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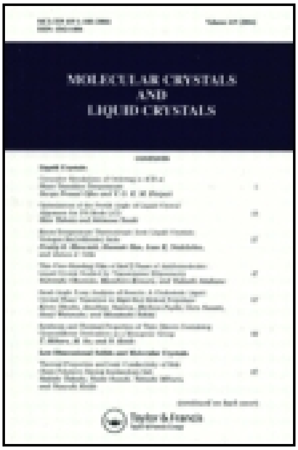

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Photo-Stimulated and Photo-Suppressed Phase Transitions

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Photo-Stimulated and Photo-Suppressed Phase Transitions

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Temperature, concentration of the solvent and pressure are the parameters that are well known to bring about phase transitions in liquid crystalline systems. In recent years a new parameter has been added to this list: light. The ability of light to alter/stabilize a particular thermodynamic phase via the photo-isomerization of the constituent molecules is an interesting tool to investigate condensed matter from a new dimension. In this talk I will describe our recent results on just two aspects of these non-equilibrium phase transitions: (i) In the case of the photo-induced isothermal nematic-isotropic transition, it is found that the time required for the system to achieve the photo-stationary state as well as to recover the original state after photo-irradiation, is a smooth function of the absolute temperature except in the vicinity of the transition; the behaviour is explained in terms of the order parameter excess between the equilibrium and photo-stimulated states. It is also found that the effect induced by photoisomerization can be suppressed by applying an external field. This novel method provides an accelerated means of recovering the equilibrium from the photo-driven state. The applied electric field is seen to make the recovery at least two orders of magnitude faster. (ii) Recently, we reported the first exception to an established phenomenon that the photo-induced transition always leads to a phase that in any case exists in the thermal cycle. A guest-host ternary mixture consisting of the photoactive guest molecules and not exhibiting smectic A phase, is seen to induce and stabilize the smectic A phase only in the presence of UV light. We have also mapped out hitherto unexplored temperature vs. UV intensity phase diagrams for various mixtures which illustrate that light mimics, in a limited sense, the role of a thermodynamic parameter like, e.g., pressure; these studies also suggest the possibility of observing a double critical point by employing the UV intensity as a fine-tuning parameter.

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1. INTRODUCTION

Molecules containing a chromophoric moiety such as azobenzene are well known to show reversible isomerization transformations upon irradiation with UV and visible light [1]. Upon absorption of UV light (~365 nm) the energetically more stable E (also known as *trans*) configuration with an elongated rod-like molecular form, transforms into a bent banana-like Z (or *cis*) 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). This latter change also occurs in the absence of any stimulation by a process known as "thermal back relaxation (TBR)". If the photoactive molecules are present in a system exhibiting liquid crystal phases then the isomerization transformations mentioned above can lead to interesting influences on phase transitions. This is owing to the fact that the *E* form of the azobenzene, as it is rod-like, is favourable for the stabilization of the liquid crystalline phase, whereas the *Z* form, which is in bent form acts like an "impurity" and therefore destabilizes the liquid crystalline phase. 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. In fact, photo-induced effects have been well studied in systems exhibiting the nematic–isotropic (N-Iso) transition [2]. Surprisingly, there have been only very few investigations on systems exhibiting other liquid crystalline transitions. In this article, we review two of our recent investigations [3–6] on such systems.

2. EXPERIMENTAL

Although, photoisomerization-related effects are large if the entire material is photoactive, from a practical point of view it is obviously better to dope small quantities of guest photoactive material into a host liquid crystalline system that exhibits the required phase sequence. For this purpose in the studies mentioned here we have employed guest-host systems, in which the host non-photoactive material is chosen with the kind of phase transition that is to be studied

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and the guest compound (hereafter referred to as EPH and obtained from Eastman Kodak), is a photoactive molecule with the molecular structure and phase transitions given in Figure 1. Figure 1 also gives such information for the different host compounds used. The fact that the photoactive compound is also liquid crystalline helps in obtaining homogeneous mixing of the guest and the host materials. The UV apparatus used for inducing photo-isomerization consisted of an intensity stabilized UV source (peak wavelength: 365 nm) with a fiber-optic guide (Hamamatsu L7212–01, Japan) along with a UV-band pass filter (UG 11, Newport). An additional IR-block filter was inserted just before the sample to prevent any effects of heat radiation from the UV source. The actual power (I_{UV}) of the radiation passing through the filter combination, falling on the sample was measured with a UV power meter (Hamamatsu, C6080–03) kept in the sample position. The Xray diffraction experiments were done with the help of an image plate set up.

