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Effect of aerosil dispersions on the photoinduced nematic–isotropic transition

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Abstract

We report differential scanning calorimetric (DSC) and dielectric measurements on the nematic–isotropic transition in the bulk and aerosil composites of a liquid-crystal mixture having a photoactive guest azobenzene compound in a non-photoactive host, 4-n-heptyl cyanobiphenyl (7CB). The DSC scans taken at different cooling rates show that, at slower rates, the bulk displays a single peak across the transition, whereas the composites in the soft gel regime exhibit a double-peak profile. Such a double-peak profile, although seen in high-resolution ac calorimetric studies, has been observed for the first time in DSC experiments. The temperature range of the region between the two peaks is comparable to that seen in ac calorimetric experiments and has similar features. This observation is significant since the appearance of the low-temperature peak in ac calorimetric data has been explained to be due to a crossover from the random-dilution to the random-field limits. This work also constitutes the first experiments on the photoisomerization driven isothermal phase transitions in liquid-crystal–aerosil composites. The studies carried out in the absence and presence of a low-magnitude UV radiation not only bring out the standard features now established for such photostimulated phase transitions, but display a few surprises. Notable among them are that (i) the photoinduced shift in the transition temperature is a non-monotonic function of the aerosil composition and appears qualitatively similar to the dependence of the transition temperature itself, and (ii) the thermal anomaly mentioned above characterizing the crossover is also seen in the temperature-dependent as well as the temporal variation of the sample capacitance for a composite in the soft gel regime. We have also evaluated, using the temporal variation of the capacitance, the different response times associated with the UV-on photochemical process as well as the UV-off thermal back-relaxation process; the response times appear to have a similar dependence on the aerosil concentration as the transition temperature.

1. Introduction

Investigations on liquid crystals (LCs) confined in restricted geometries have been attracting significant attention in the past few years [1]. The restricted geometry can be realized by using a prefabricated confining matrix such as Anopore and Nuclepore in which the voids are highly regular with well-defined pore dimensions or an irregular network like aerogels. The geometrically enforced disorder observed in these situations can also be obtained by having the liquid crystal in a network termed aerosil formed with silica spheres of ~ 7 nm diameter whose surfaces are decorated to achieve hydrophilic or hydrophobic interactions [2–12]. The advantage of the aerosil network is that the random disorder can be controlled and fine tuned by simply varying the concentration of the silica particles. The fragile hydrogen bond network that results from the interactions between the particles permits the disorder to be created *in situ*, allowing the study of the role of the quenched randomness on various phase transitions in LC materials.

The phenomenon of light acting as a stimulus and control parameter to bring about phase transitions has attracted significant interest in recent times [13]. Such photo-driven phase transitions are known in a variety of systems, including spin-crossover complexes [14], π -conjugated polymers [15], biological systems [16], and, of course, liquid crystals [17]. Azobenzene molecules are well known to show reversible isomerization upon irradiation with UV [18]. Upon absorption of UV light (typically 365 nm), the energetically more stable *trans* or E configuration, with an elongated rod-like molecular form, transforms into a bent banana-like *cis* or Z configuration. The reverse transformation of the Z isomer into the E isomer can be brought about by irradiation of visible light (in the range of 400–500 nm). The latter change also occurs in the ‘dark’ by a process known as ‘thermal back-relaxation’ in a period ranging from minutes to tens of hours depending on the system. When such azobenzene entities are incorporated into a liquid-crystalline medium, either by physical mixing or by chemical bonding, the photoisomerization can lead to spectacular results. For example, the E form, due to its rod-like shape, stabilizes the liquid-crystalline phase while the photoinduced Z isomer with its bent shape acts like an ‘impurity’ destabilizing the phase. It needs to be emphasized that these impurities can be created on demand, and their concentration controlled by the magnitude of the UV intensity. The destabilization can be significant enough to even cause an isothermal photoinduced transition from a liquid-crystalline phase, say, the nematic phase, to the isotropic phase. This phenomenon has attracted attention, not only from a basic point of view, but also for possible applications in optical switching, image storage and opto-mechanical devices [19]. Photoinduced effects have been well studied in systems exhibiting nematic–isotropic [17] and tilted smectic–smectic A transitions [20]. Recently, we reported [21] the occurrence of the smectic A phase stabilized only in the presence of light from an otherwise nematic phase. (Notice that, in this case, contrary to all earlier observations, the photoinduced phase is more ordered.) In this paper we present the first report of the influence of confinement in a fragile network on the photoinduced shift and the dynamics associated with the nematic–isotropic (N–I) transition. A point that may be mentioned regarding photoinduced transitions in restricted geometries is that since light can be confined to extremely small regions (say, diffraction-limited regions), it is possible to create a naturally confined system and also alter the conditions of the neighbourhood so as to mimic the creation of different surface conditions around the confinement.

