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## Liquid Crystals

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## The temperature dependence of nematic liquid crystalline polymer melt diffusion

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Polymer chain diffusion in the nematic mesophase was studied using a model main chain liquid crystalline (LC) polyether based on 2,2'-dimethyl-4,4'-dihydroxyazoxybenzene and mixed alkane spacers. A side chain LC polymethacrylate containing an azobenzene mesogenic group was also investigated. Tracer diffusion coefficients were determined as a function of temperature by an ion-beam depth profiling technique, forward recoil spectrometry. The results confirm that main chain LC polymer chain dynamics are dramatically affected by phase transitions and sample geometry. This behaviour is in marked contrast to the side chain LC polymer which exhibited no phase dependence on the part of the tracer diffusion coefficient.

### 1. Introduction

Significant progress is being made in the development of liquid crystalline (LC) polymers for a variety of mechanical and optical applications. In all cases, the processing of these materials is extremely important and depends on both their diffusion and rheological behaviour. Despite there being a number of papers on the rheological behaviour of main chain and side chain LC polymers [1-5], at present there exists little information concerning the diffusion behaviour of such materials [6, 7].

A large body of experimental evidence has demonstrated that self diffusion of low molar mass liquid crystals in aligned nematic melts is anisotropic. In most, but not all cases,  $D_{\parallel} > D_i > D_{\perp}$  where  $D_{\parallel}$  is the diffusion coefficient parallel to the nematic director,  $D_{\perp}$  is the diffusion coefficient perpendicular to the nematic director, and  $D_i$  is the diffusion coefficient in the isotropic phase [8, 9]. At clearing,  $D_i$  is approximately equal to the average diffusion coefficient of an unaligned, nematic phase sample,  $\langle D \rangle$ , for many samples [8]. This may allow one to describe diffusion in terms of a biased average whereby

$$D_i \approx \langle D \rangle = 1/3(2D_{\perp} + D_{\parallel}). \quad (1)$$

Diffusion of low molar mass liquid crystals has also been observed to exhibit Arrhenius behaviour [8-10]. The temperature dependence of the diffusion coefficients,  $D_{\parallel}$ ,  $D_{\perp}$ , and  $D_i$  can therefore be described as

$$D = D_0 \exp(-A/kT) \quad (2)$$

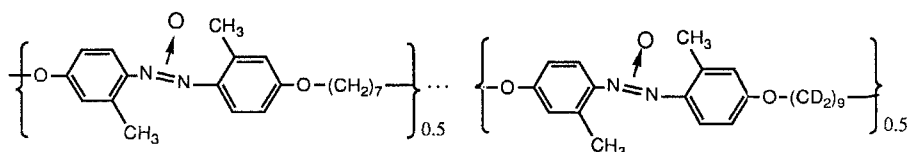
\* Author for correspondence.

where  $D_0$  is a constant,  $A$  is the activation energy,  $k$  is the Boltzmann constant, and  $T$  is absolute temperature. Only close to the clearing transition when plotted versus temperature does  $D_{\perp}$  show a steeper slope and  $D_{\parallel}$  a shallower slope than that corresponding to the average slope of  $D$  versus  $T$ . This behaviour is attributed to a lower order parameter in this temperature range [8, 10].

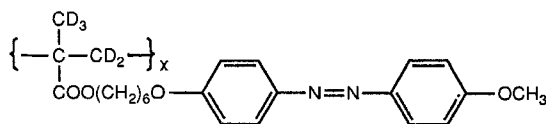
Recently, we have started to investigate tracer diffusion ( $D^*$ ) in LC polymer melts. While in low molar mass liquid crystal studies, tracer diffusion usually denotes the use of a chemically dissimilar tracer species, the tracer and matrix species in our studies may be considered to be chemically equivalent. The tracer chains used were partially deuteriated and of relatively short length, thus avoiding the problems of chemical phase separation common to LC polymers and to very high molecular weight polymers. Because chain length strongly influences polymer diffusion behaviour,  $D^*$  for polymers denotes a measurement specific to the molecular weights of the tracer and matrix chains. Molecular weights for tracer and matrix have been matched as closely as possible to approach a situation of self diffusion (i.e. perfectly matched, mono-disperse molecular weights).

