Organic Glasses with Tunable Liquid-Crystalline Order

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Liquid crystals (LCs) are known to undergo rapid ordering transitions with virtually no hysteresis. We report a remarkable counterexample, itraconazole, where the nematic to smectic transition is avoided at a cooling rate exceeding 20 K/s. The smectic order trapped in a glass is the order reached by the equilibrium liquid before the kinetic arrest of the end-over-end molecular rotation. This is attributed to the fact that smectic ordering requires orientational ordering and suggests a general condition for preparing organic glasses with tunable LC order for electronic applications.

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Thermotropic liquid crystals (LCs) undergo rapid phase transitions with changing temperature. These transitions are usually so fast that nearly no supercooling is observed. This allows LCs to serve as standards for temperature calibration at fast cooling rates (up to 2×10^4 K/s) [1,2]. Standard theories of LC transitions [3–5] do not include time as a variable, effectively assuming instantaneous transformations. We report here that the system itraconazole (ITZ) is exceptional in this regard. At slow cooling, the isotropic liquid transforms to a nematic phase and then a smectic phase, but at fast cooling, smectic ordering can be avoided altogether or avoided partially to produce glassy solids with variable smectic order. There have been reports of cooling an LC phase to form a glass that inherits the structural order in the liquid state [6–9], but to our knowledge, there have been no reports of circumventing an LC transition by fast cooling to produce glasses without the equilibrium LC order. This system provides insight on the nature of molecular motions responsible for smectic ordering and suggests a general condition for producing glasses with tunable LC order for applications in organic electronics [10–12].

We first describe the smectic ordering in an equilibrium liquid of ITZ. As Fig. 1(a) shows, upon cooling at 0.16 K/s, an isotropic liquid of ITZ (99% pure from Alfa Aesar) transforms to a nematic phase ($T_{N/I} = 363$ K) and then to a smectic phase ($T_{\mathrm{Sm}/N} = 347$ K) [13–15]. In the nematic phase, the molecules are aligned with their long axes approximately parallel to each other, while in the smectic phase, the molecules are further organized into layers [Fig. 1(a)]. Further cooling transforms the smectic liquid to a glassy solid ($T_g = 328$ K). Upon reheating, the transitions noted above are reversed, indicating their reversibility. The process of smectic ordering was confirmed by x-ray scattering [Fig. 1(b)] [14,16]. ITZ was placed in a capillary tube (0.7 mm diameter) and measured in the transmission mode (Bruker SMART APEX2 diffractometer with a Cu $K\alpha$ source) [17,18]. The sample was unaligned (no preferred orientation) as shown by the uniform rings in the 2D scattering pattern. In Fig. 1(b), the integrated scattering intensity over all azimuthal angles is plotted as a function of momentum transfer $q = 4\pi \sin\theta/\lambda$. Smectic ordering is evident from the appearance of the scattering peak at $q = 0.2$ Å^{-1}, along with its overtone at 0.4 Å^{-1}. This indicates smectic layers with a spacing of 31 Å, roughly the length of an ITZ molecule [14,19]. In Fig. 1(c), the area of the 0.2 Å^{-1} peak I is plotted as a function of temperature. At the cooling rate used (5 mK/s), I increases steadily below $T_{\mathrm{Sm}/N}$ down to ~330 K and plateaus at lower temperatures. The increase is well described by the power law $I = I_0\,[(T_{\mathrm{Sm}/N} - T)/T_{\mathrm{Sm}/N}]^x$, where $x = 0.67$ and $T_{\mathrm{Sm}/N} = 349$ K, as shown by the curve in Fig. 1(c). We have normalized the value of I by I_0 obtained from power-law fitting. The value of I is a measure of the smectic order according to $\Sigma \propto I^{1/2}$, where Σ is the amplitude of density modulation of the smectic layers [17]. The exponent $x = 0.67$ for ITZ is larger than the literature values for smectic LCs: $x = 0.17$ for 8CB [18], 0.20 for 8OCB [18], and 0.24 for cholesteryl nonanoate [17]. This means that smectic order rises more slowly with cooling in ITZ than in other systems. We performed the same experiment described above with 8CB and obtained $x = 0.21$, confirming the literature value. According to Ref. [18], the ratio I/I_0 can be directly related to the smectic order parameter $I/I_0 = \Sigma^2$, where $\Sigma = 1$ corresponds to "perfect" smectic ordering in the absence of thermal fluctuation. By this relation, our sample in Fig. 1(c) reaches a maximal smectic order of $\Sigma = 0.4$ when cooled at 5 mK/s.

