DYNAMICS IN THE PRETRANSITIONAL ISOTROPIC PHASE
OF PENTYLCYANOBIPHENYL
STUDIED WITH SUBPICOSECOND TRANSIENT GRATING EXPERIMENTS

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Transient grating optical Kerr effect measurements in the isotropic phase of the nematic liquid crystal pentylcyanobiphenyl (5CB) are presented. Subpicosecond time resolution permits the first direct investigation of the time correlation function for the local molecular dynamics of the molecules within the pseudonematic domains. Intradomain molecular relaxation is nonexponential with relaxation rates ranging from 1/1 ps to 1/300 ps. The decay characteristics are *temperature independent* to temperatures 35°C above the nematic–isotropic phase transition reflecting a decoupling of the local dynamics from the bulk viscosity.

1. Introduction

The isotropic liquid phase of nematogenic substances is characterized by considerable short range order [1]. Although macroscopically isotropic, orientational correlation between the molecules persists over a coherence length, $\xi(T)$, much larger than the molecular size. This local correlation can be visualized as microscopic pseudonematic domains in the isotropic phase.

As a consequence of this coherence length, $\xi(T)$, many static and dynamic physical properties show pretransitional behavior. Parameters, which characterize these physical properties, diverge if one lowers the temperature toward T^*, which is slightly below the nematic–isotropic phase transition T_{ni}, as expected from the Landau–de Gennes model [1,2]. One of these parameters is the collective reorientational relaxation time, τ_c, measured with dynamic light scattering (DLS) [3] and the optical Kerr effect (OKE) [4–6]. In the pretransitional region right above T_{ni}, $\tau_c \propto 1/(T-T^*)$ as predicted by the Landau–de Gennes model, i.e. as $\xi(T)$ increases the reorientation slows dramatically because of collective interactions.

Early on Flytzanis and Shen argued [7] that, besides the well-established slow collective dynamics arising from fluctuations of the order parameter, the reorientational motion in the pretransitional region should have fast contributions from local molecular reorientation. These fast contributions could actually be seen in dynamic light scattering [8] and optical Kerr effect experiments [9,10]. Because of the limited resolution in these experiments, however, the effect could only be established, and questions about the general characteristics of the correlation function for the molecular dynamics or its change with temperature could not be addressed.

In this Letter detailed experiments are presented which analyze the fast contributions to the correlation function and elucidate the time dependence of the local molecular dynamics in pseudonematic domains. By using transient grating experiments [10] it is possible to examine dynamics over the necessary broad range of time scales, i.e. from subpicosecond to tens of nanoseconds. Frequently, dynamics in liquids are discussed in terms of reorientational motions. However, OKE and DLS data provide measurements of a collective correlation function, which, in addition to rotational dynamics, monitor interaction- or collision-induced (CI) phenomena. The

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possible role of CI phenomena in the measurements presented below is discussed in section 3.

Although refined models have been discussed [11], reorientational dynamics in regular liquids can generally be described by a Debye-type small step diffusional model and hydrodynamic theory [12,13]. In a Debye model, the reorientational time correlation function is given by a sum of exponentials with decay constants $\tau_{rot,i}$ corresponding to the interactions between the molecule probed and the surrounding molecules. For hydrodynamic boundary conditions, the Debye–Stokes–Einstein (DSE) equation shows that this interaction can be described by the bulk viscosity, η, of the liquid and an effective volume, V_{eff}, of the rotating molecule:

$$\tau_{rot,i} = V_{eff,i} \eta / kT . \tag{1}$$

η depends exponentially on temperature. There is a linear relationship between the reorientational relaxation time and η/T; a fact which has been confirmed by a multitude of experiments [12,15].

As will be shown below, dynamics of molecules within pseudonematic domains of 5CB cannot be explained in the manner described above. The orientational correlation in the domains establishes a local structure that is stable on the timescale of the fast molecular dynamics. The stable local structure provides an anisotropic potential within which a molecule moves. As demonstrated by the results presented in this Letter, the ordered liquid structure influences the dynamics and gives rise to deviations from hydrodynamic theory.