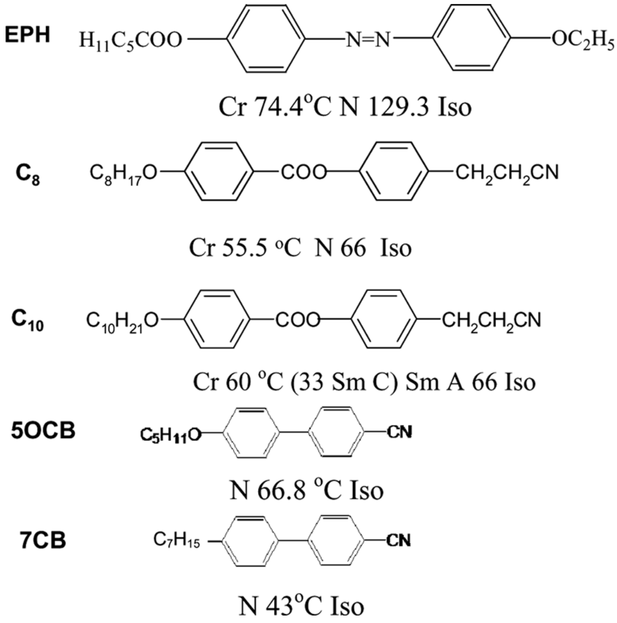

FIGURE 1 Molecular structures and phase transition temperatures of the compounds mentioned in this article.

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3. RESULTS AND DISCUSSION

3.1. Kinetics of the Thermal Back Relaxation Time of the Photoinduced Nematic-Isotropic Transition

As already stated, by irradiating the sample with UV radiation the system is photo-driven from the equilibrium nematic phase to the isotropic phase via an isothermal phase transition. The recovery of the equilibrium phase takes place spontaneously through a process known as thermal back relaxation (TBR). The starting point of the present investigations is the data given in Figure 2 showing the temperature dependence of the dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ (parallel and perpendicular to the nematic director respectively) without and with UV irradiation. Under both conditions $\varepsilon_{\parallel}$ increases and $\varepsilon_{\perp}$ decreases at the I-N transition as expected for the host molecule 5OCB used here, a system with positive dielectric anisotropy. Note that upon UV illumination the transition temperature shifts by $\Delta T = 6°C$, as a consequence photoisomerization of the guest EPH molecules from the E to Z form. Figure 3(a) shows the temporal variation of ε upon UV illumination and subsequent switch off at a representative temperature in the N phase, using which we extract various time constants of the system. Here we consider τ_{off}, the duration required for the system to recover the equilibrium ε value after the UV radiation is switched off. The detailed temperature dependence of τ_{off} is shown in Figure 3(b) and is seen to have, surprisingly, a non-monotonic variation with a substantial reduction in the finite ΔT region bracketed by the two

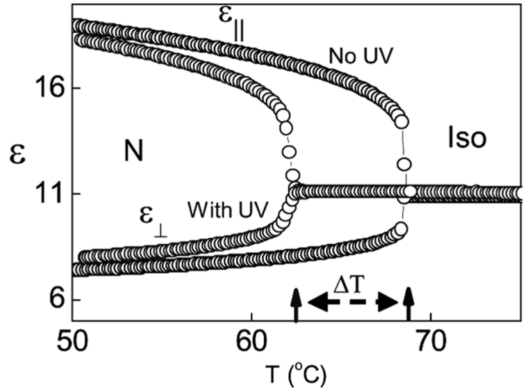

FIGURE 2 Temperature dependence of the two principal dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ without and with the UV radiation. The two arrows indicate the transition temperature $T_{no\text{-}UV}$ and $T_{with\text{-}UV}$, before and after UV irradiation.