The increase of smectic order with cooling is halted near 330 K and, with further cooling, the smectic order plateaus, even decreasing slightly. This indicates that the system has fallen out of equilibrium and its smectic order is frozen in a

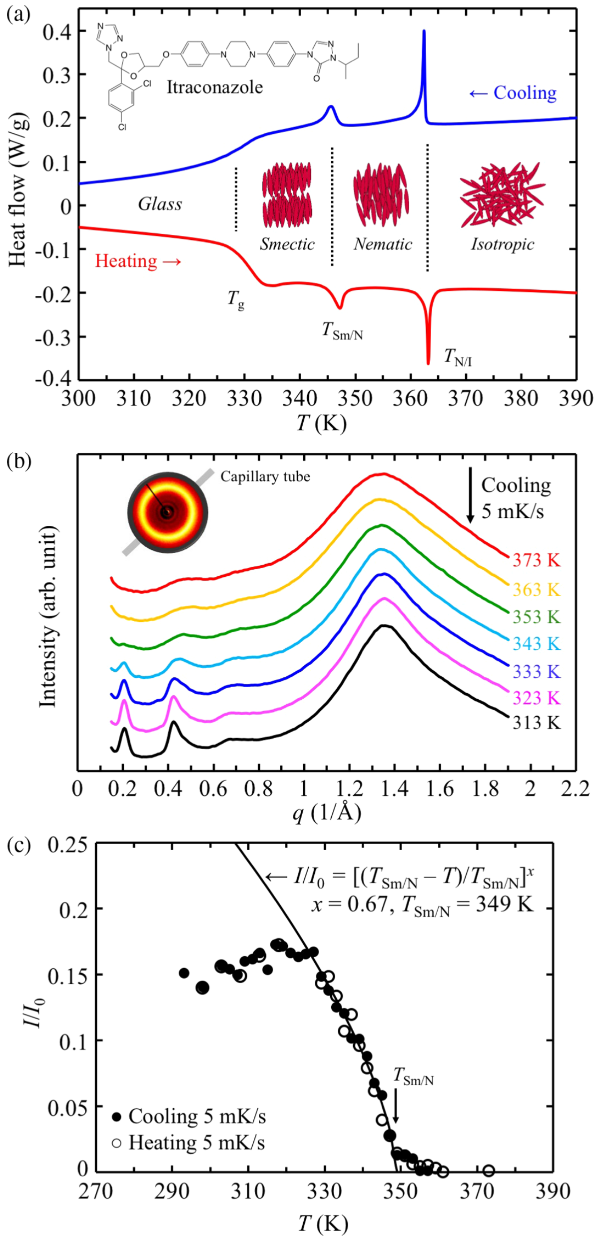

FIG. 1. (a) DSC traces of ITZ during cooling and reheating at 0.16 K/s. Note the isotropic-nematic transition ($T_{N/I} = 363$ K), the nematic-smectic transition ($T_{\mathrm{Sm}/N} = 347$ K), and the glass transition ($T_g = 328$ K). (b) X-ray scattering patterns recorded during cooling at 5 mK/s. The 2D image of x-ray scattering confirms absence of preferred orientation. (c) Area of the $q = 0.2$ Å^{-1} peak as a function of temperature during cooling and reheating. The curve is the power-law fitting of the high-temperature data (equilibrium liquid).

