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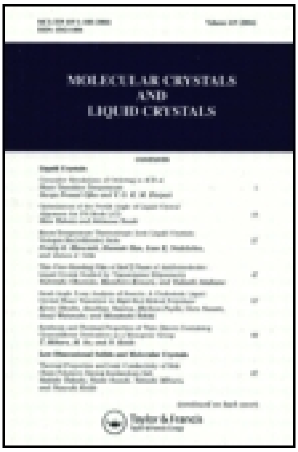

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Influence of TiO_2 Nanoparticle Doping on the Splay and Bend Elastic Constants of the Nematic Liquid Crystal 4′-butyl-4-heptyl-bicyclohexyl-4- carbononitrile, CCN47

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Influence of TiO_2 Nanoparticle Doping on the Splay and Bend Elastic Constants of the Nematic Liquid Crystal 4′-butyl-4-heptyl-bicyclohexyl-4-carbononitrile, CCN47

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Measurements are reported of the splay and bend elastic constants, and the Freédericksz threshold voltages of the nematic liquid crystal 4′-butyl-4-heptyl-bicyclohexyl-4-carbononitrile (CCN47) doped with low concentrations of titanium dioxide (TiO_2) nanoparticles. No measurable impact was found on elastic properties at frequencies of a few kilohertz, in contrast to literature reports of substantial threshold voltage changes observed for nematics subject to low (Hz) frequency applied electric fields. The results support the view that such effects are likely due to ionic influences rather than changes to elastic properties.

Keywords Elastic constant measurement; nanoparticle; nematic liquid crystal; TiO_2

1. Introduction

In recent years, there has been growth of interest in the effects of doping nanoparticles into liquid crystals. Among a wide array of nanoparticle species investigated, several authors [1–3] have studied the impact of low concentrations (typically 0.01 wt%–2.0 wt%) of insulating nanoparticles, such as ZnO, TiO_2, and Si_3N_4 on the properties of nematic hosts. Doping with insulating nanoparticles has been observed to induce a variety of valuable effects including improvements in voltage-holding ratio, a reduction in transient electrical currents associated with the movement of ionic impurities in devices, and a reduction in the Freédericksz threshold voltage for liquid crystal director switching. Doping with titanium dioxide (also commonly termed titania) nanoparticles at levels of only 0.05 wt% was found [1] to reduce the Freédericksz threshold voltage of the host nematic by around 10% when addressing sample cells with pseudo-DC ($<$1 Hz) voltages. Somewhat similar results have been found for low molar mass nematics doped with low concentrations of carbon nanotubes [4]. A "gettering-like" process was proposed to account for these observations, with the nanoparticle dopant acting as a trap for ionic impurities that would be normally be freely mobile within in the liquid crystal.

As well as being of scientific interest, changes in the electrical switching characteristics of liquid crystals may have practical applications for devices. In applications such as flat panel displays, the liquid crystal acts as the dielectric in a parallel plate capacitor.

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The energy associated with charging and discharging this capacitance scales typically as voltage-squared, and a reduction in threshold voltage therefore implies the possibility of power saving. The very low ($\ll$1%) nanoparticle concentration at which effects have been observed further holds out the possibility that nanoparticle doping may be a low cost approach to material improvements and make it interesting to seek a fuller understanding of the physical mechanisms at work.

The studies above, where a significant change to the Freédericksz voltage has been observed, have typically used low frequencies ($<$1 Hz). In several practical applications however, liquid crystals may be addressed using higher frequency (typically kHz) alternating voltages, and in a manner that ensures the sample experiences no net DC voltage over an extended time period. In the present work therefore, the investigation focused on the impact of TiO_2 nanoparticle doping on the static material properties of a liquid crystal under application of such (kHz) voltages. Specifically, we report accurate measurements of the Freédericksz threshold voltage and the splay (K11) and bend (K33) elastic constants of a negative dielectric anisotropy nematic material, 4′-butyl-4-heptyl-bicyclohexyl-4-carbononitrile (CCN47, supplied by Merck Chemicals Ltd., Southampton, UK), doped with low ($\leq$0.5 wt%) concentrations of TiO_2 nanoparticles. Under these conditions, no measurable impact was found of TiO_2 doping on static elastic properties. These results suggest that doping at low concentrations may have little impact for the order parameter of the host nematic and support the conclusions in [1,2] that the majority effects of TiO_2 doping occur at low frequencies as a consequence of changes to the population and mobility of ionic contaminants present within the liquid crystal.

