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Photoinduced nematic-isotropic phase transition: A case for the random-field Ising model

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Experiments have been carried out on a photoactive guest-nonphotoactive host system exhibiting a photoinduced nematic-isotropic phase transition. It is shown that the phenomenon of photoinduced shift in the transition temperature is similar to the induction of cooperative chiral order in ‘‘sergeant-soldier’’ copolymer systems. An expression resembling the one given by the random-field model proposed for the latter system is seen to quantitatively describe the shift in the transition temperature as a function of the magnitude of the radiation.

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I. INTRODUCTION

Reversible shape transformation of photoactive molecules resulting from photoisomerization and consequent effects on phase transitions in liquid crystals has been well studied [1–5]. For example azobenzene derivatives can exist as two geometric isomers, the *E* form and the *Z* form. In the ground state the azobenzene molecules exist in the *E* (also known as trans) form that has a rodlike shape. Upon illumination with uv radiation (~360 nm) photoisomerization takes place resulting in transformation to the *Z* (or cis) form with a bent shape. 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 rodlike shape stabilizes the liquid crystalline phase while the photoinduced *Z* isomer with its bent shape acts like an ‘‘impurity’’ destabilizing the 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. This phenomenon has attracted attention, not only from a basic point of view, but also for possible applications in optical switching and image storage [6]. A general observation [1–3] is that in a guest-host system, with the photoactive material being the guest, the shift in the transition temperature (ΔT) has a nonlinear dependence on the power of the incident uv radiation. ΔT increases steeply at lower values of the power, but saturates for higher values. In this paper we show the similarity between this behavior and the cooperative chiral order observed in the ‘‘sergeant-soldier’’ copolymer materials [7]. The latter system has been theoretically analyzed [8] using a random-field Ising model and our results show that the expressions similar to that derived for this model describe well the variation of ΔT with uv power.

II. EXPERIMENT

The experiments were done on a mixture of the host material $E7$, a commercially available room temperature nematic material from *E* Merck, and an uv active dopant *p*-(*p*-Ethoxy phenylazo)phenyl hexanoate (EPH for short) from Eastman Kodak serving as the guest compound; the concentration of EPH in the mixture was 3.8% by weight. The resulting mixture, hereafter referred to as Mixture 1, shows the nematic-isotropic (NI) transition at 67.6 °C, with no crystallization until it reaches room temperature. This guest-host system has been shown to exhibit a large photoinduced shift in the NI transition temperature [2]. The dependence of the NI transition temperature, T_{NI}, on the intensity of the uv light was determined using a pump-probe beam setup described elsewhere [9]. Essentially it consisted of an intensity stabilized uv source with a fiber-optic guide (Hamamatsu L7212-01, Japan) along with a uv-bandpass filter and an infrared-block filter. The actual power of the radiation, I_{uv}, 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 intensity of the probe He-Ne laser beam (I_{probe}) transmitted through the sample was monitored using a photodiode. The sample was sandwiched between two polyimide coated, unidirectionally rubbed glass plates with mylar spacers defining the cell thickness. The actual cell thickness was determined using an interferometric technique. The sample cells were mounted in a temperature controlled hot stage (INSTEC HS250) for the temperature dependent measurements.

III. RESULTS AND DISCUSSION

Figure 1 shows representative raw scans of I_{probe} versus temperature for a sample thickness of 39.6 μm for different values of the uv power. The temperature at which there is an abrupt change in the intensity corresponds to the NI transition. As expected this temperature shifts to lower values on irradiating the sample; the shift depends strongly on I_{uv} at lower values of the uv power, but becomes saturated at higher powers. A plot of ΔT as a function of uv power for different thicknesses of the sample is shown in Fig. 2. It is seen that for the different thicknesses both the qualitative trend and the saturated value of ΔT are the same. However, the growth rate and consequently the uv power required to attain the saturated ΔT value has a significant dependence on the thickness of the sample.

Now, let us look at the mechanism behind the photoinduced NI phase transition in a guest-host system. The guest photoactive molecules are randomly distributed in the non-

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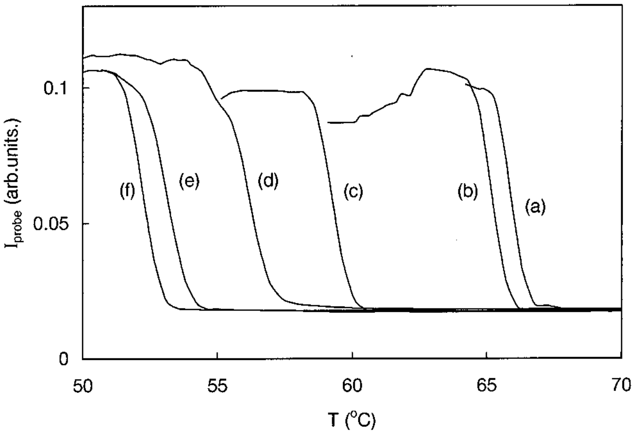