Earlier studies of main chain liquid-crystalline polymers using 4,4'-dihydroxy- $\alpha$ -methylstilbene (DHMS) as the principal mesogenic unit (80 mol%), with 2,2'-dimethyl-4,4'-dihydroxyazoxybenzene (DMAz) as an ancillary mesogenic unit (20 mol%), have demonstrated that tracer diffusion in the nematic phase, is highly anisotropic even in the absence of an applied external field [7]. Correlation of the D<sub>i</sub>IMS-based polymer diffusion data by both ion-beam and spectroscopic techniques with rheological and orientation measurements indicate that  $D_{\parallel} > D_{\perp}$  with  $D_{\parallel}$  being as yet unmeasured. In addition to the change in slope at clearing, the diffusion coefficient of these LC polymers showed changes at the melt transition,  $T_m$ . Ordinary, flexible polymers, such as polystyrene, show a steady increase in  $D^*$  with  $T$  above their glass transition temperature [11].

To determine whether the behaviour observed in our initial experiments was specific to the mesogenic structure DHMS, or could be representative of more general LC polymer behaviour, polyethers with DMAz mesogen were synthesized and tested by forward recoil spectrometry. The Arrhenius behaviour of the main chain polymer is contrasted to that of the side chain polymer containing an azobenzene mesogenic core. The structures of the tracer polymers are shown in Schematic I.



(a) d-DMAz-7,9



(b) d-PMAM

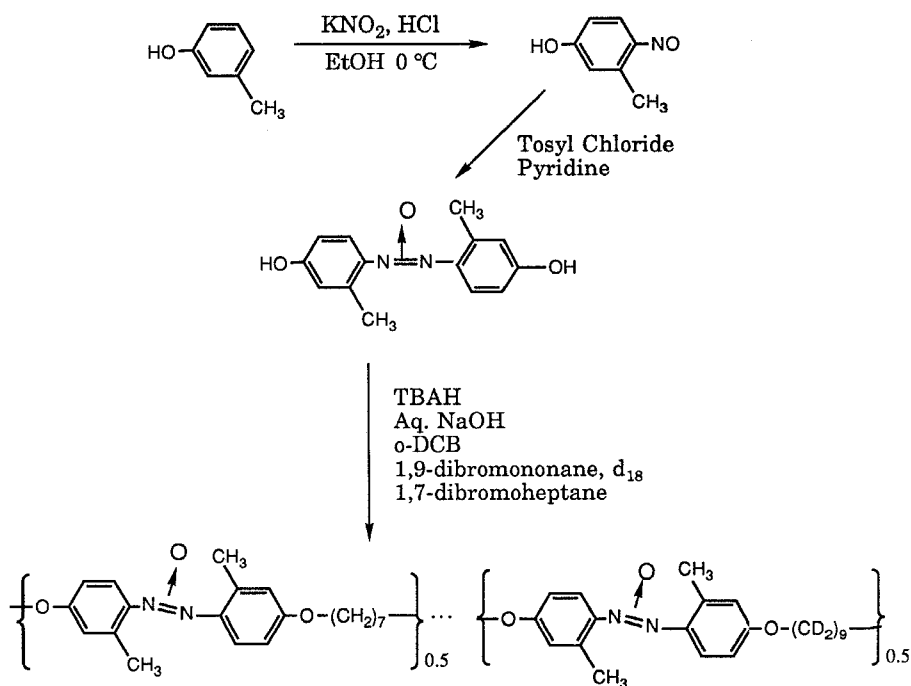
Schematic I. Structures of deuterium labelled LC polymers.

## 2. Materials and methods

### 2.1. Main chain polyether synthesis

The synthesis of the monomer, 2,2'-dimethyl-4,4'-dihydroxyazoxybenzene (DMAz), has been described in earlier publications [12, 13]. Briefly, DMAz was made by a two step process. First, the appropriate nitrosophenol was prepared from *m*-cresol and potassium nitrite after which tosyl chloride was added; the resulting condensation produced DMAz (see schematic II).