2. Background and Experimental

An untwisted, negative dielectric anisotropy nematic liquid crystal confined between parallel plates, with the director constrained to lie normal at the plates, and with an electric field applied perpendicular to these surfaces, undergoes a transition at a critical Freédericksz voltage (V_{th}) when the applied voltage is increased from zero. At the critical voltage, the director at the cell center begins to tilt away from its initial (zero volt) position. The Freédericksz threshold is given explicitly by

$$V_{th} = \pi \left(\frac{\mathrm{K33}}{\varepsilon_0 \Delta\varepsilon} \right)^{1/2} \tag{1}$$

where ε_0 is the permittivity of free space, $\Delta\varepsilon = (\varepsilon_\perp - \varepsilon_{//})$ is the dielectric anisotropy of the material, and K33 is an elastic constant for director bend distortions.

Equation (1) holds for a homeotropically aligned, negative $\Delta\varepsilon$ material. For a planar aligned, positive dielectric material, Equation (1) still holds with K33 replaced by the bend elastic constant K11. Experimentally, a measurement of $\Delta\varepsilon$ and V_{th} yields a value for K33 via Equation (1).

A value for the splay elastic constant K11 of a nematic can also be determined from measurements of sample capacitance [5,6]. In brief, the approach is to measure the capacitance, C, at a range of voltages, V, above the Freedericksz voltage V_{th}. It can then be shown [7] that the variation of capacitance with voltage conforms to Equations (2) and (3) where $\kappa = \mathrm{K11/K33}$ is the elastic constant anisotropy of the liquid crystal, $\gamma = (\varepsilon_\perp - \varepsilon_{//})/\varepsilon_\perp$ is the normalized dielectric anisotropy, and C_0 is the empty cell capacitance.

$$\frac{C_0}{C} = \frac{\int_0^{\theta_m} \left[\frac{[1+\kappa \sin \sin^2 \theta]}{(1+\gamma \sin^2 \theta)(\sin^2 \theta_m - \sin^2 \theta)} \right]^{1/2} d\theta}{\int_0^{\theta_m} \left[\frac{(1+\gamma \sin^2 \theta)(1+\kappa \sin^2 \theta)}{\sin^2 \theta_m - \sin^2 \theta} \right]^{1/2} d\theta}, \tag{2}$$

$$\frac{V}{V_c} = \frac{2}{\pi}(1+\gamma \sin^2 \theta_m)^{1/2} \int_0^{\theta_m} \left[\frac{[1+\kappa \sin \sin^2 \theta]}{(1+\gamma \sin^2 \theta)(\sin^2 \theta_m - \sin^2 \theta)} \right]^{1/2} d\theta. \tag{3}$$

Experimentally, with K33, γ, and C_0 known, K11 can be determined from a numerical fit of C versus V data to Equations (2) and (3). (θ_m is the tilt of the liquid crystal director at the cell center determined numerically during the fitting procedure.)

To obtain accurate measurements of capacitance, sample cells were constructed from indium tin oxide coated glass, spaced 25 μm apart using hard-tempered aluminum foil (Goodfellow, Cambridge). Homeotropic alignment was achieved by spin coating the alignment layer JALS2017 (JSR Company, Japan). After filling, samples were left for typically 24 h to equilibrate before making measurements. Close to V_{th}, capacitance values were recorded at 10 mV increment, allowing approximately 1 h for the cell to equilibrate between each voltage increment. Errors due to fringing fields at cell edges were minimized by patterning the ITO electrodes with a guard-ring structure. Electrical measurements were carried out at 4 kHz using an Agilent Technologies UK Ltd., Wokingham, UK E4980A LCR meter. Sample temperatures were controlled to an accuracy of 0.1°C using a purpose-built heating stage. Typical empty cell capacitances were of order 25 pF. Any variation of empty cell capacitance with temperature was recorded. Typical variation was less than 2 fF$\cdot$°C^{-1}. Measured capacitance data were fitted numerically to Equations (2) and (3) using routines written in MATLAB.

Titanium dioxide was obtained from Sigma Aldrich Ltd., Gillingham, UK as a 99.5% pure, <100 nm powdered mixture of the rutile and anatase forms. Mixing into the host liquid crystal was achieved by 6 h of ultrasonificaiton at elevated temperatures, interspersed with bouts of vigorous mechanical stirring. Uniform mixing was confirmed by optical microscopy and was further supported by the visual appearance of samples (see below).