There have been a large number of investigations of the local order and molecular reorientation in nematogenic substances using NMR [16] and ESR [17]. These investigations have either studied the motion of small solute molecules dissolved in the nematic or isotropic pretransitional phase [18–20] or considered the nematic phase [21]. The spin relaxation techniques provide a large amount of detailed information about single molecules rotational dynamics in liquid crystalline systems. These experiments, however, require assumptions about the form of the reorientational correlation function and the coupling of the spins to the molecular motions before information about dynamics on a picosecond timescale can be extracted from data. On the other hand, the OKE experiments to be described here, as well as DLS techniques, give direct model-free access to the correlation function or its Fourier transform.

Recently, a transient grating (TG) OKE approach was used to perform a temperature-dependent study of the reorientational dynamics [10] of neat biphenyl and biphenyl in solution [22]. Because of the similarities of the biphenyl and 5CB molecules a comparison with the biphenyl study can provide insights into the nature of molecular dynamics. Besides an ultrafast component (100 fs timescale) associated with librational damping/dephasing, the biphenyl experiments revealed two reorientational relaxation components. The slower one was associated with the tumbling motion of the molecule around its short axes, the fast one with motion around the long axis. Both components are accurately described by eq. (1).

The biphenyl study also demonstrated another point. DLS and TG-OKE experiments in principle contain the same information [23]. However, depending on the specific situation, one of the methods can be advantageous. Whereas the TG-OKE study of biphenyl exhibited two reorientational relaxation components following the ultrafast growth and decay of the precursor librational motions [22], a comparable DLS investigation [24] gave a single Lorentzian, corresponding to the slowest reorientational component. This illustrates that when there are several decay components, a time-resolved study can more readily observe the faster phenomena. The TG-OKE technique has another feature not found in DLS or conventional OKE experiments. As demonstrated by Etchepare et al. [25] and recently more generally [26], it permits the separation and identification of physical processes which are characterized by different symmetries of $\chi^{(3)}$. This feature of the TG-OKE experiment makes it possible to suppress the contribution of the electronic OKE to the signal and to study solely the molecular dynamics giving rise to the nuclear OKE. Like DLS, it also allows the separation of the isotropic CI phenomena from the single molecule rotational motion and anisotropic CI contributions.

The TG signal is proportional to the square of the sample response function G [10,22,23]

$$S(\tau) \propto G^2(\tau) . \tag{2}$$

Therefore, in the analysis of complex TG data it is

useful to take the squareroot of the signal before further manipulation.

2. Experimental procedures

The experiments were performed with a subpicosecond dye laser system which is described in detail elsewhere [27]. With a DCM dye the laser system generates tunable 150–200 fs pulses with pulse energies of 10–20 μJ at a 1 kHz repetition rate.

A schematic of the TG set-up is shown in fig. 1. As described in detail previously [26], the set-up provides control of the polarization of both excitation beams, the probe beam, and the detected signal. Thus it is possible to monitor exclusively the contribution of the desired physical processes to the TG signal. To avoid two-photon absorption in the 5CB sample, which becomes significant at shorter wavelengths [26], an excitation and probe wavelength of $\lambda = 665$ nm was used. Careful laser power and wavelength studies demonstrated that the results are free of artifacts.
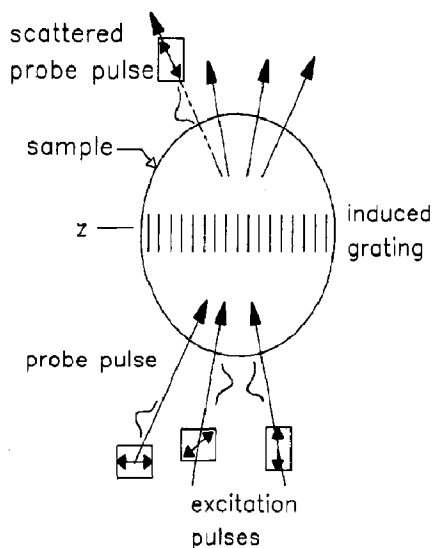

Fig. 1. Schematic illustration of the transient grating experiment. The crossed excitation pulses generate a periodic Kerr effect alignment in the sample with the wavelength of the optical interference pattern. The resulting changes in the index of refraction create a diffraction grating which Bragg scatters the probe pulse. The polarizations of all four pulses are controlled in the experiment and are used to separate various contributions to the signal.

The extensively filtered pentylcyanobiphenyl (5CB) liquid was placed in a 1 mm spectrophotometric cuvette which was inserted into a variable temperature sample holder. The sample temperature could be measured and controlled within $\pm 0.2\,^\circ$C. The experiments described here were performed in the isotropic phase of 5CB (nematic–isotropic phase transition temperature $T_{ni} = 35\,^\circ$C).