The matrix polymer, DMAz-7,9 and the tracer polymer, *d*-DMAz-7,9, were prepared with equimolar amounts of 7 and 9 carbon spacers using phase transfer catalysis [14]. 1,2-Dichlorobenzene (*o*-DCB, Aldrich 99 + per cent) and tetrabutylammonium hydrogen sulphate (TBAH, Aldrich 97 per cent) were used as obtained. The dibromoalkanes, 1,7-dibromoheptane and 1,9-dibromononane (Aldrich) were purified by vacuum distillation prior to use. The perdeuteriated 1,9-dibromononane,  $d_{18}$  (MSD Isotopes) used in the tracer polymer synthesis, was used as received. Synthesis of the matrix polymer was as follows: Under nitrogen, 0.701 g (2.717 mmol) of DMAz and 0.185 g (0.544 mmol) of TBAH were added to a 20 ml of sodium hydroxide solution (30 per cent by weight) at room temperature in a flask equipped with a mechanical stirrer. After the mixture had stirred for 15 minutes, a solution of 0.388 g (1.359 mmol) of 1,9-dibromononane and 0.351 g (1.359 mmol) of 1,7-dibromoheptane in 20 ml of *o*-DCB was added. The mixture was stirred vigorously for 20 hours at 85°C. After cooling, the aqueous layer was neutralized with 2 N HCl and decanted off. The organic layer was precipitated in acidified methanol. The tracer polymer was labelled with deuterium by incorporation of perdeuteriated 1,9-dibromononane. Schematic II illustrates the complete synthesis for *d*-DMAz-7,9.



Schematic II. Synthesis of *d*-DMAz-7,9.

The matrix polymer was purified by reprecipitation from chloroform into heptane, and then by solution precipitation from a toluene–ethanol solution. The amount of fractionated material produced was  $\sim 0.7$  g. Due to the much smaller amount of tracer polymer synthesized, the *d*-DMAz-7,9 was purified by a single reprecipitation from chloroform into heptane.

### 2.2. Main chain polyether characterization

Molecular weights were determined by gel permeation chromatography on a Waters chromatograph using Ultrastaygel® columns calibrated against monodisperse polystyrene standards. Thermal transitions were measured using a Perkin–Elmer DSC-2C differential scanning calorimeter using heating and cooling rates of  $20^\circ\text{C min}^{-1}$ . Data are presented in the table. The mesophase of DMAz-7,9 was identified optically as nematic using a Leitz polarizing microscope equipped with a Mettler FP 52 hot stage. Because of the azoxybenzene chromophore, the melt has a distinctly yellow colour. Composition was verified by proton nuclear magnetic resonance using a Varian XL-200 in  $\text{CDCl}_3$ .

### 2.3. Side chain polymer synthesis and characterization

A side chain LC polymer was prepared from its monomer form in which a methoxy azobenzene mesogenic group was attached to a methacrylate functionality by an aliphatic spacer six carbons in length. The methacrylate group was then free radically polymerized to produce poly[4-(6-methacryloyloxyhexyloxy)-4'-methoxyazobenzene]. The polymer, identified as PMAM, has had its synthesis and characterization described in previous publications [7, 15]. The tracer polymer (*d*-PMAM) consisted of a perdeuteriated methacrylate polymer backbone. See table for values of molecular weight and transition temperatures, and schematic *Ib* for the polymer structure.

### 2.4. Diffusion sample preparation

Diffusion samples were composed of a 1 micron thick matrix layer spin-coated on to a silicon substrate from a toluene solution. Matrix layers were annealed for 1 hour within the smectic or nematic regions to remove any structure induced by the spin coating. A thin, 600 Å deuterium-labelled tracer film was then spun on to glass, floated

Molecular weights and transition temperatures of LC polymers†.