2. Experimental details

The liquid-crystalline material (which we refer to as LCM hereafter) used is a 3.3% (by weight) mixture of the photoactive guest EPH (4-(4'-ethoxy phenylazo)phenyl hexanoate,

from Eastman Organics) in the non-photoactive host 7CB (4-n-heptyl cyanobiphenyl, from E-Merck). The mixture exhibits the N phase from 40.3 °C down to sub-ambient temperatures, a feature that was a necessary criterion, since the aerosil network formed by the aerosil-LC system is a fragile one, and crystallization of the material may seriously disrupt the network. For these investigations we used hydrophilic aerosil particles (Aerosil 300) with a diameter of ~ 7 nm obtained from Degussa Corporation¹. Before the preparation of the mixtures, the aerosil particles were degassed and dried at a temperature of ~ 200 °C for 12 h. Mixtures of aerosil and LCM were prepared by a simple physical mixing process as well as the solvent mixing procedure. (It may be mentioned that, as shown in an earlier investigation [12], the results are invariant with respect to the method of mixing, particularly if the quantity of the sample required is quite small (~ 15 mg).) For the physical mixing method, the weighed aerosil and LCM were physically stirred while maintaining the temperature of the system at ~ 10 °C above the clearing point (i.e., T_{NI} , the nematic-isotropic transition point). For the solvent mixing method the weighed materials were transferred to a test tube containing acetone. The solution was sonicated for 1 h, following which the solvent was slowly (over ~ 12 h) evaporated and then the test tube was connected to a vacuum line for ~ 24 h to remove traces of the solvent. Aerosil mixtures are usually characterized in terms of the aerosil density defined as $\rho_a = m_a/V_{LCM}$, where m_a is the mass of aerosil and V_{LCM} is the volume of LCM (as the density of the LC is ~ 1 g cm⁻³, ρ_a can be taken to be m_a/m_{LCM}). We have carried out studies on composites with $\rho_a = 0.03, 0.05, 0.10$ and 0.15 g cm⁻³ (the unit is dropped hereafter) as well as on LCM.

The differential scanning calorimetric (DSC) experiments were performed using a model DSC7 calorimeter (Perkin Elmer) operating on the principle of power-compensation. These experiments were performed on the bulk LCM material as well as on the aerosil composites. For this purpose the samples, having a nominal mass of 3 mg, were loaded into aluminium pans and the DSC thermograms were taken in nitrogen atmosphere. The sample was heated to 10 °C above T_{N-I} and the scans were recorded while cooling at three different ramp rates, 5, 1 and 0.3 °C min⁻¹. The transition temperature was taken to be the peak point of the exothermic peak. This provided more reliable data than the conventionally used onset point as the transition temperature owing to the fact that the thermal signatures, especially for the aerosil composite system, were weak and the onset point determined from the tangent drawn with respect to the slope of the baseline could be erroneous. It must also be mentioned that the sample (bulk or the aerosil composite) temperature was never allowed to go below the ambient temperature, thereby preventing any possible crystallization-induced effects on the results.

The dielectric measurements were done with an impedance analyser (HP 4194A/4284A). The samples were contained between two indium tin oxide-coated glass plates having a rubbed polyimide layer to facilitate alignment of the molecules parallel to the substrate surface. It must be mentioned that except for the pure LCM and $\rho_a = 0.03$ composite, the quality of the alignment could not be ascertained by optical microscopy owing to the fact that no specific texture was observed. However, as we shall see later, the dielectric data show that for all the composites the molecules do align in a planar fashion, although the extent of this could not be determined. Since, for the mixtures with higher ρ_a values, the viscosity was quite high, the standard capillary filling method to fill the sample into a prefabricated cell could not be employed. Therefore the sample was placed on one plate and the other plate was kept on top of it with the two plates being separated by Mylar spacers (~ 6 μ m thickness) located outside the electrically active area of the cell; the plates were held together by glue. The drawback of the method, however, is that the thickness and therefore the empty cell capacitance could not be accurately measured, precluding the determination of the absolute value of the dielectric constant.

¹ The aerosil samples were kindly given to us by Mr Vikas Rane of d-hindia Ltd, Mumbai.

