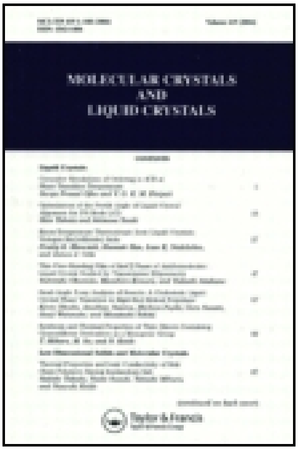

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Order and Mobility of the Fluorescent Probe 1,6-Diphenylhexatriene in a Polyester Liquid Crystal Polymer

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Order and Mobility of the Fluorescent Probe 1,6-Diphenylhexatriene in a Polyester Liquid Crystal Polymer

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We have employed time dependent fluorescence polarization to investigate a main chain semiflexible polyester type liquid crystal polymer using the fluorescent probe 1,6-diphenylhexatriene. We have obtained the second rank order parameter and the tumbling reorientational time of the probe as a function of temperature. We have found the polymer disordering to occur in a temperature range very close to the nematic-isotropic transition.

Keywords: liquid crystal polymers; time resolved fluorescence depolarization; order; mobility; DPH

INTRODUCTION

Time resolved fluorescence depolarization[1–3] has proved to be a powerful technique for investigating liquid crystals[4–9] and model membranes.[10–13] The technique consists of following the time dependence of the polarized fluorescence emitted by a suitable probe dissolved in the anisotropic system. An analysis of the fluorescence intensities and of their decay can yield order and dynamic information for the probe with a minimal perturbation of the host system, given the high sensitivity of the method and the attendant low concentration (~ 10^{-3} w/w) of the probe needed.

Although in principle quite applicable, the investigation of time dependent anisotropy has found only relatively limited application[14–18] to polymers and to

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our knowledge it has not been applied to liquid crystal polymers.[19] This is somewhat surprising since an analysis of the fluorescence anisotropy evolution can yield the second and, although not always, the fourth rank order parameter and these are of particular importance for the structural characterization of the material in a more reliable way than that offered by the often used time independent, steady state technique.[3,17,20–25] Moreover the time resolved approach can offer important information on the rotational mobility or microfluidity of the probe.

Here we report some results showing the feasibility of extending anisotropy decay experiments to the study of oriented liquid crystal polymers. In particular we consider the fluorescence polarization decays of the probe 1,6-diphenylhexatriene (DPH) dissolved in a main-chain semiflexible polyester, designated as TR-10, constituted of twin spaced *p*-oxybenzoyl diads (see Figure 1) with number-average molecular weight $\overline{M}_n$ of 27820 g mol^{-1} and ratio between weight-average and number-average molecular weight $\overline{M}_w$ / $\overline{M}_n$ of 1.73.[26]

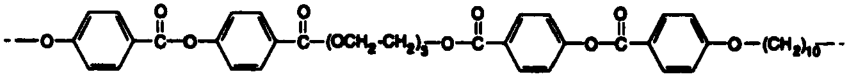

FIGURE 1 The structure of the main-chain mesogenic unit TR-10.[26]

Part of the difficulty in studying liquid crystal polymers is that of preparing suitably oriented samples. Here thin homogeneously aligned samples were prepared by carefully spreading the liquid crystal polymer on a quartz slide, obtaining a macroscopic orientation of the polymer chains parallel to the shear direction.

We have examined the order and fluidity of the polymer by determining the probe second rank orientational order parameter $\langle P_2 \rangle$ and the rotational diffusion coefficient $D_\perp$ as a function of temperature, using a suitable deconvolution procedure. Our results demonstrate the possibility of obtaining thin aligned main-chain polymeric samples and show that fluorescence depolarization can be a useful technique for investigating not only low molar mass liquid crystalline systems, but also this kind of materials.