FIG. 1. Representative plot of the temperature dependence of the probe beam intensity I_{probe} through the sample (thickness 39.6 μm) (a) before and (b),(c),(d), and (e) after exposure to uv radiation. The intensity of uv radiation used is (b) 1.2 mW/cm^2, (c) 3.9 mW/cm^2, (d) 5.5 mW/cm^2, (e) 8.6 mW/cm^2. and (f) 18.1 mW/cm^2. The nematic-isotropic transition temperature, taken at the point where an abrupt change in intensity is seen, shows increasing downward shifts with increasing level of the uv radiation.

photoactive host system. In the absence of the uv radiation, the photoactive molecules are rodlike in shape and therefore support, if not enhance, the orientational ordering of the host nematogenic molecules. In fact, in the chemical system used here the photoactive molecules are also nematogenic and thus provide a better environment for orientational ordering than if they were non-nematogenic. When illuminated with uv radiation, the photoactive molecules undergo a shape transformation to a bent form and hence act as *local impurities* for the host rodlike system. The medium being nematic, these low-concentration impurities are randomly dispersed in the system and under steady state irradiation conditions do not undergo the reverse shape transformation. Despite such conditions they impose a substantial influence on the temperature at which the cooperative orientational ordering of the system sets in. With these features in mind one can draw a parallel between this phenomenon and the sergeant-soldier cooperative chiral ordering in copolymer systems.

Polyisocyanate systems, studied by Green *et al.* [7], consist of a polymer backbone in which a pendant group is attached to each monomer. The pendant groups can be either chiral or achiral, with the backbone itself being achiral. Owing to steric considerations, the polymer assumes a helical conformation, which can be either right or left handed. If all the pendant groups are achiral, the helices of either handedness have the same energy and therefore a long chain will possess domains of right and left handed helicity, which are separated by helix reversal walls. This results in the net optical activity to be zero. If on the other hand, a fraction of the pendant groups are chiral, there is a preference for one sense of helicity leading to a non-zero optical activity. Green *et al.* [7] found that the magnitude of the optical activity is extremely sensitive to the presence of the chiral pendant groups. Even at low concentrations of chiral moieties there is a large amplification of the optical activity, which can taken to be a measure of the chiral order parameter. The *sergeant* chiral units drive the *soldier* achiral units to adapt, in a cooperative way, the chiral order. To explain this behavior Selinger and Selinger [8] introduced an approximate theory based on the random-field Ising model [10] in which the free energy of the system has contributions from the energy cost of a helix reversal and an effective field due to the local chiral bias of the chiral units. The randomness comes from the distribution of the placement of the chiral units along the polymer chain. According to this model the chiral order parameter M can then be expressed as $M \sim \tanh(rK)$, where r is the concentration of the monomer units and K is a parameter dependent on, amongst other factors, the domain size of the polymer chain between helix reversals. This approximate theory as well as numerical simulations based on this model were found to describe the experimental data well [8].

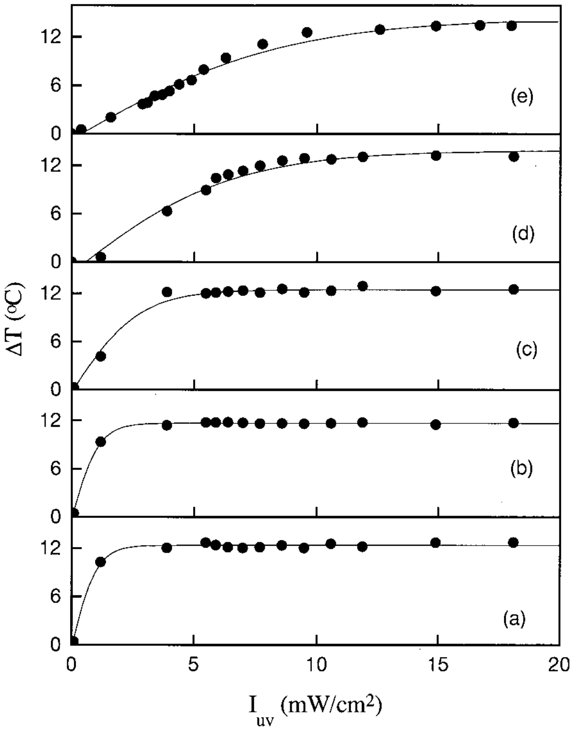

FIG. 2. Plot showing shift in the transition temperature ΔT as a function of I_{uv}, the power of the incident uv radiation for different sample thicknesses: (a) 4.4 μm, (b) 13.2 μm, (c) 26.9 μm, (d) 39.6 μm, and (e) 56 μm. The circles represent the experimental data and the lines fit to Eq. (1).