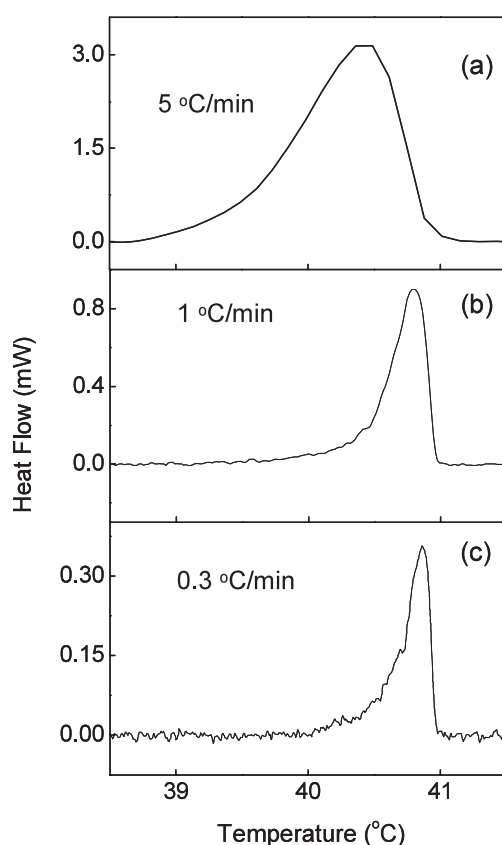


Figure 1. Differential scanning calorimetry (DSC) scans for the bulk (non-aerosil) sample obtained across the nematic–isotropic transition at three different cooling rates. Notice that there is only a single peak at all the rates.

3. Results and discussion

3.1. Thermal analysis

Figures 1 and 2 show the DSC scans obtained across the $I-N$ transition for the pure LCM and $\rho_a = 0.03$ composite at three representative cooling rates, 5, 1 and 0.3 °C min^{-1} . With decreasing cooling rate the peak height decreases, a feature known for the bulk material but also seen here for the composite. The point to be highlighted in these scans is that at all the rates a single peak is observed for the bulk sample; the composite shows a rate-dependent behaviour. Specifically, the thermal profile which appears like a single peak at 5 °C min^{-1} has a flat top with a slight depression when the rate is reduced to 1 °C min^{-1} . The latter feature develops into a twin-peak profile for the 0.3 °C min^{-1} scan. The double-peak profile was seen for composite $\rho_a = 0.05$ also, except that the temperature range between the two peak points is decreased from 0.3 °C for $\rho_a = 0.03$ to 0.17 °C for $\rho_a = 0.05$, perhaps suggesting that the range decreases as the concentration of the aerosil increases further. Indeed for higher- ρ_a composites we do not see the two-peak profile. The observation of such a two-peak profile assumes significance for the following reason. The $\rho_a = 0.03$ and 0.05 composites lie in the regime referred to as the soft gel region. In this region the density of aerosil particles exceeds the ‘gelation’ (percolation)

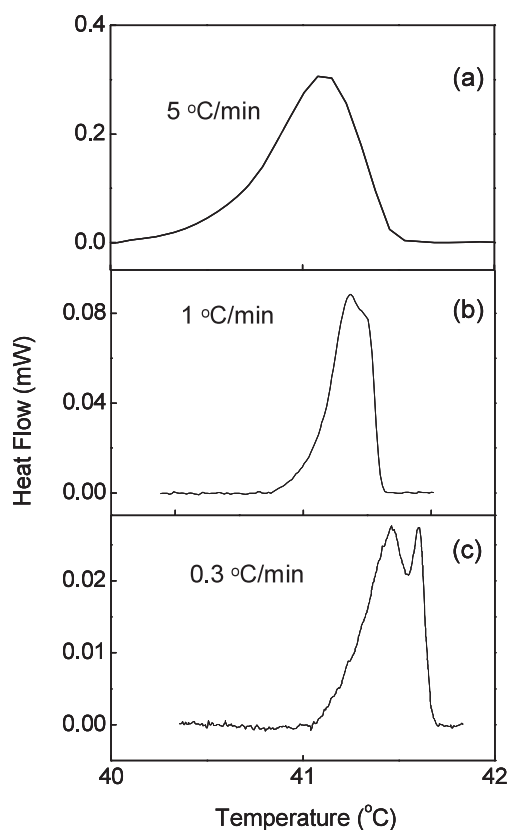


Figure 2. DSC scans for the $\rho_a = 0.03$ composite obtained across the nematic–isotropic transition at three different cooling rates. While for the fastest rate, $5\text{ }^\circ\text{C min}^{-1}$ there is a single peak, there are clearly two peaks for the lowest rate, $0.3\text{ }^\circ\text{C min}^{-1}$. The profile obtained with the intermediate rate has a flattened top, suggesting that there may be two peaks.