Polymer	$M_n$	$M_w$	$M_{\text{peak}}$	$M_w/M_n$	$T_m/^\circ\text{C}$	$T_{\text{SN}}/^\circ\text{C}$	$T_i/^\circ\text{C}$
Matrix							
DMAz-7,9	19 K	27 K	27 K	1.4	85	—	120
PMAM	36 K	133 K	119 K	3.7	—	95	140
Tracer							
<i>d</i> -DMAz-7,9	9 K	20 K	21 K	2.2	78	—	125
<i>d</i> -PMAM	20.4 K	74 K	97.5 K	3.6	—	95	140

†(1) The two melting peaks for DMAz-7,9 and *d*-DMAz-7,9 are visible on DSC trace only after annealing. The shoulder on the peak at clearing reduces with annealing, see figure 1. The  $T_m$  reported is for the second melt transition. (2) PMAM and *d*-PMAM data previously reported in [7]. The temperature reported is for the smectic to nematic transition,  $T_{\text{SN}}$ . (3) Molecular weights are measured by gel permeation chromatography.

on to water, and picked up by the matrix layer. Samples were diffused by annealing the bilayers in either a water bath or a silicon oil bath; both media produced identical values for the diffusion coefficient. Forward recoil spectrometry (FRES) was then used to profile the deuterium concentration versus depth [16, 17]. Diffusion coefficients,  $D^*$ , were obtained by fitting diffusion profiles with a solution to Fick's second law.

FRES is an ion-beam technique which requires solid, highly planar samples. As such, it has not been utilized for low molar mass liquid crystal experiments. FRES, as a mass transport technique, provides data that are comparable in many aspects to radioactive tracer techniques and to forced Rayleigh scattering, both of which have been used to measure diffusion in low molar mass liquid crystals [18–20]. Mass transport techniques are macroscopic, and thus measure diffusion on the same long time scale. Microscopic techniques in contrast, measure short time-scale motion, and thus can result in different conclusions about long-time behaviour. FRES probes an area approximately  $2.5\text{ mm} \times 7.5\text{ mm}$ , and a depth of approximately  $0.5\text{ microns}$ . Sample-to-sample variation is small, and the error in the diffusion coefficients reported is typically 10–25 per cent.

### 3. Results and discussion

Some physical parameters and phase transition temperatures of the matrix and tracer polymers are reported in the table. The main chain polyether, DMAz-7,9 (see schematic 1a), showed an increase in the tracer diffusion coefficient,  $D^*$ , with temperature,  $T$ , prior to formation of the nematic phase, whereupon there was a sharp change in slope (see figure 1). In the nematic phase,  $D^*$  was found to be nearly independent of  $T$ , and to increase rapidly at the onset of clearing.

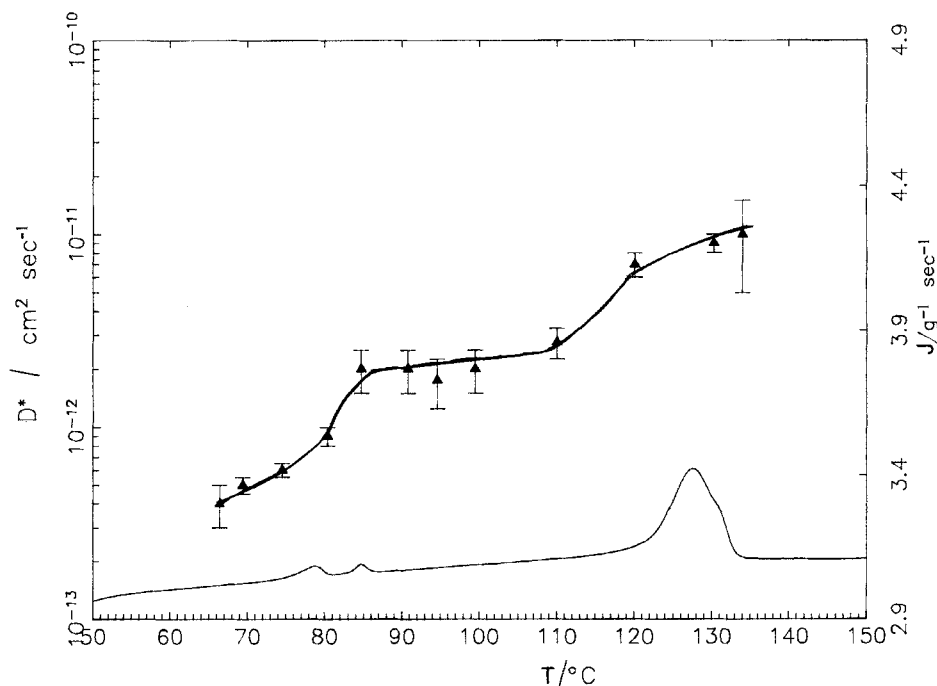


Figure 1. Tracer diffusion coefficient versus temperature for DMAz-7,9 ( $\blacktriangle$ ). The thin line denotes the DSC scan trace.