THEORY

We consider the aligned liquid crystal polymer as providing a uniaxial anisotropic environment for the probe. Fluorescence depolarization in oriented mesophases has been theoretically described in Reference 4. The relevant equations for a cylindrically symmetric probe in a local uniaxial domain, assuming both the absorption and emission transition moments parallel to the symmetry axis and an experimental setup with forward geometry[5] with the laboratory Z axis parallel to the director, i.e. here the alignment direction of the polymer, are:

$$I_{ZZ}(t) = \left[\frac{1}{9} + \frac{4}{9}\langle P_2\rangle + \frac{4}{9}\phi_{00}(t)\right] F(t) \tag{1.a}$$

$$I_{ZX}(t) = \left[\frac{1}{9} + \frac{1}{9}\langle P_2\rangle - \frac{2}{9}\phi_{00}(t)\right] F(t) \tag{1.b}$$

where $\langle P_L\rangle$ is the L-th rank order parameter of the probe, $\phi_{00}(t)$ its long axis rotational correlation function and $F(t)$ the intrinsic fluorescence decay function.[4] These intensities give the following form for the polarization ratio $r(t) = [I_{ZZ}(t) - I_{ZX}(t)] / [I_{ZZ}(t) + 2\, I_{ZX}(t)]$ describing the anisotropy in fluorescence intensities:[4]

$$r(t) = [\langle P_2\rangle + 2\phi_{00}(t)] \;/\; [1 + 2\langle P_2\rangle] \tag{2}$$

The orientational correlation function[27] $\phi_{00}(t) = \langle D^2_{00}(\omega_0) D^{2*}_{00}(\omega_t)\rangle$, where $D^2_{00}(\omega_t)$ is the second-rank Wigner rotation matrix that gives the molecular orientation at time t, can be calculated using the diffusional model[27,28] with a $P_2 - P_4$ effective orientational potential as suggested by maximum entropy considerations:[29,30]

$$-U_{probe}(\beta, T)/kT = a_2(T)P_2(\cos\beta) + a_4(T)P_4(\cos\beta) \tag{3}$$

Here P_L (cos β) are L-th rank Legendre polynomials, β is the angle between probe symmetry axis and director and a_2 (T) and a_4 (T) are temperature dependent solute-solvent interaction coefficients. In this case we consider only a pure P_2 potential where just the first item in Equation 3 is present. Given the effective potential, the probe order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ can be calculated using the Boltzmann relations:

$$\langle P_2\rangle = \frac{1}{Z}\int_0^{\pi} P_2(\cos\beta)\exp[-U_{probe}(\beta,T)/kT]\sin\beta\, d\beta \tag{4.a}$$

$$\langle P_4\rangle = \frac{1}{Z}\int_0^{\pi} P_4(\cos\beta)\exp[-U_{probe}(\beta,T)/kT]\sin\beta\, d\beta \tag{4.b}$$

where the pseudopartition function Z is:

$$Z = \int_0^{\pi} \exp[-U_{probe}(\beta,T)/kT]\sin\beta\, d\beta \tag{5}$$

The applicability to liquid crystal polymers of the rotational diffusion model, originally developed for low molar mass systems, has been justified by various studies employing NMR and dielectric relaxation (see Reference 31 and refs therein) and in this work we shall assume its validity without further argumentation.

EXPERIMENTAL

Obtaining the fluorescence intensities I_{ZZ} and I_{ZX}, described in the previous section, requires the probe to be incorporated in an aligned sample. In practice the probe was dissolved in chloroform, a good solvent for both DPH and the polymer, and then added to the polymer at room temperature. After homogeneization the solvent was evaporated under vacuum. The alignment of the polymer proved difficult given its rubbery consistency when heated and its solid-like behaviour at room temperature. We have thus prepared thin homogeneously aligned samples by bringing the liquid crystal polymer into the isotropic phase, allowing it to cool just below the N-I transition and then suitably spreading it on a quartz slide by means of a glass rod. Adopting this simple procedure we were able to obtain a macroscopic orientation of the polymer chains parallel to the shear direction with good sample reproducibility. The alignment was checked with the help of a polarizing microscope and was found to be of good quality and stable with time during a period of at least days. The sample was thermostated by an oil circulation and the nematic-isotropic transition temperature, determined by monitoring the light intensity transmitted between cross polarizers (see Figure 2), was found to be 142 °C, in good agreement with DSC measurements.

