Nonphotochemical laser-induced nucleation of nematic phase and alignment of nematic director from a supercooled thermotropic liquid crystal

Xiaoying Sun and Bruce A. Garetz*
Department of Chemical and Biological Sciences, Polytechnic Institute of New York University, Brooklyn, New York 11201, USA

Michele F. Moreira and Peter Palffy-Muhoray
Liquid Crystal Institute, Kent State University, Kent, Ohio 44240, USA

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A nonphotochemical laser-induced phase transition was studied in a supercooled 4′-*n*-pentyl-4-cyanobiphenyl (5CB, also referred to as PCB and K15) liquid crystal, using linearly polarized 45 ps light pulses at a wavelength of 532 nm. The laser induced nucleation from the metastable supercooled isotropic phase to the nematic phase during slow cooling (0.001 °C/min) and high light intensity (3.9 MW/cm^2). The resulting nematic director tended to be aligned along the direction of the plane of polarization of the light. At the intensities used, there is no observable laser-induced realignment of the director once the sample is in the nematic phase, nor any permanent laser-induced ordering when the sample is illuminated only in the stable isotropic phase during slow cooling. These experimental results are consistent with a mechanism based on optical Kerr alignment.

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I. INTRODUCTION

Nonphotochemical laser-induced nucleation (NPLIN), a phenomenon in which intense laser pulses induce supersaturated solutions to nucleate, was discovered by Garetz *et al.* [1,2] and has also been demonstrated to control polymorphism in some systems through "polarization switching," in which the polymorph formed depends on the polarization state of the laser beam [3,4]. There is growing evidence that crystallization from solution is often a two-step process: the formation of a liquidlike solute cluster, followed by the organization of that cluster into an ordered phase [5]. Garetz *et al.* have hypothesized that NPLIN involves the electric-field-induced alignment of molecules or groups of molecules in a prenucleating solute cluster, aiding the cluster in organizing into a crystal-like entity, through the optical Kerr effect [6].

The liquid crystalline state exhibits optical properties that display a sensitivity to external electric and magnetic fields not seen in other fluids, owing to strong correlations between molecules [7]. There is a substantial body of literature from the 1980s concerning the laser-induced molecular reorientation in isotropic, nematic, smectic, and cholesteric phases, induced by the optical torque associated with the optical Kerr effect. These effects are responsible for "giant" optical nonlinearities in liquid crystal systems [8], and more specifically for the optical Freedericksz transition in nematic liquid crystals—a second-order transition in which the nematic director undergoes a change in direction in response to an applied optical field [9]. More recently, there have been numerous reports of enhanced molecular reorientation in dye-doped nematic liquid crystals, owing to dye excited state–liquid crystal interactions [10].

NPLIN has been observed in supersaturated solutions of urea in water, ethanol, and methanol, as well as aqueous solutions of a variety of organic acids and amino acids. All of these cases have involved two-component solutions. The aim of this paper is to see whether NPLIN is a more general phenomenon in which light can induce a phase transition from a metastable isotropic state to an ordered state in a single-component system, for example, an isotropic → nematic transition in a single-component thermotropic liquid crystal. In this case, the metastable state is the supercooled isotropic state, rather than the supersaturated state in the case of a two-component system. Furthermore, we investigate whether the polarization of the incident light controls the ultimate order in the resulting nematic phase.

II. EXPERIMENTAL

A. Laser exposure protocol

In our earlier studies of nucleation from two-component solutions, the preparation of supersaturated solutions was straightforward, because such solutions are metastable over a fairly wide range of concentrations and can survive for several weeks before spontaneously nucleating. A one-component thermotropic liquid crystal, however, exhibits a very narrow temperature range of about 1 °C [11], in which it can exist in a supercooled isotropic state, and the temperature at which the supercooled isotropic state spontaneously nucleates depends on the cooling rate.

In a laser-induced nucleation experiment on a thermotropic liquid crystal, we wish to expose the sample to laser pulses while the sample is in the supercooled isotropic state. In practice, this is difficult to achieve, because the supercooled temperature range is so narrow. An easier alternative is to expose the sample to laser pulses throughout the cooling process. This can work as long as one can demonstrate that exposing the isotropic phase and the nematic phase to laser pulses of the same intensity has no appreciable effect on the sample order.