3. Results and discussion

The data in figs. 2a–2c show typical TG-OKE results obtained in the 5CB sample at 41.7°C, i.e. about 7°C above the nematic–isotropic phase transition. The three plots depict the OKE behavior on three different timescales. The ultrafast dynamics ($\tau < 5$ps) in fig. 2a have been recorded with polarization configurations which allow separation of the electronic and nuclear OKE and monitoring of their respective contributions to the TG signal [26]. The plot of the electronic-only TG-OKE represents the instrument response function of the experimental set-up as the relaxation time of the electronic OKE (10^{-15} s) is fast compared to the laser pulse duration. The nuclear OKE on the subpicosecond timescale is dominated by a strong slightly delayed signal with decay constants on a 100 fs timescale. A response of this kind has been found in all ultrashort laser pulse OKE studies performed so far [22,28–31]. This response is due to a coherent excitation of molecular librations and CI interactions in the liquid. The optical pulse exerts a torque on the molecules, which react with a certain inertial delay. The induced anisotropy then decays because of thermalization and dephasing of the librations. As has been discussed in detail recently [22], this ultrafast librational dynamics gives rise to the anisotropy which decays on slower timescales by reorientational diffusion. Possible contributions from CI phenomena and coupling between rotational and translational degrees of freedom are discussed below.

The dynamics are shown in fig. 2b on a timescale which is compressed by two orders of magnitude compared to fig. 2a. The large dynamic range of the observed dynamical phenomena is emphasized by fig. 2c which shows the OKE decay on a timescale compressed by another order of magnitude. The data
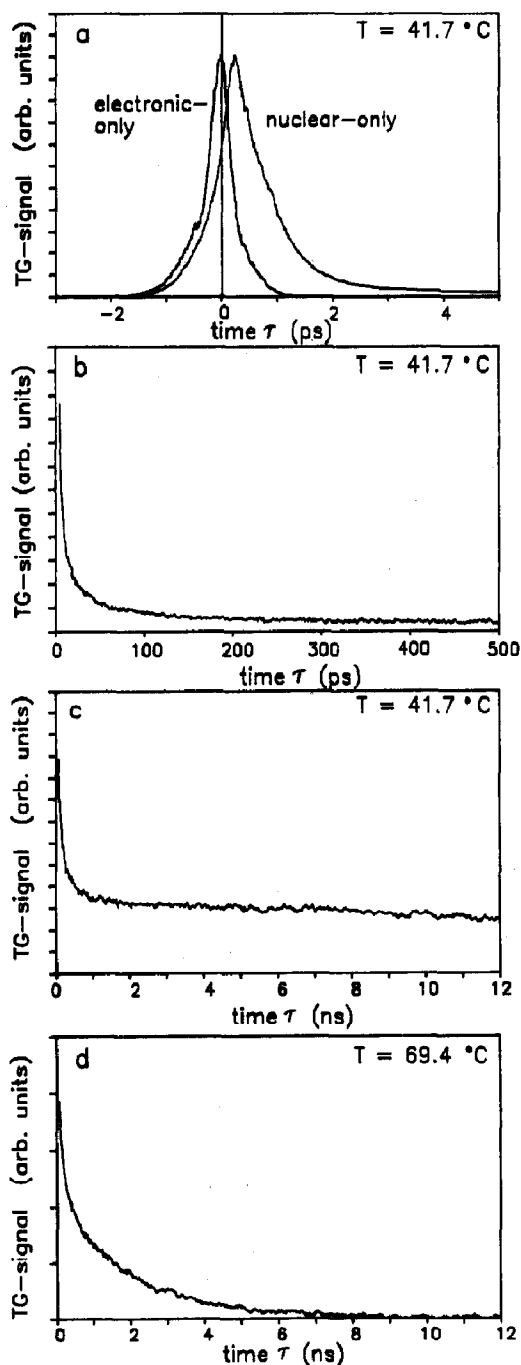
Fig. 2. Optical Kerr effect transient grating signals $S(t)$ for a pentylcyanobiphenyl (5CB) sample (a–c) $T=41.7°C$, (d) $T=69.4°C$. (a) Ultrafast timescale behavior. Signals 1 and 2 are recorded with the electronic-only nuclear-only TG-OKE polarization configurations, respectively [26]. (b) Intermediate timescale behavior of the signal, recorded with the crossed grating configuration. (c) and (d) Slow timescale behavior of the signal, recorded with the crossed grating configuration at two temperatures.

in figs. 2b and 2c were recorded with a crossed grating configuration, which suppresses any contribution from laser-induced phonons [10,26]. Note that the flat part of the curve in 2a is the steep part of 2b, and the flat part of 2b is the steep part of 2c.