Time-dependent fluorescence depolarization experiments were performed using the fluorescence probe DPH with a concentration of 1×10^{-3} g DPH/g TR-10. No miscibility problem or evidence of segregation of probes was found at this concentration, also judging from a comparison of the fluorescence spectra of DPH in this and in simple solvents. A previously described[5] single photon counting apparatus equipped with a nanosecond flash-lamp was employed. The flash-lamp was filled with N_2 at a pressure of 1 atm and operated at a 30 kHz repetition rate with an electrode gap of 0.8 mm. The fluorescence was excited at a wavelength of 358 nm and observed at 430 nm with collinear geometry.[5,8,9] Intensities were collected in a range of temperatures from 50 to 160 °C within the aligned and isotropic phase. At every temperature the excitation polarizer was kept vertical and the emission polarizer periodically rotated collecting for 40 s alternatively the parallel (I_{ZZ}) and the perpendicular (I_{ZX}) intensity. Typically, decay curves were measured over 512 channels with a width of 0.1 ns and a maximum peak height of ~ 10^4 photon counts for the parallel polarizers configuration; flash collection was alternated with fluorescence every 60 min. A separate

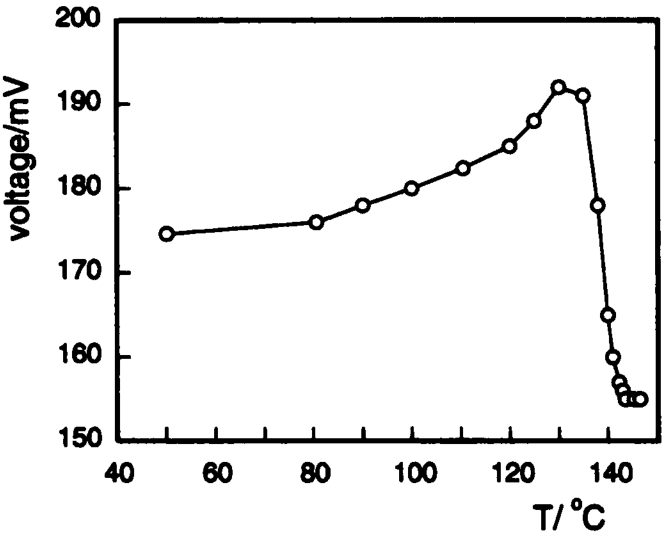

FIGURE 2 Output of the light intensity meter used to find the nematic-isotropic transition temperature of the sample

series of measurements was performed with vertical excitation and magic angle observation (54.7°) in order to obtain the fluorescence lifetimes τ_F of the probe.[5]

DATA ANALYSIS

Fluorescence anisotropy decays for a probe performing rotational diffusion in an oriented mesophase are in general a sum of a rather substantial number of exponentials. Experimental fluorescence intensities have been deconvoluted using the Target Analysis procedure[5] with a modified Gauss-Newton-Marquardt non linear least-squares fitting. Aim of this procedure of analyzing experimental data is not to perform a fit to a sum of free exponentials but rather to choose a model potential and fit the smaller number of parameters that the model involves. In practice, assuming a pure P_2 potential, all measurements in the nematic or in the isotropic phase are individually analyzed and the reduced chi square χ_r^2 is minimized in terms of the probe order parameter $\langle P_2 \rangle$ and of the probe rotational diffusional coefficient $D_\perp$.

The correction factor accounting for the different sensitivity of the detection system to the vertical and horizontal polarization was determined according to the procedure proposed in Reference 32 and was found to be 1.05. All the analyses were performed with an original software package developed by our research group.

RESULTS AND DISCUSSION

We start with the results of the magic angle measurements. Deconvolution of these data gave the fluorescence lifetimes of DPH, that are shown in Figure 3 as a function of temperature.