threshold, and consequently a network is formed by diffusion-limited aggregation through hydrogen bonding of the silica spheres. The gel is soft owing to the fact that the links among the silica particles can easily break. It may be mentioned that rheological studies in this region have shown that the aerosil composites exhibit soft glass behaviour generally seen for materials such as foams, emulsions, particulate suspensions, and slurries [22]. More importantly, specific heat measurements carried out using high-resolution ac calorimeters [4, 23, 24] have shown that these soft gels exhibit two closely spaced and sharp specific heat features. Combining high-resolution calorimetric, light-scattering and microscopy techniques, Caggioni *et al* [23] propose that in the LC–aerosil systems the nematic order develops from the isotropic phase through a two-step process. They argue that a double peak in the calorimetry data is due to a crossover from a random-dilution regime, where the silica gel couples to the scalar part of the nematic order parameter, to a low- T random-field regime, where the coupling induces distortions in the director field. Although this double-peak profile was clearly seen in the ac calorimeter scans, there have been no reports of such an observation in DSC scans [24] on aerosil–liquid-crystal systems. In fact, earlier we had reported [12] a weakly polar liquid-crystal–aerosil composite with a profile that could be deconvoluted to extract the presence of two peaks. In contrast, in the present set of investigations we observe a clear separation of the two peaks.

It should also be noted that just as in the case of the ac calorimetric scans, the DSC scans show that the high-temperature peak is much sharper compared to the low-temperature peak. This is to be expected, since the high-temperature region is associated with the appearance of the domains from the isotropic phase, and it has a weak coupling to the aerosil network. The coupling becomes stronger across the temperature where the second peak is seen, thus broadening it. But curiously, in the present case, as well as in all the cases reported to date, the temperature difference between the two peaks is always a fraction of a degree, suggesting that the network gains strength even for small values of the nematic orientational order. For both the bulk material and the composite the transition temperature as identified by the peak temperature seems to be a linear function of the cooling rate (in the case of the composite we considered the value for the second peak where it could be separated). The transition enthalpy, calculated as the area under the peak (cumulative area under the two peaks for the slow cooling scans in the case of the aerosil composite), showed a weak dependence on the cooling rate, diminishing by 14% for the bulk sample and 11% for the aerosil composite. This is in agreement with the fact that the nematic–isotropic transition is a first-order transition and therefore the transition enthalpy would remain finite even when the cooling rate is extremely small. The absolute value of ΔH was itself smaller by 18% for the aerosil case, suggesting that the transition becomes weaker in the presence of the quenched disorder. Since a clear splitting of the peaks was seen for the aerosil case at $0.3\text{ }^\circ\text{C min}^{-1}$ scanning rate, the individual ΔH values for the two processes was obtained by a peak profile fitting routine; it was seen that the high-temperature process, associated with the random-dilution limit, has a three times smaller ΔH value than the one connected with the random-field region. A final point to be mentioned is that the peak temperature, taken to be the transition temperature here, increases by $<0.5\text{ K}$ when the cooling rate is reduced from 5 to $0.3\text{ }^\circ\text{C min}^{-1}$. Since a similar shift is observed even for the melting peak of indium (taken as the DSC standard), we do not ascribe the increase in the transition temperature to any feature inherent in the sample.

3.2. Dielectric measurements

Figures 3(a)–(c) show the temperature dependence of the capacitance obtained with the planar alignment of the molecules for the LCM as well as two representative ($\rho_a = 0.03$ and 0.15) aerosil composites. It should be pointed out that for better comparison the data are presented as normalized capacitance obtained by taking the ratio of the measured capacitance to the capacitance value at T_{NI} value in the absence of the UV radiation. The first point to be noted is that the capacitance variation for the composite $\rho_a = 0.03$ looks qualitatively different from that of the bulk sample. Whereas the data vary smoothly through the transition region with a step-like change at the transition for the bulk sample as well as composites $\rho_a = 0.05, 0.1$ and 0.15 , the $\rho_a = 0.03$ composite shows an additional small peak at a temperature slightly lower than the main step. In fact the temperature difference of $0.3\text{ }^\circ\text{C}$ between the point at which the capacitance deviates from the isotropic value and the peak point of the smaller feature is comparable to the starting point of the high-temperature anomaly and the peak point of the low-temperature peak in the DSC scan for this composite (compare inset of figure 3(b) with figure 2(c)). Thus a crossover from the random-dilution regime to the random field seems to have a small, but noticeable, influence on the dielectric constant of the medium. A similar anomaly is not seen for $\rho_a = 0.05$, perhaps due to the smaller temperature range of the intermediate region. Also seen in figure 3(b) is that the illumination with UV increases the difference in temperature between the main step and the small peak from 0.3 to $1.5\text{ }^\circ\text{C}$, although broadening both the features. This perhaps suggests that the region of random dilution can be conveniently enhanced by the presence of the UV light. DSC experiments performed in the