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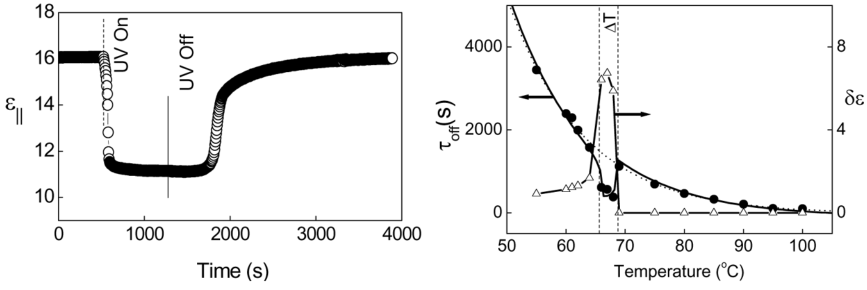

(a) (b)

FIGURE 3 (a) The temporal variation of the dielectric constant upon UV illumination and subsequent switch off in the N phase but within the ΔT region. (b) Thermal variation of τ_{OFF} (●) and $\delta\varepsilon$ (Δ). The solid line through τ_{OFF} data is a fit to Eq. (1).

transition temperature without ($T_{no\text{-}UV}$) and with UV ($T_{with\text{-}UV}$). The experiments also show that $\delta\varepsilon$, the difference in the dielectric anisotropy ε_a ($= \varepsilon_{\parallel} - \varepsilon_{\perp}$) between the equilibrium and photostimulated situations, is finite only in the ΔT region. We have used [5] this feature and the proportionality of ε_a on the orientational order parameter of the N phase to explain the non-monotonic variation of τ_{off}. Adapting Maier-Saupe model for the latter feature, we have established a simple correlation between τ_{off} and $\delta\varepsilon$ as

$$\tau_{off} = \mathrm{A} + \mathrm{B}\,\exp\left(\frac{-W}{k_B T}\right) - C\delta\varepsilon \tag{1}$$

A least-square fitting of the data to Eq. (1) is shown in Figure 3(b) as a solid line and is seen to describe the data well.

3.2. Electric-Field Assisted Acceleration of the Photostimulated Nematic-Isotropic Transition

Here again, mixture of the photoactive guest compound EPH (3.4% by weight) with a strongly polar host LC, 4-heptyl-4-cyanobiphenyl (7CB) exhibiting a room temperature nematic mesophase was used [6]. Upon illumination of the sample with UV light ($I_{uv} = 1\,\mathrm{mW/cm^2}$) the transition temperature T_{NI} diminishes by $\Delta T = 7°C$. Figure 4 shows the fixed frequency dielectric constant data obtained for a planar sample in the absence of an electric field (except for the probing field) and when a DC voltage of 40 V is applied. It should be noted that since the material has a positive ε_a, application of a voltage V (above a Freedericksz

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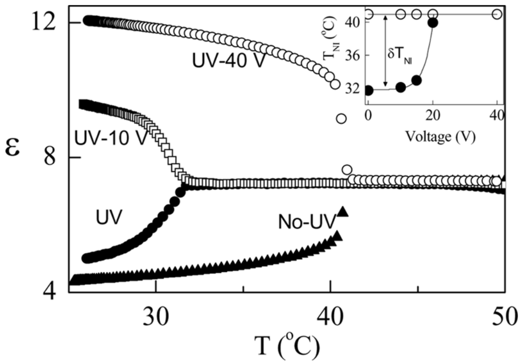
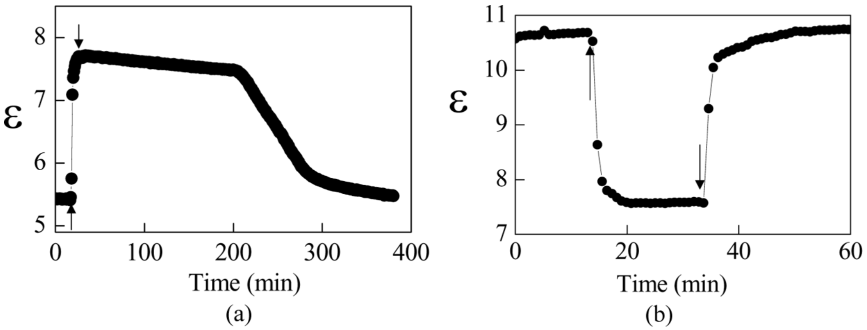


