonstrating the relative orientation of the nematic host director and the platelet normals.
applied electric field (V μm$^{-1}$)

Figure 21. Scattering plots of log(intensity) as a function of $Q$ at 2 V μm$^{-1}$ with a frequency of 1 kHz. 5 wt% Permanent Rubine with ST474 stabilizer showing: (a) Bragg peak for Rubine at 0.35 Å$^{-1}$ and nematic peak from 5CB at 0.26 Å$^{-1}$; (b) particle-form scatter; (c) schematic of field-induced orientational ordering in 5CB. 1 wt% Novoperm Carmine with ST474 stabilizer showing: (d) Bragg peak for Novoperm at 0.54 Å$^{-1}$ and nematic peak from 5CB at 0.26 Å$^{-1}$; (e) particle-form scattering; (f) schematic of field-induced orientational ordering in 5CB. (Online version in colour.)

Figure 22. Bragg order parameter as a function of applied field at 1 kHz for: (a) 5 wt% of Permanent Rubine with stabilizer ST474 in ZLI2293 and 1 wt% Graphtol Carmine with PX2SA in E7 and (b) 1 wt% Novoperm Carmine with PX2SA in 5CB and with ST2762 in ZLI2293. (Online version in colour.)

Figure 21d,e shows the orientational ordering of Novoperm Carmine with ST474 in 5CB. The scattering plots from both the particle-form scattering and Bragg peak align parallel to the applied field. This demonstrates that the particles have a strong tendency for the short dimension to align parallel to the applied field and the internal planes tending to align perpendicular to it. The
Table 3. A summary table comparing the Bragg orientational order parameter with both the calculated and measured device field response.

<table>
<thead>
<tr>
<th>pigment suspension</th>
<th>sample</th>
<th>X-ray orientational order parameter</th>
<th>calculated device field response</th>
<th>measured device field response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanent Rubine</td>
<td>5 wt% in dodecane</td>
<td>−0.27 ± 0.01</td>
<td>0.87 ± 0.01</td>
<td>0.91 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>5 wt% + ST474 in ZLI2293</td>
<td>0.48 ± 0.01</td>
<td>0.67 ± 0.01</td>
<td>0.73 ± 0.01</td>
</tr>
<tr>
<td>Novoperm Carmine</td>
<td>10 wt% in dodecane</td>
<td>−0.07 ± 0.01</td>
<td>0.97 ± 0.01</td>
<td>0.97 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>1 wt% + ST2762 in ZLI2293</td>
<td>0.85 ± 0.26</td>
<td>1.81 ± 0.63</td>
<td>1.38 ± 0.01</td>
</tr>
<tr>
<td>Graphtol Carmine</td>
<td>5 wt% in dodecane</td>
<td>−0.21 ± 0.01</td>
<td>0.90 ± 0.01</td>
<td>0.91 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>1 wt% + ST474 in ZLI2293</td>
<td>−0.35 ± 0.04</td>
<td>0.76 ± 0.05</td>
<td>0.77 ± 0.03</td>
</tr>
</tbody>
</table>

The nematic host director still aligns in the same direction parallel to the applied field. Therefore, the platelet normals align parallel to the nematic director and the applied electric field, as portrayed qualitatively in figure 21f.

Figure 22a shows that both Permanent Rubine and Graphtol Carmine have a much higher order parameter in the nematic host than in dodecane, approaching −0.5. This is the theoretical minimum, indicating a very high degree of alignment of the particles’ planes. It should also be noted that some of the samples were significantly pre-aligned while measuring the particle-form scattering and have not unaligned prior to the wider angle measurements.

As discussed, Novoperm Carmine particles in the nematic host show the opposite orientational ordering to that found in dodecane with order parameters tending to one (figure 22b). They have a high degree of orientational order with the platelet normals tending to be parallel to the host director.

9. Comparison between X-ray order parameters and the device field response

The expected device field response for suspensions in dodecane has been estimated using the material order parameters measured by Bragg scattering. For concentrations below the nematic phase, a random to homeotropic switch is assumed, so equation (2.5) is used to estimate the device response from the Bragg order parameters for an applied field of 2 V µm⁻¹. These values are compared with the measured responses in table 3.

For the suspensions in liquid crystal hosts, a planar to homeotropic switch is assumed, so equation (2.6) has been used. It can be seen in table 3 that there is a strong correlation between the predicted device field response determined from equations (2.5) and (2.6), using the Bragg order parameter and the measured device field response.

10. Discussion

It has been demonstrated that substantial orientational order can be imposed on a suspension of anisotropic pigment particles. This has been measured by two X-ray scattering methods. It was found that the response of the particle-form scattering to an applied field was a useful indicator of the polydispersity of the particles size, but could give only qualitative results for the order parameter. However, the Bragg scattering from internal planes gave accurate values of the volume-weighted order parameter. When these order parameter values were input into a simple model for the optical response of the suspensions to a high-frequency electric field, the predicted changes in absorbance were very close to those observed. This supports the model of anisotropic particles being reoriented by the field and suggests that it could be developed into a viable display technology.
The suspensions in dodecane of all three pigments showed a concentration dependence of their properties that suggested a nematic was forming at about 25–30 wt%. The onset of a Schlieren texture, the changes in the effective structure factor, $S(Q)$, and the increase in the field-induced orientational order all support this conclusion. At lower concentrations, the ordering generally decreased with concentration, suggesting that an aspect of the inter-particle interactions opposes the field-induced ordering. Further investigation of this point is required because it suggests there is an influence that is antagonistic to the formation of a well-ordered nematic phase. As the electric field was increased, no threshold was observed, as might be expected from a Fredericks transition. This suggests that even in the nematic, the main effect of the field is to increase the orientational order parameter of the particles in the material rather than simply reorient the directors.

The suspensions in liquid crystal hosts did show much higher degrees of order, and a threshold was observed with increasing field in Permanent Rubine. It was probably not seen in the Carmines because the samples had been previously aligned and had retained their director orientation within the sample tube. This suggests that the particles are anchored to the host director, and that the field effect is mostly a reorientation of the host director. In the samples that have been studied, the Permanent Rubine and Graphtol Carmine both aligned with the host director parallel to the larger face of the platelet, whereas for Novoperm Carmine, it was perpendicular. This could be rationalized by assuming different surface–director interactions. For instance, it might be that the first two have surfaces that induce planar anchoring, whereas the stabilizer on Novoperm Carmine was better for promoting homeotropic anchoring. The suspensions in nematic hosts also degraded on repeated switching, which indicates inadequate stabilization. It is clear that the stabilization of particles in nematic hosts requires further investigation.

The principle that suspensions of anisotropic pigment particles show an electro-optic response has been demonstrated for platelet-shaped particles. Furthermore, by the addition of the particles into a liquid crystal host, an extremely high degree of orientational order can be achieved. However, several improvements must be made before a material suitable for applications is developed. To achieve a high contrast between two aligned states, the estimates in §2 indicate that rod-shaped particles with longitudinal transition dipoles would be very much superior. The polydispersity of the particle size has a negative impact on the order parameter, particularly for suspensions in non-mesogenic hosts such as dodecane where the smaller particles have a weaker response to the field. However, this seems less important for nematic hosts, possibly because nearly all the particles are well anchored to the director. It is clearly desirable to investigate the effects of polydispersity in more detail. Nevertheless, we have shown that there is a potential to develop a material that would allow the strong absorbance of pigment particles to be electrically switched between absorbing and transparent states for un-polarized light.

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