glassy state. (The slight decrease of smectic order with cooling in the glassy state might be related to tension [20] caused by the larger thermal expansion of ITZ relative to the silicate container [21].) Upon reheating [open symbols in Fig. 1(c)], the smectic order retraces the cooling curve; that is, the order remains frozen in the glassy state and decreases in the fluid state as T approaches $T_{\mathrm{Sm}/N}$. This latter result indicates that, above 330 K, our measurement obtains the equilibrium smectic order, since the same order is observed during cooling and reheating. This conclusion is further supported by the result of Benmore *et al.* [16] who performed similar measurements on ITZ, but without a reheating step, using a larger capillary tube (2 mm in diameter) and slower cooling rate (2 mK/s). They found a similar increase of smectic order with cooling; our fitting of their data to a power law yields $x = 0.68$ and $T_{\mathrm{Sm}/N} = 349$ K, in excellent agreement with our value.

We now show that cooling at different rates can prepare ITZ glasses with and without smectic order. Figure 2(a) shows the x-ray scattering patterns of ITZ glasses prepared at several cooling rates R_c. At a low R_c, the $q = 0.2$ Å^{-1} peak is present, indicating smectic order, but the peak decreases and eventually vanishes with increasing R_c. For each as-prepared glass, smectic order is relatively stable in the glassy state, as the order remains frozen during heating within the glassy state and evolves with temperature only after the sample enters the equilibrium liquid state. This latter behavior is already seen in Fig. 1(c) and is shown again in Fig. 2(b). Here the glass was prepared by cooling at 18 K/s to be free of smectic order [the red trace in Fig. 2(a)]. Upon heating (red triangles), no smectic order was observed up to 328 K. Upon further heating, the smectic order reached a maximum and, above 340 K, assumed the equilibrium value established above in Fig. 1(c) [replotted in Fig. 2(b)].

In Fig. 2(c), the ratio I/I_0 for each as-prepared glass (measured at 298 K) was plotted as a function of R_c. The two curves are model predictions to be discussed later. It is evident that a range of smectic order can be obtained by preparing an ITZ glass at different cooling rates, with $I/I_0 \approx 0.14$ for the slowest cooling rates used and $I/I_0 = 0$ for $R_c > 20$ K/s. The corresponding range for the smectic order parameter $\Sigma = (I/I_0)^{1/2}$ is from 0.4 to zero [18].

We now consider why cooling at different rates can trap different smectic order in the glass of ITZ. We argue that the smectic order obtained is the order reached by the equilibrium liquid before the kinetic arrest of the end-over-end molecular rotation. The formation of smectic layers not only introduces translational order, but also increases orientational order. For ITZ, the orientational order parameter $S = \langle 3/2 \cos^2\theta - ½\rangle$, where θ is the angle between the molecule's long axis and the nematic director, rises sharply at the isotropic-to-nematic transition and has another jump at the nematic-to-smectic transition (from 0.5 to 0.75) [14]. This increase of orientational order during smectic ordering is a general prediction of the mean-field theory of liquid crystals [4]. Thus, to form smectic layers, the average molecule must reorient relative to the director (while simultaneously adjusting its center of mass). This orientation occurs through a rotation about the short axis (end over end), since the mere spinning about the long axis or the