FIGURE 4 Temperature dependence of the dielectric constant ε obtained with (●) and without (○) the UV radiation, and also under the influence of the applied DC field.

threshold, which in this case is 2 V) reorients the molecules to be along the electric field direction; the extent of reorientation is controlled by the magnitude of the voltage (as seen for the data with 10 V), reaching saturation at higher values. Thus the measured dielectric constant in the N phase would be $\varepsilon_\perp$ and $\varepsilon_\parallel$ in the absence and presence of voltage respectively; consequently in the two cases ε would decrease/increase on transforming from the isotropic phase. The salient feature to be note is that upon application of the electric field, the finite ΔT value realized by UV illumination is diminished. This is an unusual feature that has not been reported till date. UV-Vis absorption measurements show that the electric field actually aids the recovery of the E isomer. The temperature-voltage *phase diagram* (inset of Fig. 4) thus suggests that the electric field opposes the formation/existence of the Z isomers. This feature provides a convenient and novel tool to control the E-Z isomer ratio. A remark must be made at this point: whereas the phase line obtained without UV (open circles in the inset of Fig. 4) represents an equilibrium transition, the boundary obtained with the UV illumination is a non-equilibrium one owing to the tendency of the Z isomer to spontaneously (given enough time) return to the E form. Therefore the features of the latter line are dependent on various extrinsic parameters such as the amplitude of the UV intensity, E-Z conversion efficiency of the photoactive guest molecule and the kinetics of the back relaxation (although in the present case it is a dynamic equilibrium situation since the UV light was kept on throughout the measurements).



(a) (b)

FIGURE 5 The time-resolved variation of ε, measured at a fixed temperature of 2°C below the no-UV T_{NI}, after the UV radiation is turned on (upward arrow) and subsequently switched off (downward arrow) for the (a) no voltage and (b) 20 V cases respectively.

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Figure 5(a) shows the temporal dependence of the dielectric constant obtained by maintaining the planar sample in the N phase in the finite ΔT region. Turning the UV radiation on, the value of $\varepsilon_\perp$ starts increasing rapidly and saturates after about 4 minutes of exposure and achieves a 'photo-stationary' state subsequent to the photochemical transition to the isotropic phase. When the radiation is switched off and the sample is left in the dark the reverse isomerization takes place, the sample transforms back into the N phase and consequently $\varepsilon_\perp$ decreases. The switching kinetics for this TBR is, as seen in the previous section, very slow compared to the photochemical transformation. Figure 5(b) shows the temporal variation of the dielectric constant in the presence of a DC bias voltage of 20 V when the UV light is turned on and subsequently off. The drastic decrease in the responses associated with the TBR process is striking. Whereas τ_{off} reduces by a factor of about 20, the delay time (the time duration between the instant at which the UV illumination is put off and the instant at which ε starts varying substantially) diminishes by more than two orders of magnitude but, τ_{on} (the time for the transition following the E-Z transformation) is hardly affected. UV/Vis absorption data show that the application of the field does drastically accelerate the reverse isomerization. This feature seen for polar as well as non polar LCs, is quite promising from the view point of E-Z photoisomerization of photoactive molecules in general and in particular for the dynamic holograms and optical storage devices, and obviates the need for the radiation of a longer wavelength to achieve the recovery. By proper arguments, we have [6] ruled out the dielectric coupling of

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the field to the director or the flexoelectric coupling to be the cause for the observed behaviour. Electrode polarization appears to be the driving force. Further measurements are in progress.