The plot in fig. 2c suggests a change in the nature of the dynamics for $\tau < 1$ ns and for τ on the slower, nanosecond timescale. The $\tau > 1$ ns data can be fit by a single exponential with a decay constant $\tau_c = 60 \pm 10$ ns. The large error margin is due to the limited extent of the probe delay τ, which is small compared to the decay time. We have performed the same kind of TG-OKE experiments on the 5CB sample with 1064 nm 100 ps excitation pulses and much longer probe pulse delays. These measurements clearly established the monoexponential character of the nanosecond timescale decay and reduced the error margin [32]. The value of the decay time τ_c is in good agreement with earlier long time scale measurements ($t > 10$ ns) of the OKE in 5CB [33]. This decay is the collective reorientation time associated with the pseudonematic domains.

The emphasis of this Letter is on the relaxation dynamics on the intermediate timescale 3 ps $< \tau < 1$ ns, which characterize local motions within the pseudonematic domains. To analyze these data, we have taken the squareroot of the TG signal in figs. 2a–2c, which is proportional to the sample response function, and we have subtracted the slow timescale exponential decay, discussed in the preceding paragraph. The response function that is obtained from this procedure contains only intermediate timescale local molecular dynamics. A semilogarithmic plot of this reveals a distinct nonexponential character with time constants between 1 and 300 ps, that is not suitable for presentation in a semilog plot. If a single exponential is forced through the slowest part of a semilog plot, a decay constant of ≈ 300 ps is obtained. To depict the entire intermediate timescale dynamics and illustrate the broad range of decay constants the data are presented with a double logarithmic representation in fig. 3. The actual data decayed over 15 factors of e. Therefore, the square root of the data presented in fig. 3 varies over about 7 factors of e. The plot appears essentially linear over ≈ 1.5 orders of magnitude change in time. For $\tau > 100$ ps it starts to deviate because of a slowest decay constant of ≈ 300 ps, and for very short times, $\tau < 3$ ps,
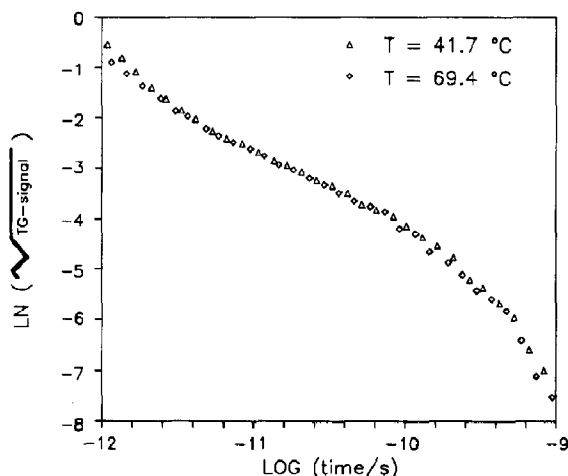
Fig. 3. Intermediate timescale dynamics of 5CB at $T=41.7°C$ and $T=69.4°C$. Double logarithmic plot of $\sqrt{S(t)}$ after subtraction of the slow timescale collective reorientation exponential decay. The bulk viscosities at these temperatures are 18.35 and 6.35 cP, respectively.

the decay may still be influenced by the ultrafast librational dynamics and CI phenomena.

If one increases the temperature of the 5CB sample, the coherence length, ξ, and the collective reorientation time, τ_c, change rapidly; $\tau_c \propto \eta/(T-T^*)$. This is illustrated in fig. 2d which shows the slow timescale decay for $T=69.4°C$. τ_c decreases from 60 ns at 41.7°C (fig. 2c) to 4 ns at 69.4°C (fig. 2d) in accordance with theory [1,2,32].

Although the collective reorientation displays a dramatic temperature dependence, the intermediate timescale behavior is quite different. If, as before, one subtracts the slow collective contribution from the sample response function, one obtains a decay for the local relaxation dynamics at 69.4°C, which is indistinguishable from the behavior at 41.7°C. As displayed in fig. 3, the data at the two temperatures fall on the same curve. Measurements at a variety of other temperatures also fall on the same curve [32]. The deviation at very short times, $\tau < 1.5$ ps, is due to differences in the laser pulse durations when the two measurements were made and their influence on the convolution with the sample response function.