*Author to whom correspondence should be addresed.

Also, at the end of a cooling run, the sample will be in the nematic phase, whether or not it has been exposed to laser pulses. One must be able to determine whether the nematic phase has resulted from spontaneous nucleation or from laser-induced nucleation. If our hypothesis that the laser helps to align molecules is correct, then the order of the nematic phase that results from laser-induced nucleation should be distinguishable from the order that results from spontaneous nucleation. For example, the nematic director might be randomly oriented in the case of spontaneous nucleation, while it may tend to be aligned parallel to the plane of polarization of the laser pulses in the case of laser-induced nucleation.

B. Surface preparation

The nematic director is also controlled by surface preparation. When rubbed polyimide is used as the coating surface, the nematic director tends to align parallel to the rubbing direction of the surface, producing a strong anchoring effect that would compete with any laser-induced effect. Planar alignment along the surface, with the director in a plane parallel to the surface, but with random azimuthal angle within that plane, is the preferred alignment for our laser-induced nucleation experiments. Janossy and Kosa were able to obtain planar alignment and demonstrated director gliding by coating the cell windows with soft polymer films of either poly(ethyl methacrylate) (PEMA) or poly(methyl methacrylate) (PMMA), and we have chosen to employ their method by coating our windows with PMMA [12].

C. Sample preparation and processing

The 4′-*n*-pentyl-4-cyanobiphenyl (5CB, also referred to as PCB and K15) was obtained from EM industries and used without further purification. A sample cell consisting of two indium tin oxide (ITO)-coated glass windows with a path length of 12 μm was filled with 5CB. The windows were coated with PMMA (T_g=110 °C) to induce planar alignment. A polymer solution was prepared by dissolving 500 mg of PMMA from Aldrich in 50 ml of isopropyl alcohol, which was spin coated onto the ITO-coated glass windows. The sample was surrounded by an aluminum hot stage (Instec Inc. model HS1) with circular apertures. The sample area is 38×63 mm with a viewing window of 9.0 mm diameter. The hot stage aperture has a 5 mm diameter to allow pump and probe lasers to enter and exit the sample.

The isotropic→nematic transition temperature in 5CB is approximately 34 °C [13]. For a cooling run, the sample is heated up to 40 °C, held there for 30 min, and then cooled down to 30 °C at different rates ranging from 0.1 °C/min to 0.001 °C/min.

D. Optical setup

In order to monitor the phase and order of the sample, the cell is placed between crossed polarizers. The polarizer-analyzer pair can be rotated while maintaining a fixed angle of 90° between them. The probe beam consists of the output of a linearly polarized 4 mW cw HeNe laser (wavelength 633 nm) with 2 mm diameter, directed through a quarter-wave retardation plate to produce circular polarization. This beam then passes through the cell-polarizer assembly, and is finally incident on a Hamamatsu silicon photodiode with the area size of 5.8×5.8 mm as shown in Fig. 1. The quarter-wave plate ensures that the intensity of the light exiting the first polarizer and entering the sample is constant, independent of the polarizer orientation. When the sample is in the isotropic state, no light is transmitted through the crossed polarizers, and the photodetector signal is close to zero. When the sample is in the nematic state, but with random director orientation over the dimensions of the probe laser beam, some light is transmitted through the crossed polarizers owing to the sample birefringence, resulting in a detector signal that is nonzero and approximately independent of the orientation of the polarizer-analyzer pair. If the sample is in the nematic state with uniform director orientation over the probe laser beam area, the detector signal is nonzero, with an amplitude that is a sinusoidal function of the polarizer-analyzer pair orientation, proportional to the transmitted light intensity given by