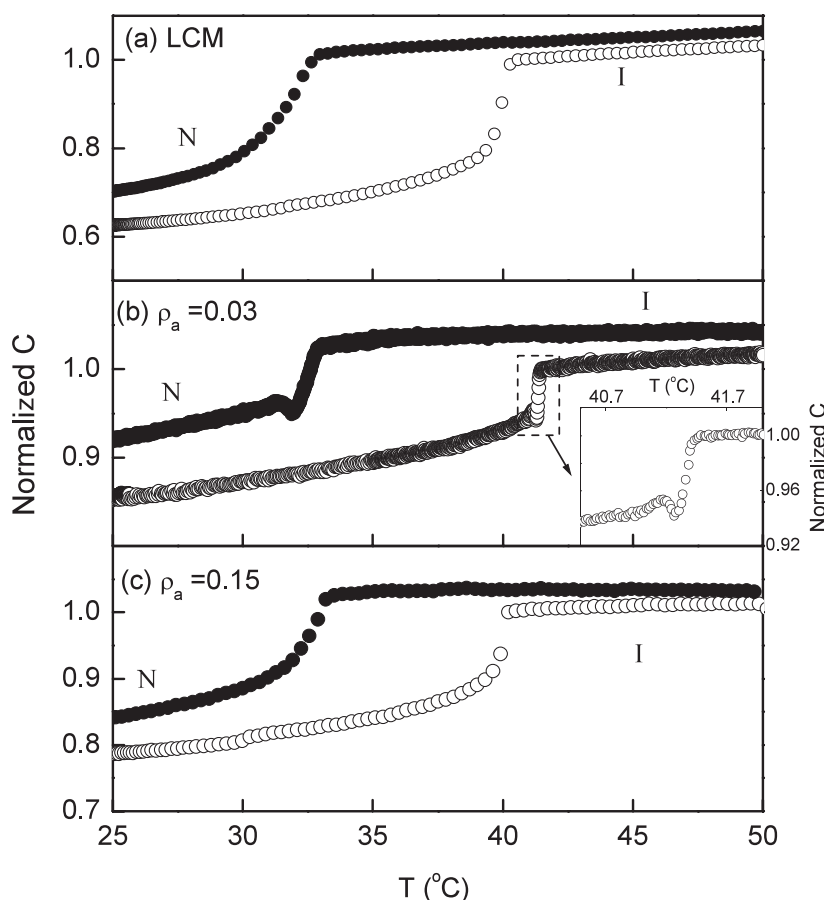


Figure 3. Temperature dependence of the normalized capacitance (C) for the (a) bulk and (b) 0.03 g cm^{-3} , (c) 0.15 g cm^{-3} aerosil composites. The isotropic to nematic transformation is signified by the step-like change. In all cases the UV-illuminated sample shows a significant shift in the transition temperature. The data for $\rho_a = 0.03$ composite show an additional peak (clearly seen in the inset) that is associated with a similar feature seen in the DSC scan for this composite. The solid circles represent data obtained with UV whereas the open circles show data obtained without UV.

presence of the UV light would be useful in this regard. A common feature noticed in all the cases is that the photoisomerization of the EPH molecules following the UV illumination results in a substantial shift of the N–I transition temperature. Of course, the temperature at which the transition temperature occurs in the absence of the UV radiation itself varies between the LCM and the composites. In bulk samples, reduction in the transition temperature owing to photoisomerization has been reported in the literature [17]. But what we find more interesting is the data shown in figure 4 featuring T_{NI} and $\Delta T_{\text{NI}}^{\text{UV}}$, the photoinduced shift in T_{NI} , as a function of the aerosil density. Not only do both parameters have a non-monotonic variation with ρ_a , but the behaviour of $\Delta T_{\text{NI}}^{\text{UV}}$ follows that of T_{NI} ! Several theoretical attempts have been made to explain the non-monotonic variation of T_{NI} in aerosil mixtures [4, 10, 22].

The effect of the aerosil network on the nematic orientational order parameter (OOP) is the basis of these theories. In the pinned-boundary-layer (PBL) models the orientational anchoring at the silica (aerosil) surface is so strong that the LC material in the boundary layer is quenched