An Arrhenius plot of the DMAz-7,9 diffusion data in figure 2 illustrates the low activation energy ( $\sim 3 \text{ kcal mol}^{-1}$ ) for diffusion in the nematic plateau region. In the region between the polymer glass transition and its melting point, the activation energy for diffusion is higher than for the nematic region ( $\sim 14 \text{ kcal mol}^{-1}$ ). This observation reconfirms our previous work on other LC polyethers [7, 17]. Above  $T_{\text{NI}}$ , DMAz-7,9 exhibits biphasic behaviour until  $134^\circ\text{C}$ .

In contrast, PMAM (see scheme 1b) showed simple Arrhenius behaviour across the two phase transitions, the clearing transition ( $T_{\text{NI}}$ ) and the smectic–nematic transition ( $T_{\text{SN}}$ ), with an activation energy of  $22 \text{ kcal mol}^{-1}$  (see figure 2). Tracer diffusion behaviour of PMAM is qualitatively identical to conventional, amorphous polymers in that diffusion increases steadily with temperature.

The difference in chain dynamics between main chain LC polymers and either side chain polymers or conventional polymers is the effect of backbone conformation. Side chain systems have been shown to possess nearly random-coil conformations of their backbone in the nematic phase in contrast to the more extended chain conformations expected of nematic main chain LC polymers [6]. Additionally, the PMAM samples used for FRES showed no macroscopic alignment in the nematic phase when measured with IR dichroism. Any orientational effects were therefore absent.

By analogy with low molar mass liquid crystals [8], and our previous results on LC polyethers [7, 17] the plateau present in the DMAz-7,9 diffusion data in figure 1 is suggestive of a system in which only the  $D_{\perp}$  component of diffusion is being probed in the nematic state for a macroscopically aligned sample. In such a system,  $D_{\perp}$  may be expected to increase at the expense of  $D_{\parallel}$  as diffusion becomes more isotropic above  $T_{\text{NI}}$  and the order parameter decreases [21]. This suggestion of orientation has been confirmed in a structurally similar polymer based on DHMS by orientation measurements using IR dichroism, which show that the chains align parallel to the

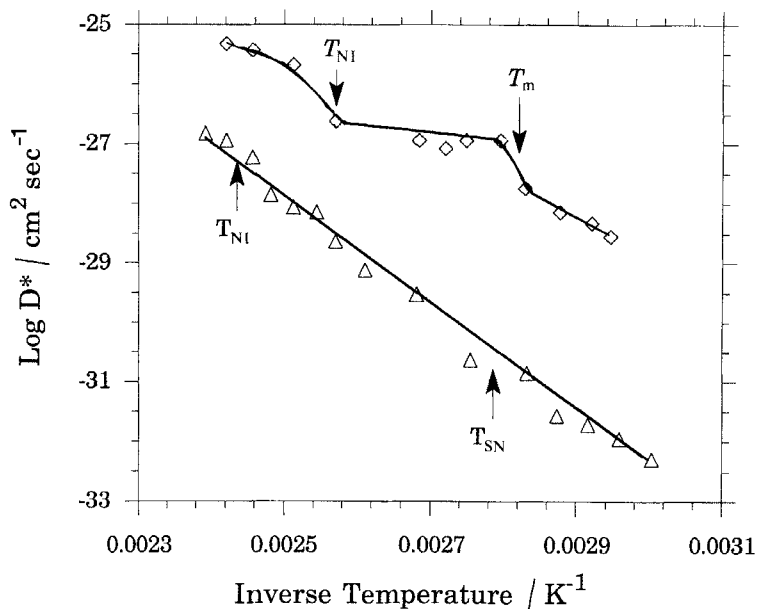
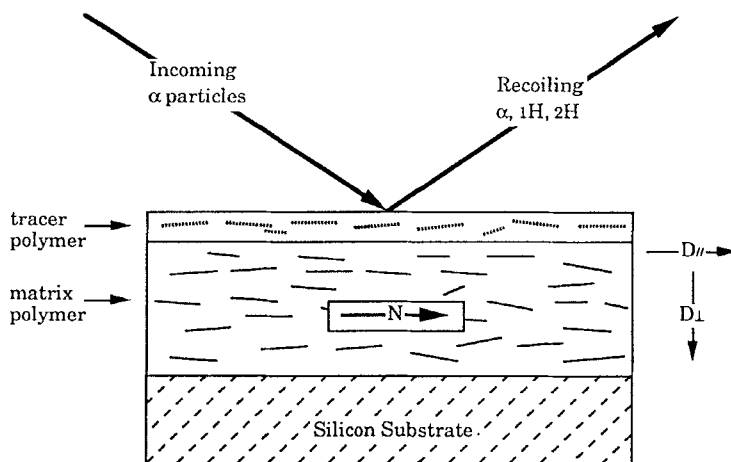