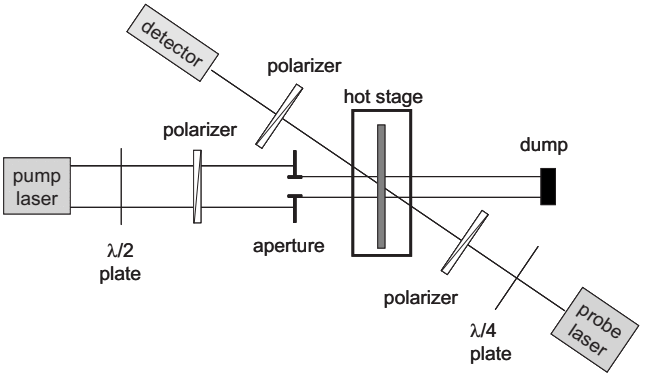

FIG. 1. Optical setup. Linearly polarized high-intensity pump laser illuminates a sample in the hot stage, and the probe laser detects the presence of any sample birefringence.

$$I = I_0 \sin^2 2\theta \left[1 - \cos\left(\frac{2\pi d \Delta n}{\lambda} \right) \right],$$

where θ is the angle between the polarizer and the director, λ is the light wavelength, d is the sample thickness, and Δn is the birefringence of the nematic material.

In order to induce nucleation and alignment, a second, linearly polarized pump laser beam is directed through a half-wave retardation plate followed by a polarizer, which allows the rotation of its plane of polarization without loss of intensity. It is then incident on the sample cell, making an angle of about 5° to the propagation direction of the probe beam. The pump laser is a Continuum frequency-doubled, mode-locked Nd:YAG laser with a pulse duration of 45 ps, a pulse repetition rate of 10 Hz, a wavelength of 532 nm, a beam diameter of 5 mm, and a peak intensity of 3.9 MW/cm^2.

E. Polarized optical microscopy

An additional means of characterizing the final nematic state is to view the sample using polarized light microscopy

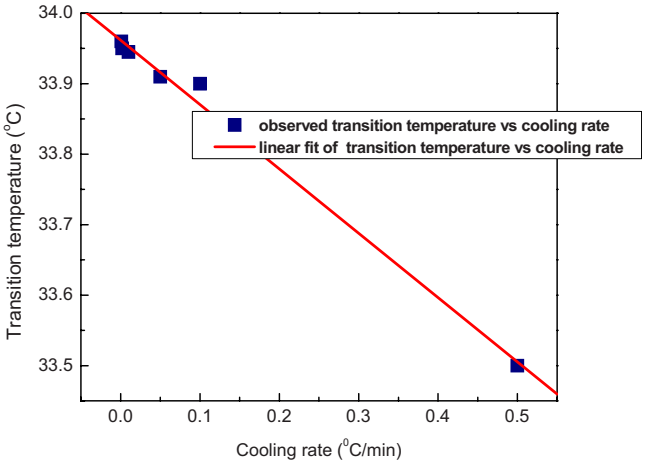

FIG. 2. (Color online) Observed isotropic-nematic transition temperature vs cooling rate. Symbols represent the temperature at which the sample begins to scatter light for a given cooling rate, as measured by a decrease in the probe laser signal.

(POM). The sample was removed from the hot stage and viewed in a Nikon OPTIPHOT-POL microscope connected to an Optronics CCD camera.

F. Characterization of the supercooled state

The supercooled isotropic state can be characterized by recording the spontaneous isotropic→nematic phase transition temperature at different cooling rates, plotting the observed transition temperature as a function of the cooling rate, and linearly extrapolating the transition temperature T_{NI}, to a zero cooling rate. The observed transition temperature is determined by plotting the probe laser transmission intensity as a function of temperature, and noting the temperature at which the transmission signal begins to drop. The temperature range of the supercooled state is approximately between the extrapolated T_{NI} and $T_{NI}-1$ °C [11].

III. RESULTS

A. Isotropic-nematic transition temperature

A sample of 5CB was heated to 40 °C, held there for 30 min, and then cooled to 30 °C at different rates of 0.1, 0.05, 0.01, 0.002, and 0.001 °C/min, while monitoring the probe laser transmission. The observed transition temperature as a function of the cooling rate is shown in Fig. 2. When the cooling rate decreases, the transition temperature increases. Extrapolating the observed transition temperature to a zero cooling rate gives a value of 33.96 ± 0.01 °C for T_{NI} [13].

B. POM of spontaneous nucleation of the nematic phase

Figure 3 shows a sequence of polarized light micrographs showing the nucleation process for 5CB upon cooling below T_{NI}. The cooling rate was 0.001 °C/min for the obtained image sequence. The time between each image is about 15 min. One can see the growth of individual droplets at early times, which merge into each other and coarsen at later times via defect annihilation. Micrographs at the later times suggest that the liquid crystal has planar alignment along the surface, with no preferred director orientation within the plane of the surface.