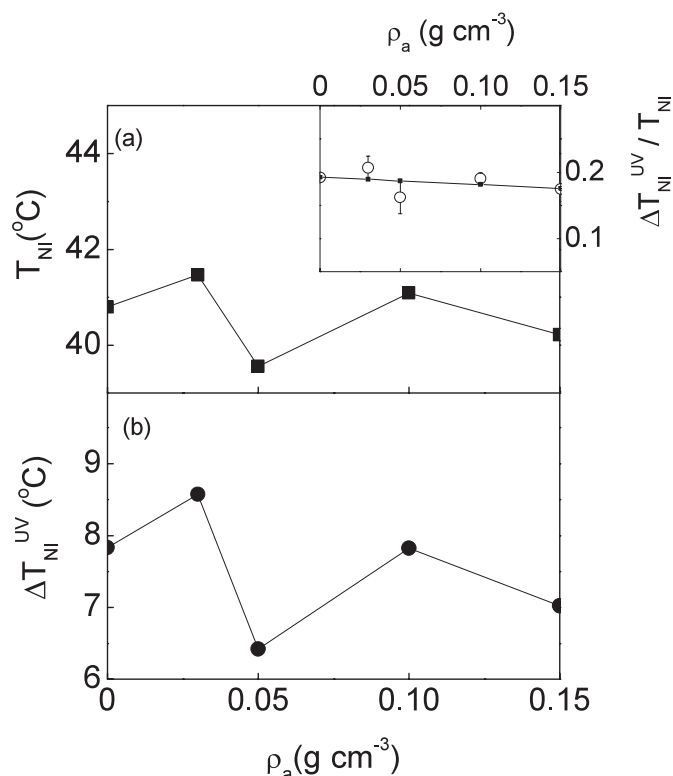


Figure 4. Influence of the aerosol composition on the transition temperature T_{NI} (top panel) and $\Delta T_{\text{NI}}^{\text{UV}}$, the UV-induced shift in the transition temperature (bottom panel). The line drawn through the data is only a guide to the eye. The inset shows that the ratio of the two parameters is only weakly dependent on the aerosil concentration. The line drawn through the data points is a fit to a straight line and the error bars indicate 95% confidence limit.

and the remaining LC behaves as pure bulk material. In the random-field (RF) model the quenched LC is simply distributed randomly in space, leading to a reduction of the average order in the remaining material, affecting the latent heat of the N–I transition. It must be further noted that whereas the PBL model does not predict a transition temperature shift, the RF model has a variation that is far steeper than in the experiments. A recent model is by Caggioni *et al* [23], who consider a crossover from a random-dilution regime to a random field. Despite this concerted effort, none of the models has been completely successful. It is with this background that we look at the ρ_a -dependence of $\Delta T_{\text{NI}}^{\text{UV}}$, the photoinduced shift in the transition temperature. In the case of bulk samples it is not difficult to visualize that the reduction in the transition temperature takes place owing to the photoisomerization which causes the photoactive molecules to change their shape from rod-like to bent-shaped, with the latter then acting as an impurity in the environment of the host rod-like molecules. Such a shape change can be expected to decrease the OOP and in cases where the reduction is substantial to bring about an isothermal transition from the nematic to the isotropic phase. If the PBL model were to be operating then except for the boundary layer the LC should have behaved as the bulk one. In such a case there should not have been any variation in the transition temperature when the aerosil concentration was increased, contrary to the experimental observations, shown in figure 4. In contrast the results favour, at least conceptually, the ideas of the RF model that