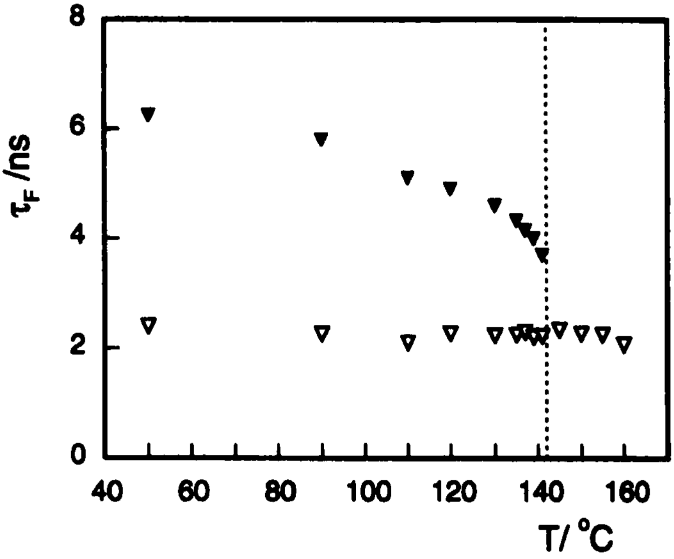

FIGURE 3 The fluorescence decay times τ_1 (empty triangles) and τ_2 (full triangles) for the probe DPH determined at a series of temperatures within the aligned and isotropic range of the liquid crystal polymer TR-10. Here and in the following figures the N-I transition temperature is indicated by the dotted line

The kinetic of the probe fluorescence decay was found to be biexponential in the aligned phase with a short component τ_1 having a characteristic time of ~ 2.3 ns, essentially temperature-independent, and a longer one τ_2 with a decay time steadily decreasing from ~ 6.5 ns at 50°C to ~ 3.5 ns close to the N-I transition temperature. The first component always gave the major contribution, in agreement with the shortening of DPH fluorescence lifetime in polar systems.[33] Beyond the N-I transition temperature, in the isotropic phase, only the short component survives, giving a mono-exponential decay of the fluorescence intensities.

We have then analyzed, with the previously mentioned model, three series of anisotropy measurements in the aligned and one in the isotropic phase. The order parameter of DPH (see Figure 4) shows a flat region with $\langle P_2 \rangle \sim 0.7$ for temperatures between 50 and 120°C, then a fairly rapid decrease to a value at the transition of about 0.3 or less. This behaviour is apparently at some variance with other order parameter results for similar polyesters with different spacers[34] determined by deuterium NMR of labelled spacer chains. In that case the order parameter, although strictly not comparable, retains high values (~ 0.8) apparently up to the transition. A closer look shows that actually the experimental results are only available up to ~ 15°C from the transition. Thus the extrapolation in Reference 34 may not be justified if, as we find here, most of the disordering takes place in the near neighborhood of the N-I transition.

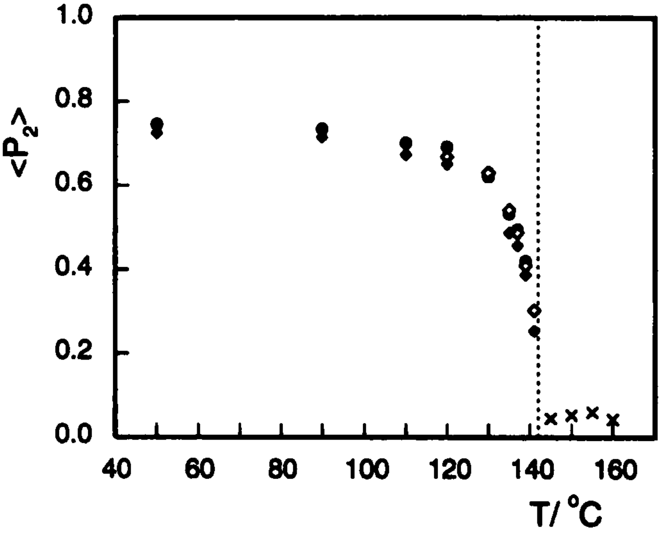

FIGURE 4 The second-rank order parameter $\langle P_2 \rangle$ for DPH in TR-10 as a function of temperature obtained from three series of measurements in the aligned phase (full circles, empty diamonds, full diamonds) and from one in the isotropic phase (crosses). The results correspond to the Target Analysis using a pure P_2 potential and transition moments parallel to the long axis

In general terms the order parameter of a main chain polymer like that shown in Figure 1 is expected to depend on the length and flexibility of the spacers[35] with the mesogenic units becoming similar to Maier-Saupe (M-S) systems[19] if the spacers are completely flexible, rendering the rod-like segments essentially independent.

In Figure 5 we plot the probe order parameter in reduced temperature and we compare it with the M-S mean field curve. As we can see, the behaviour of $\langle P_2 \rangle$, although qualitatively similar, shows a marked deviation from mean field in the already mentioned sudden disordering of the system close to the transition.