Let us now draw the correspondence between the polymer system mentioned above and the photoinduced NI transition. The contribution to the free energy comes from the orientational ordering of the host molecules and the local orientational entropy due to the guest photoactive molecules. When the uv radiation is present, the photoactive molecules are bent and therefore introduce a local region of higher orientational entropy compared to the regions of the host molecules. This is similar to the regions of higher chiral bias where the chiral units are present on the polymer chain. The amplified chiral cooperative response of the polymer system can be compared with the amplication of the local disorder due to the bent photoactive molecules leading to an isothermal transition from the nematic to the isotropic phase. Thus, perhaps one can consider ΔT, the shift in the NI transition temperature to be analogous to the chiral order parameter of the polymer. The role played by the fraction of the chiral units is taken by the number of photoactive molecules in the bent form (Z isomer). In the following this number is considered to be directly proportional to the magnitude of the uv power, I_{uv}.

There exist two important differences between the two systems, though. First, while in the polymer case, the effect of the sergeant chiral units is to enhance the ordering of the whole system, the sergeant bent photoactive molecules lead to a higher disordering of the entire medium. The main implication of the reverse role of the sergeants is that whereas the cooperative effect increases with decreasing temperature for the polymer, it decreases with decreasing temperature for the NI case. Second, in the polymer system, the chiral and achiral units are covalently bonded together by the polymerization process, and they cannot redistribute themselves. In contrast, in the liquid crystalline system, the photoactive dopants are free to redistribute themselves in the host ‘‘solution.’’ Thus it may appear that this is a case of annealed randomness, as opposed to quenched randomness. But based on observations described below, we feel that it is a case of quenched randomness. Before uv illumination of the sample, the field of view under a polarizing microscope is that of a uniform birefringent material. Upon illumination and consequent photoisomerization, only the illuminated region transforms to the isotropic phase, while the nonilluminated portion remains in the nematic phase. By illuminating through a patterned mask we found that the isotropic regions are highly localized without getting diffused into the nonilluminated regions. From the fact that the concentration of photoactive molecules is quite small, along with the observation that the region of illumination gets transformed to the isotropic phase and remains localized, we can infer that the effect of uv on the photoactive molecules gets amplified substantially. Within the time scales of measurement, which are much shorter than the thermal back relaxation time (even in the absence of uv irradiation) the photoinduced disorder can be considered quenched [11]. With these analogies in mind we fitted the data shown in Fig. 2 to the following expression, which is similar to the one proposed for the polymer case:

$$\Delta T = \Delta T_{sat} \tanh(A^{*} I_{uv}). \tag{1}$$

Here ΔT_{sat} stands for the saturated value of ΔT, the parameter A represents contributions coming from the conversion efficiency of the paraticular photoactive molecule and also accounts for the depletion effect experienced by the radiation as it passes through the sample. The fitting shown as solid lines in Fig. 2 indicate that Eq. (1) describes the data well for all sample thicknesses. The thickness dependence of the value of A obtained from the fit, is presented in Fig. 3 and shows the expected result that its magnitude, being largely controlled by the depletion effect, should be inversely proportional to the thickness of the sample.

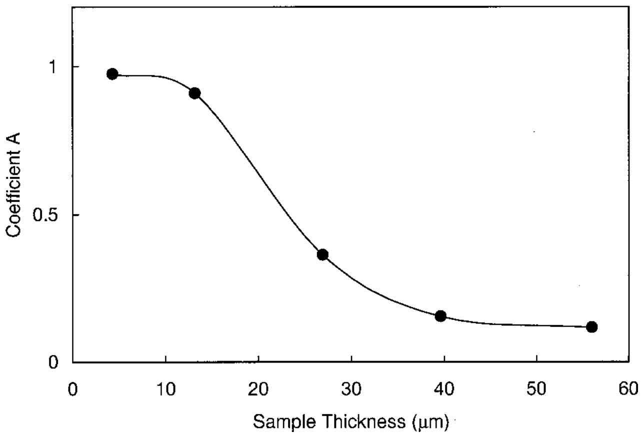

FIG. 3. Thickness dependence of the coeffcient A in Eq. (1). The circles are from the fit of the data to Eq. (1) and the solid line is a guide to the eye.

In summary, our results suggest that the magnitude of the photoinduced shift in the nematic-isotropic transition temperature can be analyzed in terms of a random-field Ising model. More experiments and a rigorous theory should be able to shed more light on this phenomenon.

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[11] A significant feature that should be noted is that in our case the ‘‘disorder’’ is created ‘‘on-line.’’ Of course, given enough time (through thermal back relaxation) and in the absence of the uv irradiation, the disorder vanishes. Thus under steady state uv illumination conditions the localized disorder can be considered as quenched.