The negligible change of the intermediate time scale dynamics between $T=41.7°C$ and $T=69.4°C$ is startling. The respective viscosities of the 5CB samples at 41.7 and 69.4°C are 18.35 and 6.35 cP [34].

Hydrodynamic theory and the DSE equation (1) predict a linear relationship between τ_{rot} and η/T and therefore a change of reorientational diffusion constants by a factor of ≈ 3.

As mentioned in section 1, hydrodynamic theory has been confirmed for biphenyl, the parent of 5CB, by TG-OKE experiments performed in this laboratory using the identical equipment and techniques [22]. For the sake of comparison with the 5CB results, typical biphenyl data are shown in a double logarithmic presentation in fig. 4. The viscosities of biphenyl for the two temperatures shown, $T=124°C$ and $T=58°C$, are 0.67 and 1.93 cP, respectively. The change of the viscosities by a factor of ≈ 3 leads to a change of the reorientational decay constants by a factor of ≈ 3 [22] and, as displayed in fig. 4, a correspondingly large change in the sample response function with temperature. Note that fig. 3 covers one more decade of time than fig. 4, and still the 5CB data for the two temperatures are indistinguishable.

As mentioned in section 1, the TG-OKE experiments described in this paper measure a time correlation function of single molecules as well as higher order polarizabilities. Single molecule polarizability reflects only rotational motion whereas higher order polarizabilities are sensitive to translational and librational intermolecular motions (called CI effects). Therefore, the intermediate timescale decay
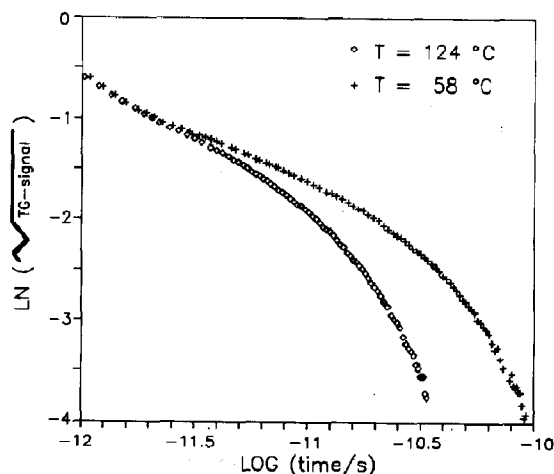

Fig. 4. Reorientational dynamics of biphenyl at $T=124°C$ and $T=58°C$. Double logarithmic plot of $\sqrt{S(t)}$ with $S(t)$ being the TG-OKE signal. The bulk viscosities of biphenyl at these temperatures are 0.67 and 1.93 cP, respectively.

could, in principle, contain contributions from single molecule rotational motion as well as intermolecular translational motion in the pseudonematic domains.

The contributions of *isotropic* CI effects [35,36] in the experiment can be inferred from the polarization dependence of the signal [26,32]. The contribution to the signal from *isotropic* CI effects is down by more than a factor of 10^6. Because the signal depends on the square of the size of the effect, the *isotropic* CI effects are less than one part in a thousand of the total OKE effect.

To estimate the importance of *anisotropic* CI effects is more difficult. To be of significance, the *anisotropic* CI effects would have to be a thousand times greater than the *isotropic* contribution. Furthermore, the type of positional correlations between molecules generally associated with CI effects would have to exist out to a time of one nanosecond. This would have to be the case if a substantial part of the intermediate time scale decay is because of CI phenomena. This seems unlikely. Intermolecular correlations would be expected to decay on a much faster timescale of a few picoseconds. Frenkel and McTague [35] have shown for small diatomic molecules that a timescale separation between rotational and intermolecular motions is generally not possible. However, an extrapolation of these results to much larger molecules is not straightforward as, e.g. the point-polarizability approximation would not seem to be good for nematogens [37]. Also, at higher temperatures, when the pseudonematic domains are becoming vanishingly small (above 85°C), the intermediate timescale decay begins to show a T dependence which scales with η/T [32]. This also suggest that the intermediate timescale decay is associated with single molecule dynamics.