3. Results

The liquid crystalline material 4′-butyl-4-heptyl-bicyclohexyl-4-carbononitrile (CCN47, supplied by Merck) was chosen as the host for investigation. These properties of CCN47 have been characterized in previous studies [8,9]. A benefit of this material for our studies was that the presence of a smectic-A (SmA) phase below the nematic (N), resulting in a pronounced temperature variation of elastic constants and threshold voltages, thereby enabling us to probe for the effects of nanoparticle doping across a range of material values. Furthermore, negative dielectric anisotropy materials find application in technologically important so-called “normally black” displays, making the material interesting for comparison with previous studies [1,2] of nanoparticle doping into positive anisotropy materials. The phase transition temperature sequence of CCN47 is Crystal 28 SmA.30.6 N 59.7 Isotropic.

Figure 1 shows the effects of TiO_2 doping on the appearance of samples. Samples are increasingly whitened as more TiO_2 was added. The uniformly scattering appearance of the doped samples provides some further quantitative evidence for a uniform distribution of the TiO_2 throughout the liquid crystal.

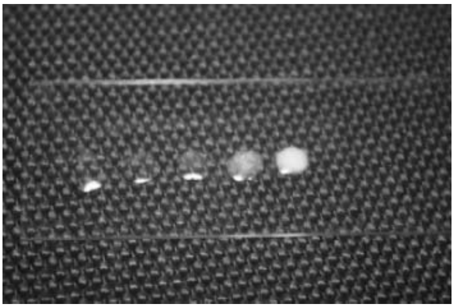

Figure 1. Samples of nematic liquid crystal CCN47 doped with (from left to right) 0 wt%, 0.04 wt%, 0.08 wt%, 0.5 wt%, and 1 wt% TiO_2.

Figure 2 shows differential scanning calorimetry traces for pure CCN47 and for CCN47 doped with 0.08 wt% TiO_2. The data were recorded for a cooling rate of $1^{\circ}C \cdot min^{-1}$. The nematic-to-isotropic and (lower temperature) nematic-to-smectic transitions are clearly seen. At the low doping concentrations of TiO_2 used in our work, we found the transition temperatures of doped samples to be unaltered versus those of the pure host.

Figure 3 shows measurement results for the Freédericksz threshold of samples. By careful measurement in guard-ring cells, we estimate that we are able to determine V_{th} to an accuracy of around 10 mV. From Figure 3, it is apparent that at this measurement resolution, we find no evidence for a variation in V_{th} under the application of the 4 kHz drive voltage. This holds even for the highest TiO_2 concentrations in our study (0.5 wt%). These results contrast with the marked (~10%) changes in V_{th} reported in [1] for samples doped with a 10-fold lower concentration (0.05%) of TiO_2, under pseudo-DC (<1 Hz) drive voltage conditions.

Figure 4 shows measured values of the nematic bend elastic constant, K33, for samples of CCN47 doped with various concentrations of TiO_2. The vertical extent of the data point

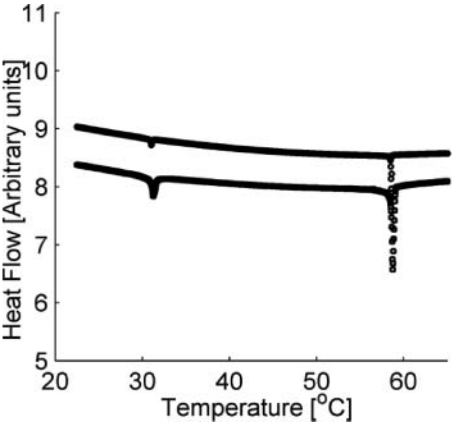

Figure 2. Differential scanning calorimetry traces cooling at $1^{\circ}C \cdot min^{-1}$ for pure CCN47 (upper line) and CCN47 + 0.08 wt% TiO_2 (lower). The higher and lower temperature peaks correspond to the isotropic-to-nematic and nematic-to-smectic transitions, respectively.