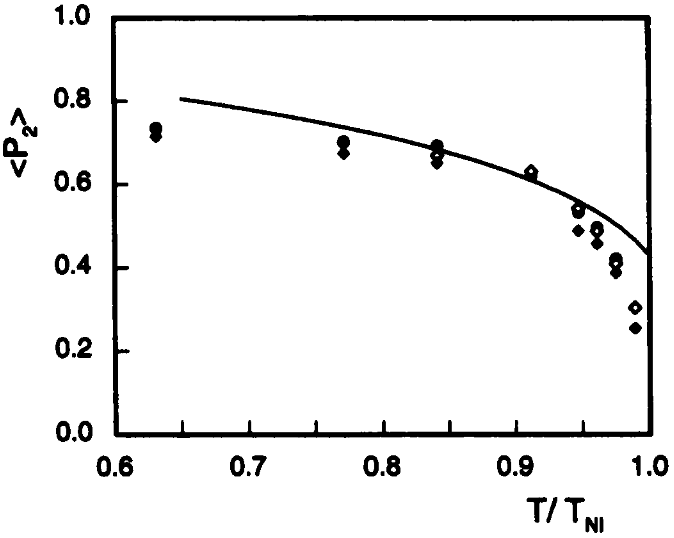

FIGURE 5 The second-rank order parameter $\langle P_2 \rangle$ for DPH in TR-10 as a function of the reduced temperature T/T_{NI} obtained from the three series of measurements in the aligned phase (see Figure 4 for the notation). The continuous line is that expected for a Maier-Saupe effective potential

Not surprisingly in this same temperature interval the dynamics of the system rapidly unlocks as shown by the tumbling diffusional time of DPH which assumes values in the nanosecond range (see Figure 6). It is interesting that near the N-I transition the probe reorients on a time scale similar to that of ordinary liquid crystals such as ZLI-1167[5] showing for the polymer near disordering a large effective fluidity. This large variation in fluidity shows that the use of the orientationally frozen probe approximation, normally employed in the interpretation of steady state fluorescence anisotropies for polymers,[22,23] can have serious limitations. Indeed the fact that the assumption of still molecules can be valid or not in the experiment temperature range is in favour of using a time dependent technique like the present one where possible.

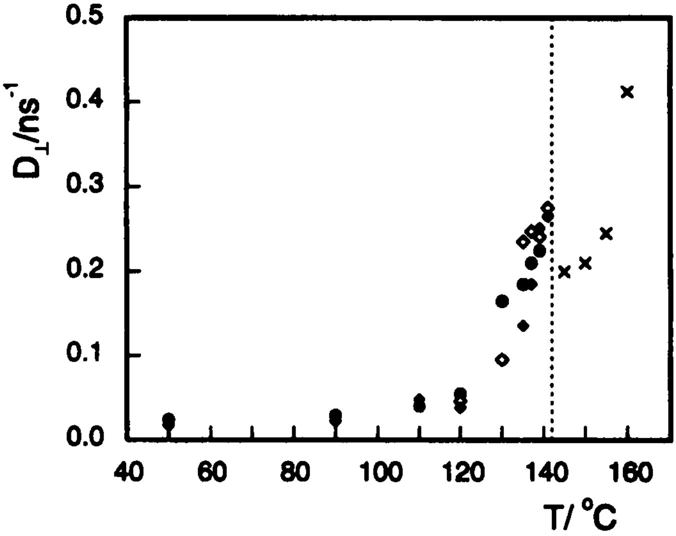

FIGURE 6 The rotational diffusion coefficient $D_\perp$for DPH in TR-10 as a function of temperature. The notation for the series of measurements is the same as in Figure 4. The results correspond to the Target Analysis using a pure P_2 potential and transition moments parallel to the long axis

CONCLUSIONS

We have employed the fluorescence polarization technique to investigate order and dynamics in a polyester liquid crystal polymer. We have developed a method to mechanically align this type of polymeric liquid crystals and shown that it is feasible to perform time dependent fluorescence depolarization studies in this kind of aligned materials. The Target Analysis approach[5] has been used to extract information about the temperature dependence of both the order parameter $\langle P_2 \rangle$ and the rotational diffusion coefficient $D_\perp$ for the fluorescence probe molecule employed. We have found that the order parameter and the reorientation of the DPH probe show deviation from Maier-Saupe mean field type behaviour, with the material maintaining high order and viscosity up to the close neighborhood of the nematic-isotropic transition temperature.

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