While they cannot be totally ruled out, the discussion given above indicates that CI effects are not of major importance in the intermediate timescale, temperature independent decays shown in fig. 3. However, there is another type of translational effect which should be considered. The rotational and translational degrees of freedom of the molecules within the pseudonematic domains may be intimately coupled so that orientational correlation is partly transferred to positional correlation. Even in semidilute solutions of rod-like molecules, rotations

and translations are coupled. Under these circumstances a discussion in terms of single molecule *rotation* is insufficient. However, we believe that even in this case the main conclusion concerning the decoupling of local reorientation (translational) motions from the bulk viscosity, put forward in the following discussion, remains unaltered.

In contrast to a simple liquid, in the pretransitional region of 5CB reorientational relaxation takes place within an anisotropic potential of the local liquid structure which persists for times characterized by the collective reorientation time, τ_c. The timescales of local reorientational relaxation and complete local structure randomization are widely separated. The interaction of the rotating molecule with this highly correlated environment and its dynamics within this structure are independent of the bulk viscosity over a large temperature range. When the temperature is increased, the rate of structural randomization increases and the viscosity decreases. However, as long as the rate of structural randomization (the slowest component in the TG-OKE decays, figs. 2c and 2d) is long compared to the rate of local reorientational relaxation, the local relaxation is decoupled from the bulk. The local relaxation occurs on a potential surface which is essentially fixed on the timescale of the relaxation. The distinct timescales and temperature dependences of the local reorientational relaxation and the domain structure randomization suggests that the local relaxation causes the anisotropy responsible for the TG-OKE signal to decay by returning the local structures essentially to their original configurations. Once the local structures have returned to their original configurations on a picosecond timescale, the remaining anisotropy is a property of the bulk domains. It decays with τ_c, the collective reorientation time on a nanosecond timescale.

The pretransitional isotropic phase of a liquid crystal is composed of domains which are internally structured like the nematic phase. Each domain has a director. In a macroscopic volume, there are a large number of domains, and the directors point in random directions. Therefore a macroscopic volume is isotropic. The optical field induces an anisotropy which on a long timescale (> 1 ns) decays with a rate $1/\tau_c$. This is the rate of the loss of initial directional correlation among the molecules that make up a do-

main. In the isotropic phase, domains decay, and new domains are formed. The long lived anisotropy is due to a small net alignment of the domains' directors by the optical field, and it can only decay by a randomization of the domains' structures.

The intermediate timescale (3 ps $< t <$ 1 ns) anisotropy decay of 5CB is fundamentally different in nature. When the optical field is applied, the individual molecules will attempt to align with the field. The nematic structure of the domain means that the molecules have a net projection onto the director, but the individual molecules are arrayed with a spread of angles relative to the director. Depending on the director direction relative to the applied field, the optical pulse will enhance or decrease, on average, the angles relative to the director. The new structures can be thought of as characterized by local order parameters which are higher or lower than the ones consistent with thermal equilibrium.

To illustrate this idea, consider two special cases. The first is the subensemble of domains which have their directors along the applied field. The molecules will partially align with the field, and therefore the average angle made with the director will be smaller. This corresponds to a higher value of the order parameter. In contrast, consider the subensemble of domains which have their directors perpendicular to the applied field. Partial alignment with the field will make the average angle with the director greater, corresponding to a lower value of the order parameter.

In the sample there are domains with directors pointing in all directions relative to the applied field direction. Therefore there will be a broad distribution of modified order parameters. It is reasonable to postulate that the intermediate timescale dynamics are the reorientational motions (with possible associated translational motions) which restore the local structures to their equilibrium spread of angles. One is observing the relaxation to the equilibrium local order parameter. The slow timescale dynamics are the relaxation of the bulk anisotropy induced by partial orientational alignment of the domains' directors.

Although a certain degree of decoupling of local solute motions from the bulk motions in the pretransitional region of a liquid crystal has been observed in NMR experiments [18], to our knowledge temperature independent liquid crystal dynamics

have not been observed previously. We have extended the measurements described here to high temperatures ($T = 120°C$), where the coherence length decreases to a value comparable to the size of a single 5CB molecule. In these circumstances, one would expect 5CB to begin to behave as a simple liquid, and indeed we observe a change of the intermediate timescale response function with temperature. These measurements together with detailed TG-OKE data for the reorientational relaxation of 5CB in n-heptane solutions will be published elsewhere and will greatly amplify the results presented here [32].

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