C. Average director orientation in spontaneous vs laser-induced nucleation

5CB samples were exposed to trains of pump laser pulses in which the plane of polarization was set at various angles (0°, 45°, and 90°) measured relative to laboratory horizontal. The resulting nematic phase was analyzed using the probe

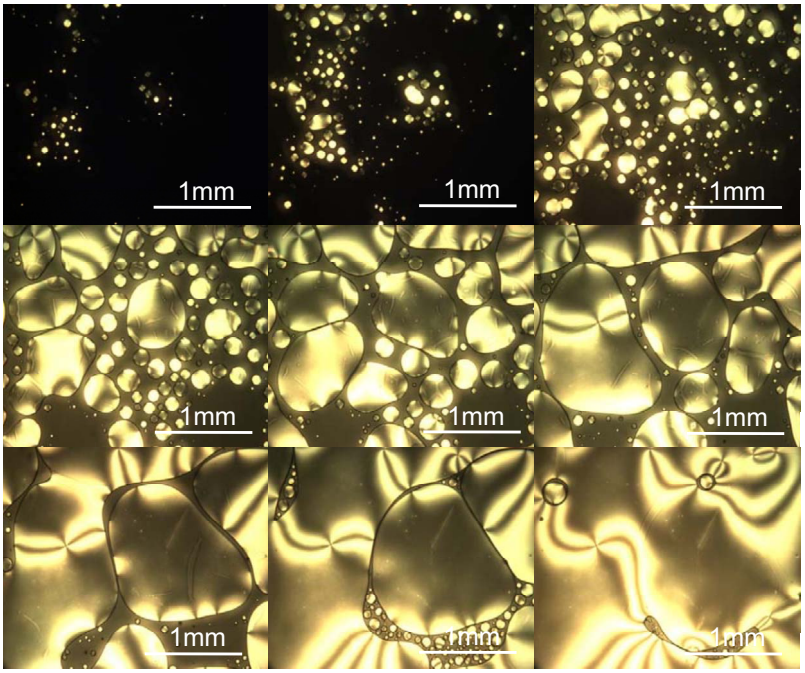

FIG. 3. (Color online) POM micrographs showing nucleation and growth of the nematic phase of 5CB. Sequence of images each separated by about 15 min showing the growth of nematic domains from the isotropic phase. The cooling rate was 0.001 °C/min.

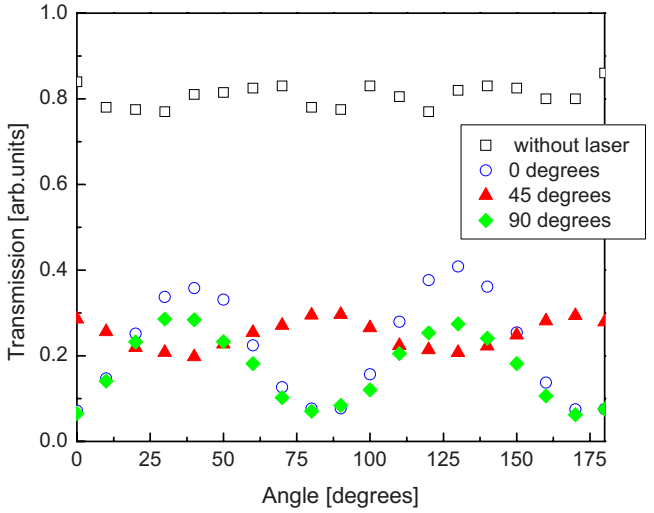

FIG. 4. (Color online) Transmission dependence on the polarizer angle of the nematic phase between crossed polarizers. Symbols represent different polarization angles of the incident linearly polarized pump pulses with respect to the laboratory horizontal. The transmission scale is in arbitrary units.

laser by rotating the polarizer and analyzer through 180° in increments of 10°, always keeping the polarizer and analyzer crossed at 90°, and recording the transmitted probe laser intensity as a function of the polarizer angle. The results are shown in Fig. 4.