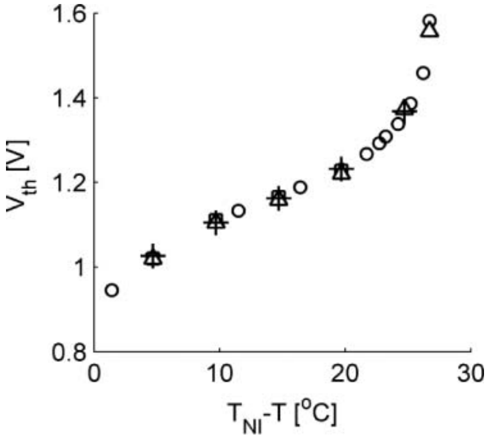

Figure 3. Measured values of the Freédericksz threshold voltage, V_{th}, versus reduced temperature for samples of CCN47 (circles); CCN47 + 0.04 wt% TiO_2 (squares); CCN47 + 0.08 wt% TiO_2 (triangle); and CCN47 + 0.5 wt% TiO_2 (crosses) doped with various concentrations of TiO_2. Vertical error bars are estimated as 10 mV and are too small to be made visible in the figure.

markers in Figure 3 is representative of the measurement accuracy (5%). K33 shows a (power law – see [9]) divergence as the sample temperature is lowered toward the smectic-A phase at $T_{NI} - T = 30.1°C$. In common with the measurements of V_{th} of Figure 3, within the limits of measurement accuracy no impact was found for low concentration of TiO_2 on the bend elasticity of CCN47 across the full temperature range of the nematic.

Finally, K11 was determined for CCN7 + TiO_2 samples from measurements of the capacitance versus voltage characteristics, fitting data to Equations (2) and (3). This procedure is more complex than the measurement of K33 (which proceeds from Equation (1)) and results in larger experimental errors, estimated as 10%. This error is reflected in the error bars on the measured K11 values in Figure 5 and it is apparent that at this measurement resolution, no change in K11 was observed as a result of doping.

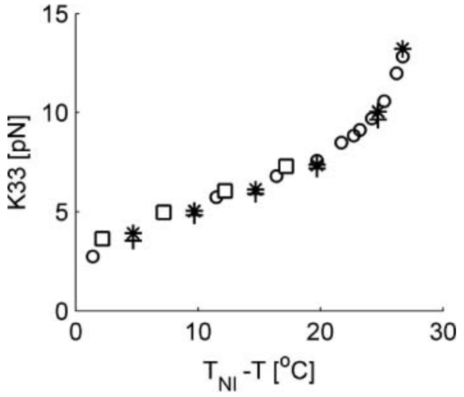

Figure 4. Measured values for K33 for CCN47 (circles); CCN47 + 0.04 wt% TiO_2 (squares); CCN47 + 0.08 wt% TiO_2 (stars), and CCN47 + 0.5 wt% TiO_2 (crosses). Data markers have been sized to approximately represent the 5% measurement error.

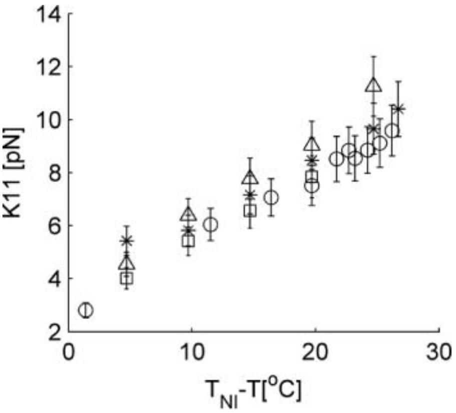

Figure 5. Measured values of K11 versus reduced temperature for CCN47 (circles); CCN47 + 0.04 wt% TiO_2 (squares); CCN47 + 0.08% TiO_2 (stars); CCN47 + 0.5% wt TiO_2 (triangles). Error bars are 10%.

4. Discussion and Conclusion

Previous authors have reported pronounced effects of TiO_2 nanoparticle doping for the switching behavior of liquid crystals at low frequencies. Using dielectric spectroscopy, Tang et al. [2] have shown that low-level TiO_2 doping in nematics impacts the behavior of space charges and electrical double layers in samples, clearly highlighting the importance of ionic effects for observations at low frequencies. The presence of low-frequency ionic effects however, does not preclude the possibility that doping may have additional consequences for the liquid crystal. In [4], the authors raise a question of the extent to which changes in rotational viscosity observed in samples doped with low concentrations of carbon nanotubes, may be a result of changes to the order parameter, s, of the host. In mean field theory, the elastic constants in the nematic phase are coupled to order parameter, with K11 and K33 scaling as s^2 in some theories [10]. The fact that no impact of low-level TiO2 doping was observed for K11 and K33 would imply that, for the present material at least, the impact of low-level TiO2 doping on nematic order parameter must be rather small. The results then support the conclusions in [1,2] that the majority of the observed impacts of low-concentration TiO_2 doping for nematics driven at low frequencies are most likely a consequence of changes to the population and mobility of ionic species present in samples.

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