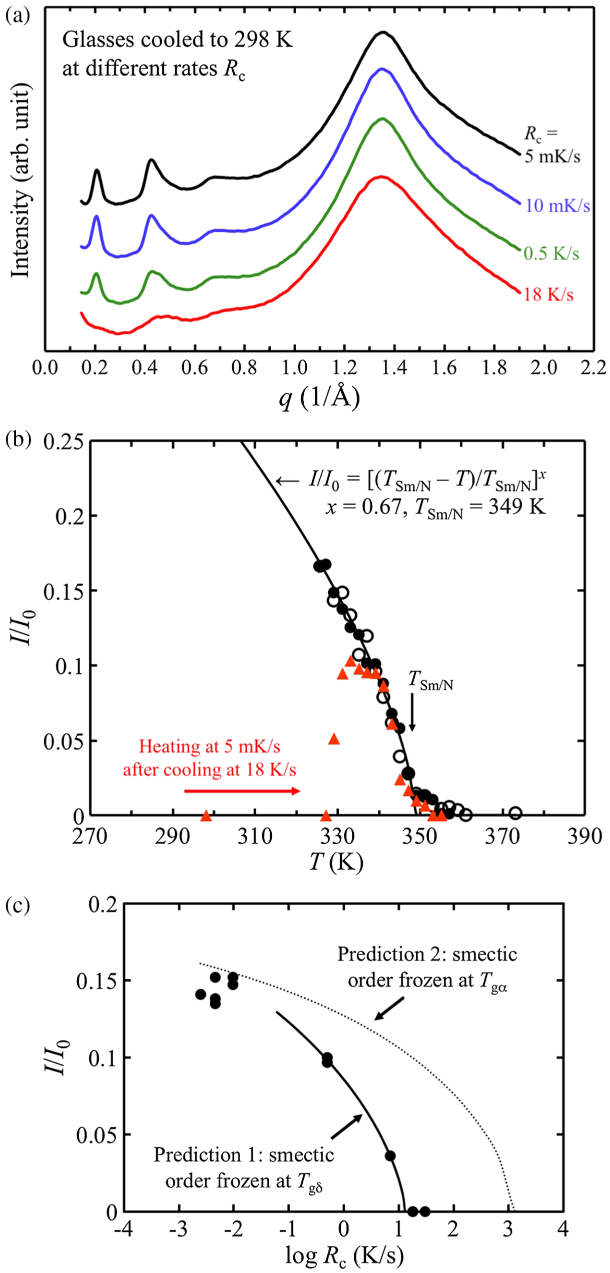

FIG. 2. (a) X-ray scattering of ITZ glasses prepared at different cooling rates R_c. Slow-cooled glasses show smectic scattering at 0.2 and 0.4 Å^{-1}, but fast-cooled ones do not. (b) Formation of smectic order in a fast-cooled ITZ glass ($R_c = 18$ K/s) during heating (red triangles). The solid and open circles are from Fig. 1(c) and represent equilibrium smectic order. For this fast-cooled sample, smectic order was initially absent, but developed above 328 K. Above 340 K, the system reached equilibrium. (c) Smectic order of glasses prepared at different cooling rates. The curves are predictions assuming smectic ordering is controlled by different molecular motions (see text).

precession of the long axis about the director does not change the order parameter S.

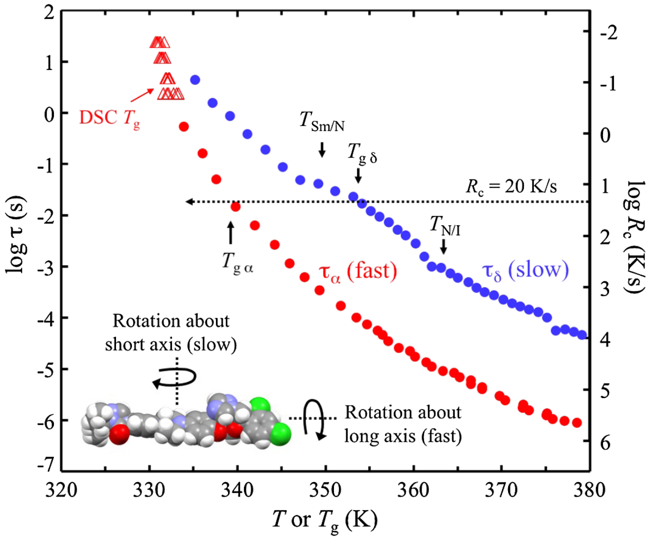

FIG. 3. Fast (red circles) and slow (blue circles) relaxation processes in ITZ from dielectric spectroscopy (Ref. [14]). DSC T_g onset (triangle) is shown as a function of cooling rate R_c (right axis). The two y axes are related by $\tau R_c = 0.4$ K.