Although we used a quarter-wave plate to ensure constant probe laser intensity when rotating the first polarizer, the intensity varied slightly with the polarizer angle. Therefore, we recorded the probe laser signal as a function of the polarizer angle with the sample and analyzer removed, to generate a correction function. Signals obtained with the sample and analyzer in place were normalized by this function to correct for angular variations in the probe laser intensity.

For spontaneous nucleation there was a very weak dependence of transmission as a function of angle, indicating an approximately random average director orientation in the sample. For the laser-induced nucleation, there was a strong sinusoidal dependence of intensity on the angle, indicating a preferential alignment of the average director. In all cases, the intensity maximum was shifted in phase by about 45° from the angle of the pump polarization, which is consistent with the induced average director alignment being parallel to the plane of pump polarization. This sinusoidal dependence was reproducible, although the modulation depth varied considerably from run to run.

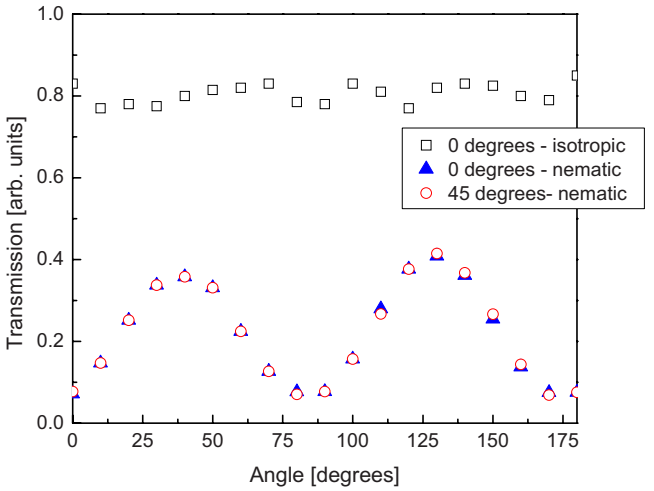

FIG. 6. (Color online) Angular dependence of transmission through the nematic phase between crossed polarizers when the laser illuminates the isotropic or nematic phase only. Solid triangles correspond to the sample exposed to the pump laser polarized at 0° throughout the cooling process. Open circles correspond to the same ordered nematic sample at 20 °C later exposed to the pump laser polarized at 45°. Open squares correspond to the sample exposed to the pump laser polarized at 0° during the cooling run, but only while the sample is in the isotropic phase. The pump laser was shut off before nematic droplets appeared, as determined by the first detectable decrease in the transmitted intensity of a probe laser. Transmission scale is in arbitrary units.

Figure 5 shows polarized optical micrographs obtained from nematic samples that nucleated with and without exposure to laser pulses. The samples were heated to the isotropic phase and cooled to 34 °C at a cooling rate of 0.001 °C/min. One sees a large number of disclinations without the laser, but almost uniform texture with the laser, consistent with the transmission data shown in Fig. 4.

Additional cooling experiments were performed in which only the stable isotropic phase was exposed to the pump laser. In that case, the transmission behavior was indistinguishable from that in the absence of the laser. Additional experiments were performed by reexposing an ordered, laser-induced nematic phase to a pump laser with various polarization directions. In those cases, the transmission behavior was indistinguishable from that obtained from the nematic phase before reexposure to the laser (see Fig. 6); the nematic order is apparently unaffected by the second pump-laser exposure.

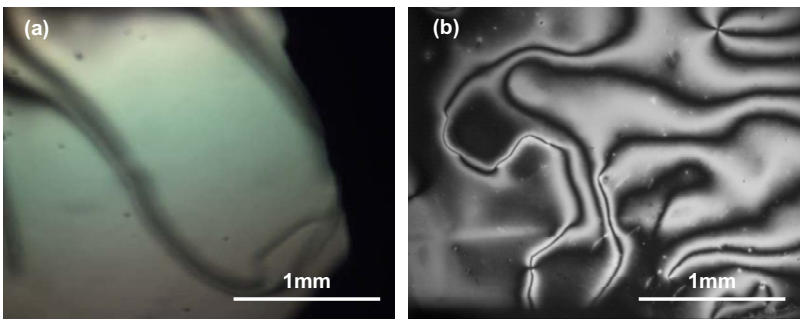

FIG. 5. (Color online) Polarized optical micrograph of the 5CB nematic phase obtained between cross polarizers. (a) with laser and (b) without laser. The cooling rate was 0.001 °C.