3.3. Dynamic Self-Assembly

In all the cases reported till recently, the photo-induced transition always leads to a phase that in any case exists in the thermal cycle, including the unusual case where we had reported [7] photoisomerization-driven disorder to order transition. Recently we described the first exception to such an established principle [3] and mapped out novel type of intensity-temperature phase diagrams of these non-equilibrium isothermal phase transition systems. For these investigations we used mixtures of C8 and C10 (see Fig. 1 for the molecular structures) as the host material, and EPH (at a fixed concentration of 4 weight %) as the guest component (In this section X indicates, in weight %, the composition of C10 in C8). For $X > 66$ the mesophase sequence is nematic (N)–smectic A (Sm A)–reentrant nematic (N_R) phase and only N mesophase for $X < 66$. When $X = 80$, in the Sm A and high temperature N phases, photoisomerization results in N and isotropic phases respectively, an expected feature, since UV irradiation leads to a "melting" of the phase, or in other words, that it leads to a transition to a less ordered state. But the N_R phase transforms to a more ordered state, viz., Sm A phase in the presence of UV illumination. The appearance of the smectic phase was confirmed using two different tools: (i) Xray diffraction, in which the low angle diffuse peak typical of the N_R phase becomes – upon UV illumination – very sharp, the width of the peak reaching the limits of the instrumentation used, which is characteristic of the Sm A phase, and (ii) bend elastic constant (K_3) measurements using the magnetic field Freedericksz transition method. In the N_R phase the threshold field (a measure of the K_3 value, in the geometry used) has a very weak dependence with the sample temperature. Measurements made after the photoillumination is switched off, exhibit a strong dependence of the threshold field as a function of time. This is a clear proof that the photoinduced Sm A phase, with an infinite K_3 value relaxes back to the N_R phase. The attractive aspect of these features is that the UV intensity required to achieve this phenomenon is very small (<100 microwatt/cm^2). As an extension of this scenario, we performed experiments on the ternary mixture with a concentration ($X = 55$) that lies outside the parabolic N-SmA-N_R phase boundary. It should be emphasized that this mixture exhibits only the N phase in the thermal cycle. Figure 6 shows the temperature-dependence of the transmitted

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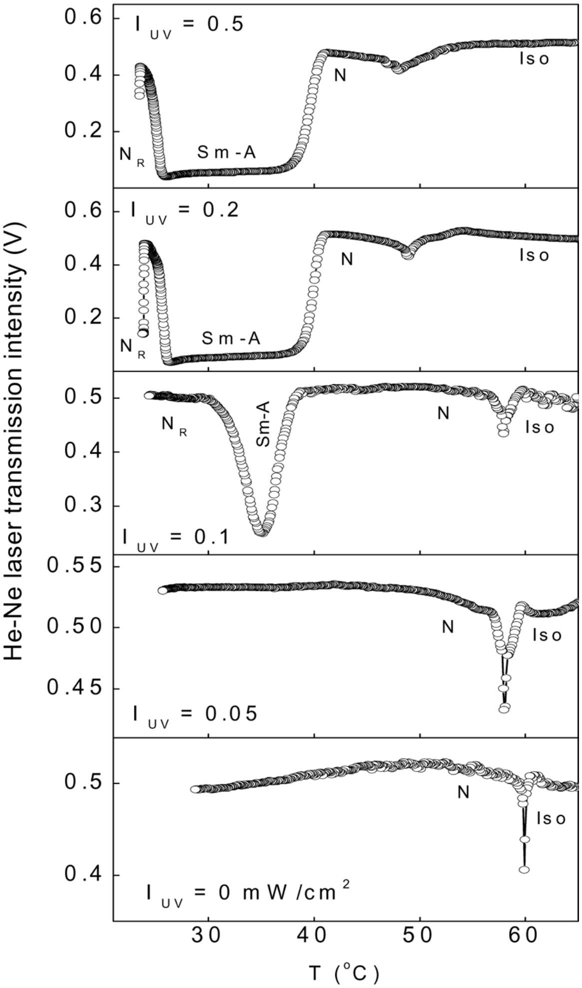

FIGURE 6 He-Ne laser transmitted intensity scans for different values of I_{UV} for the $X = 55$ mixture.