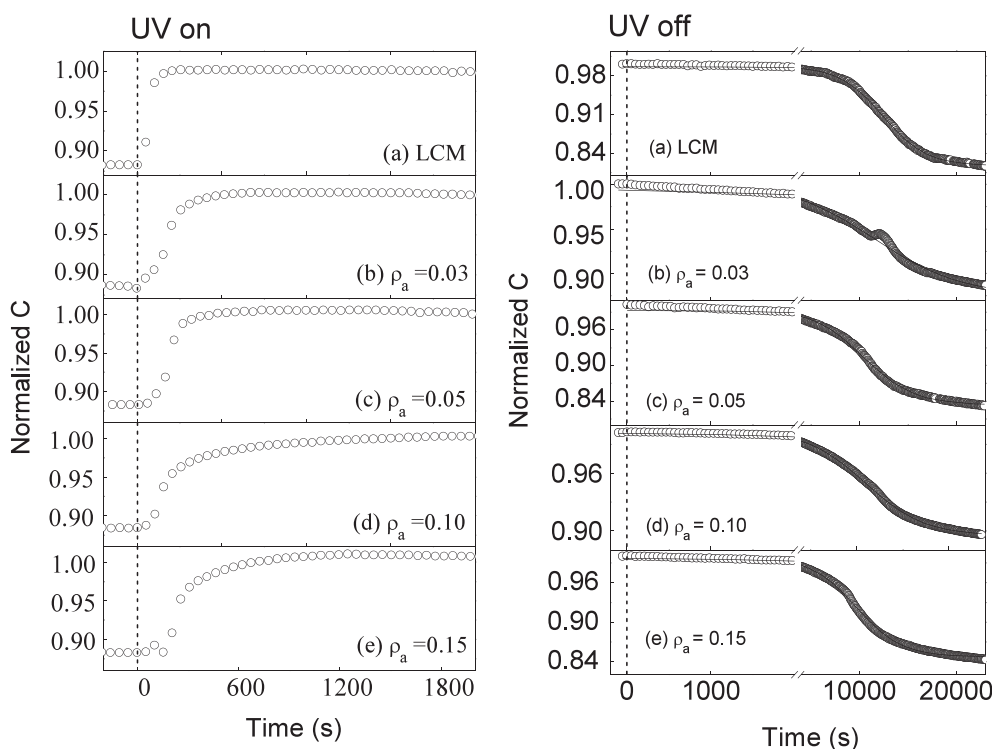


Figure 5. Temporal variation of the normalized capacitance (C) for the (a) bulk and ((b)–(e)) the composites upon turning the UV on (left panels) and subsequently off (right panels); the concentration of the aerosil is indicated in the panels. For a better presentation a break in the axis is provided in the right panels. The UV on process is quite fast unlike the UV-off process. The UV-off data are well described by a sigmoidal function, shown as the solid line through the data. The anomaly seen in the case of the $\rho_a = 0.03$ composite is again associated with that seen in the DSC scan.

the effect of the network on the order parameter would be spread over the entire material. What is more interesting is the fact that the ρ_a -dependence of the ratio of $\Delta T_{\text{NI}}^{\text{UV}} / T_{\text{NI}}$ can be approximated by a linear relation which is nearly constant with respect to the concentration (see the inset of figure 4). These features point to the fact that the same parameters that govern the behaviour of T_{NI} also control the variation of $\Delta T_{\text{NI}}^{\text{UV}}$. Any theoretical model that attempts to explain these trends should thus look for ways to account for the order parameter in the presence of the aerosil network. Even on the experimental front different kinds of behaviour have been observed as far as the dependence of the OOP on the aerosil concentration is concerned. Whereas Arcioni *et al* [25] in an ESR study find that the decrease of the OOP with increasing aerosil concentration appears to be roughly linear in the range studied, Jin and Finotello [9] found that the order parameter is almost independent of the aerosil concentration up to ~ 10 wt%; the different behaviour could also be because of the different types of aerosil used in the two studies: in the former they were hydrophobic whereas for Jin and Finotello [9] they were hydrophilic, as is in our case.

Next we look at the dynamics of the photoinduced transition as well as the thermal back-relaxation of the system to recover the equilibrium nematic phase. Figure 5 shows the temporal variation of the capacitance upon turning the UV on (left panels) and subsequently off (right

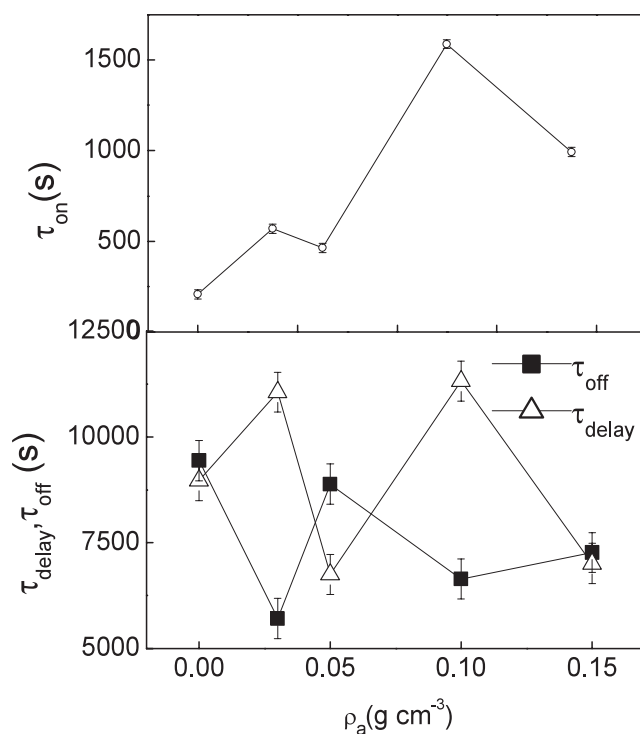


Figure 6. Dependence of τ_{on} , the UV-on response time, and τ_{delay} and τ_{off} , respectively the delay in the initial response and the total time taken to complete the back-relaxation when the UV is switched off. Notice that all the responses vary non-monotonically with the aerosil composition. However, the overall variation is more for the UV-on response than those in the UV-off process.