D. Discussion

For a nematic liquid crystal with homeotropic alignment and strong surface anchoring, there is a threshold CW laser intensity below which no molecular reorientation is induced, given by [14]

$$I_{th} = \frac{\pi^2 c K n_e^2}{d^2 n_o (n_e^2 - n_o^2)},$$

where c is the speed of light, n_o and n_e are the ordinary and extraordinary refractive indices, K is a Frank elastic constant, and d is the sample thickness. For a cw pump laser, the threshold intensity for laser-induced director reorientation in the nematic phase is about 100 W/cm^2 [9]. The threshold of optical-field-induced director reorientation in planar cells, such as our samples, is about four orders of magnitude greater [15] because of the tendency of the polarization of the optical field to follow the the principal axes of the dielectric tensor. Nematic liquid crystals with homeotropic alignment can reorient when exposed to 20 ns laser pulses, but the threshold intensity is considerably higher ($\sim$100 MW/cm^2) [8], because the liquid crystal response to the light is weaker by approximately the factor of the ratio of the laser pulsewidth to the nematic reorientation time. The reorientation response to 45 ps laser pulses is expected to be even weaker, by an additional factor of $\sim 0.5 \times 10^3$, and the threshold for reorientation with picosecond pulses is expected to be higher by this same factor. Thus, the laser intensity of 3.9 MW/cm^2 in our experiments is more than four orders of magnitude too small to induce nematic reorientation. While our geometry is homogeneous rather than homeotropic, and the surface anchoring is weak rather than strong, we would still expect our pump laser pulses to be much too weak to induce realignment of the bulk nematic liquid crystal, and this is consistent with our experimental observations. The absorption coefficient of 5CB at 532 nm is 0.1 cm^{-1} [14], so the heat absorbed by the sample from the pump laser is negligible ($\sim$0.5 μW). We therefore conclude that the observed alignment in our laser cooling experiments is due to the effects of laser light on the emergence of the nematic phase.

It is well known that optical fields can induce nematic order in the isotropic phase [15], the degree of order is given by [14]

$$S(t) = \frac{\rho \Delta\alpha}{3 \nu c \varepsilon_0 n_i} \int_{-\infty}^{t} I(t') e^{-(t-t')/\tau} dt',$$

where ρ is the number density, $\Delta\alpha$ is the polarizability anisotropy, ν is a viscosity coefficient, τ is the response time, ε_0 is the permittivity of the vacuum, and n_i is the refractive index of the isotropic phase. The response time depends on temperature, and is given by

$$\tau = \frac{\nu}{a_o (T - T^*)},$$

where a_o is a material constant with the units of energy density and T^* is a critical temperature, slightly below the nematic-isotropic transition temperature T_{NI}. Our conjecture is that, as the isotropic phase is cooled, nematic fluctuations parallel to the polarization of the pump beam are enhanced and nematic order is induced. Above nematic-isotropic transition temperature, nematic domains form and decay via fluctuations. Slightly below the nematic-isotropic temperature, the enhancement of nematic order by the laser leads to the preferential nucleation of domains whose directors are along the polarization of light and whose size is greater than the critical size. We are not aware of detailed models of nematic droplet nucleation. Both experimental observations and simple estimates, based on dimensional analysis, of the critical droplet size suggest that it is of the order of micrometers [16]. Thermal fluctuations are not expected to appreciably reorient such large domains during growth. Such domains will therefore grow, and lead to bulk nematic alignment parallel to the laser light. We call this process laser-induced nucleation of the nematic phase.

IV. CONCLUSIONS

We have demonstrated that linearly polarized picosecond laser pulses can induce nucleation of the nematic phase from the supercooled isotropic phase in 5CB aligned with the director parallel to the electric field of the incident laser light. These results provide evidence that nonphotochemical laser-induced nucleation involves the optical Kerr alignment of molecules, and that it is a general phenomenon that can occur in a variety of symmetry-breaking phase transitions.

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