He-Ne laser intensity in the absence of UV radiation, and when the system is illuminated with UV light of different intensities. The probe intensity trace was quite similar in the scans with no-UV and when UV light of $I_{UV} = 0.05$ mW/cm^2 magnitude is shined. A dramatic change was seen upon increasing I_{UV} to 0.1 mW/cm^2. Two additional signatures were seen in the probe intensity at temperatures below the Iso-N transition. These two signals got widely separated in

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temperature when the UV intensity was further increased. Thus in the case of no UV and very low UV intensities there is only the Iso-N transition, whereas above it we have two more transitions. Remarkably, the signatures for the additional transitions are very similar to the phase transitions seen at temperatures below the Iso-N transition obtained for mixtures that exhibit the Sm A phase ($X > 66$). Most importantly the original behavior is recovered after the thermal back relaxation has taken place. In other words, the Sm A phase appears and exists only as long as the photoisomerization situation is prevalent, and points to a dynamic self-assembly scenario. The photoinduced phase being smectic was unequivocally established not only by microscopic texture observations, but also with the help of Xray and Freedericksz transformation measurements discussed above. The UV intensity required to induce the Sm A phase shows a strong increase as the concentration of the mixture (X) decreases (Fig. 7) and appears qualitatively similar to the concentration dependence of the "maximum pressure of smectic stability" (P_M) seen in the high-pressure experiments [8] on binary systems exhibiting the N-Sm A-NR sequence. The strong response of the system to the magnitude of the UV intensity provides us a powerful tool to look at a new dimension to phase diagrams, viz., temperature vs. intensity diagrams. Such phase diagrams are shown in Figure 8 for a few value of X, and suggest the possibility of observation a "double critical point" using UV intensity as a control parameter.

In summary, two illustrative cases of the rich variety of phenomena which can be realized in guest-host systems consisting of photoactive guest molecules are presented. The systems described display influence of applied field on photoisomerization, photo-driven disorder to

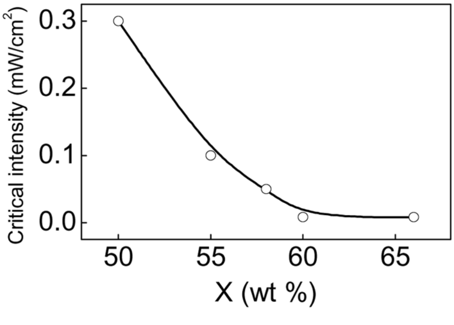

FIGURE 7 Diagram showing critical intensity to photoinduce the Sm A phase as a function of concentration. Notice that as the concentration decreases the intensity increases.

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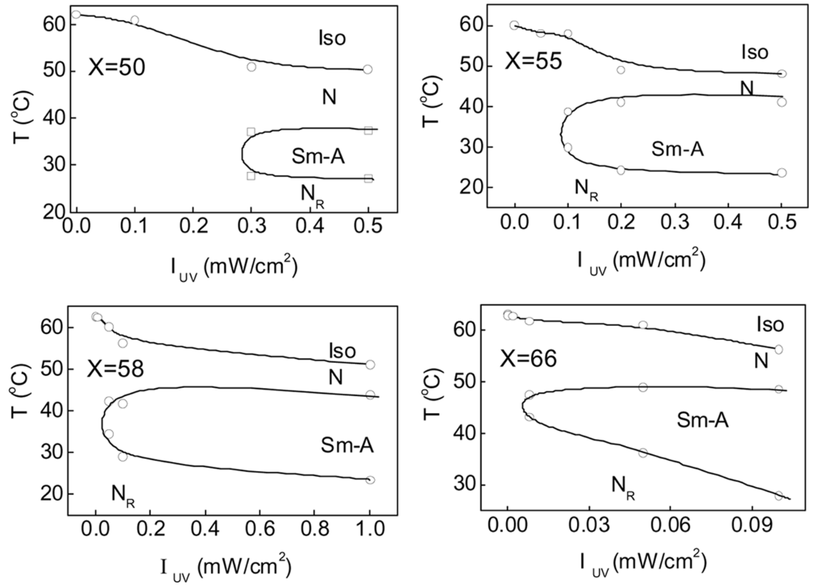

FIGURE 8 Temperature-UV intensity phase diagrams for different concentrations X.

order transition and dynamic self-assembly of a layered phase. These studies indicate that light can mimic the role played by a thermodynamic parameter like temperature, thus providing a new tool to investigate phase transitions and the associated critical phenomena.

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