panels) when the sample was kept at a constant temperature in the equilibrium nematic phase. For the purpose of comparison the capacitance data have been normalized with respect to those in the isotropic phase. The LCM and the composites show a very clear increase in the capacitance, indicating the occurrence of the isothermal N–I transition. Even at a qualitative level it is seen that the time taken to undergo the transition is much shorter for the pure LCM than for the composites. It is interesting to note that the decay of the capacitance with time after the UV is switched off can be described by a sigmoidal function (shown as solid line through the data in figure 5), a feature characteristic of isothermal kinetics of phase transitions such as crystallization [26]. It is to be noticed that except in the case of the composite $\rho_a = 0.03$, the data vary smoothly in the UV-off region. For the $\rho_a = 0.03$ composite there is a step in the temporal data. It is tempting to associate this step (although not seen for $\rho_a = 0.05$) with the low-temperature thermal anomaly seen in the DSC as well as the capacitance versus temperature data sets. For a quantitative comparison, we define τ_{on} to be the period over which the entire change in capacitance takes place, upon turning the UV on. In a similar fashion, when the UV is turned off the delay time τ_{delay} is the period between the instant at which the UV is switched off and the capacitance changes significantly, and τ_{off} is the duration over which the capacitance recovers its equilibrium value (the value before UV is shone) after the delay time. Figure 6 shows that even though τ_{on} increases as ρ_a is increased it does so in a non-monotonic fashion. This is in fact true for the thermal back-relaxation time as well as the delay time. Whereas the response time for the UV-on process and the delay time are synchronous with the

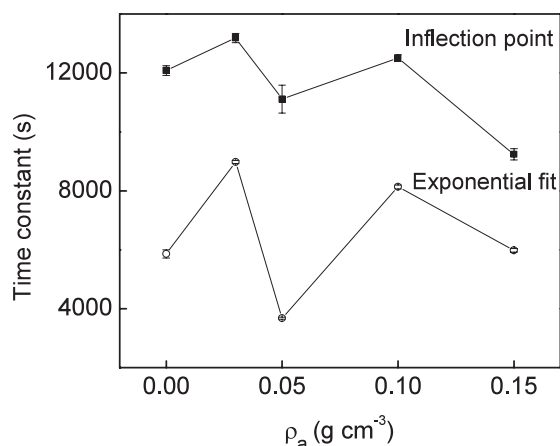


Figure 7. Aerosil concentration dependence of the time constants for the UV-off process evaluated using an exponential function (open circles) and inflection point in the data (closed symbols). The lines are merely guides to the eye.

change in T_{NI} , the thermal back-relaxation time has the opposite behaviour as a function of ρ_a . Perhaps a possible OOP change with increasing aerosil concentration is the cause for the different behaviours of the response times. It is possible that a similar feature is responsible for the trend seen in the ESR studies [25] for the tumbling diffusion coefficient associated with the rotation dynamics of the system. OOP measurements for the same concentrations as studied here would help in understanding the behaviour of both T_{NI} and ΔT_{NI}^{UV} .

The advantage of using a sigmoidal function, mentioned above, to describe the temporal variation of the capacitance during the UV-off process is two-fold: (i) data over the entire temperature range can be fitted with a single expression and (ii) it serves to look at the data as qualitatively analogous to the isothermal kinetic behaviour of phase transitions observed in other systems. However, the temporal behaviour can also be characterized in two other ways. The first is to describe the data in terms of a first-order kinetics through a single-exponential function characterized by a time constant. This involves considering the data beyond the delay time and in the case of $\rho_a = 0.03$ excluding the data near the second bump. The fitting was reasonably good for all concentrations. The second method is to take the instant at which the data go through an inflection point. This was conveniently determined by taking the first derivative of the capacitance with respect to time and noting the time at which a negative peak is seen. Figure 7 shows the time constant obtained by these two methods. It is seen that the qualitative behaviour is not very different from that for τ_{delay} presented in figure 6, establishing the non-monotonic behaviour of the associated kinetics.

In summary, we have carried out DSC and dielectric measurements on the nematic–isotropic transition in the bulk and aerosil composites of a liquid-crystal mixture of a photoactive guest azobenzene and a non-photoactive host. The DSC scans taken at slower rates for a particular composite in the soft gel regime have a double-peak profile (across the nematic–isotropic transition) similar to that seen hitherto only in high-resolution ac calorimetric data. In contrast, the bulk has a single peak at all rates investigated. It may be mentioned here that in general random quenched disorder can lead to interesting effects, like, for example, the appearance of a double-peak profile in current versus magnetic field diagrams in certain superconductors [27]. The dielectric experiments, which are first such measurements on the photoisomerization-driven isothermal phase transitions in liquid-crystal–aerosil composites,

bring out several interesting features including the dependence of $\Delta T_{\text{NI}}^{\text{UV}}$ on T_{NI} itself. DSC experiments in the presence of UV light, being planned, are expected to shed more light on these results.

Acknowledgments

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