The rates of molecular rotations in a liquid crystal can be obtained by dielectric spectroscopy [22]. Similar to other LCs [9,23,24], ITZ shows two relaxation processes (Fig. 3) [14,25]. The fast process has been associated with the glass transition detected by differential scanning calorimetry (DSC) [14,23] and is termed the α process. This process is attributed to molecular rotation about the long axis and precession of the long axis about the nematic director, whereas the slow process (called the δ mode) is attributed to molecular rotation about the short axis (end over end). The rates of the two processes can be significantly different in a liquid crystal; this is a result of a nematic potential that favors the alignment of the long axis along the director and reduces the average rate of end-over-end rotation [26].

The existence of two relaxation modes (α and δ) means that there are two glass transition temperatures for a given cooling rate R_c, $T_{g\alpha}$, and $T_{g\delta}$. Each T_g can be obtained from the condition $\tau\,(T_g)\,R_c = C$, where $\tau\,(T_g)$ is the relaxation time at T_g and C is a constant [27,28]. For ITZ, we find $C \approx 0.4$ K from its DSC T_g (onset) measured on cooling and the corresponding τ_α value (the two data sets were extrapolated slightly to overlap in temperature). In Fig. 3, the DSC T_g is plotted using the second y axis for R_c. Note the smooth connection of the DSC T_g with the τ_α curve (but not the τ_δ curve), which supports the previous assignment [14,25] that the DSC T_g is associated with the fast dielectric relaxation. The value $C = 0.4$ K for ITZ agrees with that for the non-LC glass former indomethacin ($C = 0.5$ K) [29,30], but note that C depends on the definition of T_g; for example, for DSC T_g measured on heating, $C \approx 2$ K [31].

Using the same condition of kinetic arrest, we obtain the glass transition temperature $T_{g\delta}$ for the end-over-end rotation for each cooling rate. According to our hypothesis, at each cooling rate, equilibrium smectic order is obtained as long as the temperature is above $T_{g\delta}$ and the maximal smectic order is given by $I/I_0 = [(T_{\mathrm{Sm}/N} - T_{g\delta})/T_{\mathrm{Sm}/N}]^{0.67}$. This result is shown in Fig. 2(c) as the solid curve. The prediction accurately reproduces the observed smectic order as a function of cooling rate with no adjustable parameters. This provides strong support for the notion that the end-over-end molecular rotation controls smectic ordering. Above the critical cooling rate of ~20 K/s, the end-over-end rotation is kinetically arrested above $T_{\mathrm{Sm}/N}$, frustrating smectic ordering. At slower cooling rates, smectic order can develop up to the value at $T_{g\delta}$. To further test our hypothesis, we calculate the smectic order expected with the alternate assumption that the ordering process is limited by the kinetic arrest of the fast α relaxation at $T_{g\alpha}$. The result of this calculation is shown as the dotted curve in Fig. 2(c). Clearly, this prediction deviates from the experimental results.

In conclusion, contrary to the notion that it is difficult to supercool LC transitions, we have shown that smectic ordering in ITZ can be frustrated and even eliminated by increasing cooling rate, enabling the formation of glasses with different smectic order. The smectic order parameter Σ is tunable over a significant range (0–0.4). The smectic order trapped in the glass at a given cooling rate corresponds to the order reached by an equilibrium liquid before the kinetic arrest of the end-over-end molecular rotation. This arises because a significant increase in nematic order must occur at the formation of smectic layers. Our result suggests that, at fast enough cooling, all smectic ordering can be arrested, with the critical cooling rate given by the T_g for the end-over-end rotation. For 8CB, the critical cooling rate is estimated to be 10^7 K/s, just above the current capability of fast DSC [2] and below that of computer simulations [32]. Since an isotropic-to-nematic transition also requires an increase of nematic order, our argument for the freezing of smectic order should apply to nematic ordering as well. For ITZ, the critical cooling rate to frustrate nematic ordering is predicted to be ~1000 K/s. This study suggests a need for LC theories in which both thermodynamics and kinetics are considered in describing the evolution of order parameter. These findings are relevant for creating glasses with tunable LC order for organic electronics and motivate other modes of glass preparation where molecular relaxation can be controlled [33,34].

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