Figure 2. Natural log of the diffusion coefficient versus inverse temperature for DMAz-7,9 ( $\diamond$ ) and PMAM ( $\triangle$ ). A subset of the PMAM data appears in [7].



Schematic III. The geometry of LC polymer diffusion using forward recoil spectrometry. The arrow, N, represents the nematic director.

plane of the substrate. Since FRES measurement requires that the plane of the substrate is perpendicular to the plane of depth profiling, mass transport is measured perpendicular to the direction of chain alignment. (see schematic III.) FRES, therefore, measures only  $D_{\perp}$  in aligned, homogenous samples.

If we are correct in our assessment of diffusion behaviour, we have a system with high diffusional anisotropy when compared with analogous nematic low molar mass liquid crystals [18, 22–25]. Various macroscopic and microscopic techniques measure  $D_{\parallel}/D_{\perp}$  for self-diffusion of *p*-azoxyanisole, a structure very similar to DMAz, as 1.2–1.48 [22, 23]. In their nematic phase, *p*-hexanoyl-benzylidene-*p'*-aminoazobenzene (C6-AA), has a  $D_{\parallel}/D_{\perp}$  of 2.6 and *p*-methoxy-benzylidene-*p'*-*n*-butylaniline (MBBA) has a  $D_{\parallel}/D_{\perp}$  of 3 when measured with magnetic resonance techniques [24].

In comparison, the diffusional anisotropy in LC polymers will be influenced by chain conformation much more than will their low molar mass counterparts. Polymer chains, if extended in a nematic melt, as is evidenced in LC polyesters based on DMAz [26], will have a far greater axial ratio than do low molar mass liquid crystals. This chain extension will result in a large morphological anisotropy within the melt, which can influence the diffusional components. Polydispersity will have an effect on the  $D_{\parallel}/D_{\perp}$  value due to the strong weight average molecular weight dependence of  $D^*$  at constant temperature. Measurements on DHMS-7,9 have shown that  $D^*$  decreases rapidly with increasing molecular weight of both matrix and tracer species [27].

Since the geometry of the FRES experiment makes it unsuitable for a measurement of  $D_{\parallel}$  in these polyethers, other techniques need to be identified. A preliminary analysis using equation (1) indicates that for a biased average system,  $D_{\parallel}$  for DMAz-7,9 should exceed  $1 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ . This puts the experiment in a range of  $D^*$  values attainable by electron paramagnetic resonance techniques as well as forced Rayleigh scattering. Molecular weights and sample alignment may be adjusted to the requirements of each technique.

#### 4. Conclusions

Diffusion of main chain LC polyethers within their nematic melt shows a number of characteristics similar to the diffusion behaviour of low molar mass liquid crystals.



Diffusion is sensitive to phase transitions and shows different activation energies depending on phase. Diffusion in LC polymers appears to be at least as anisotropic as for small molecule liquid crystals. The side chain LC polymer investigated in this study possesses diffusion behaviour that is qualitatively indistinguishable from ordinary amorphous polymers, and exhibits none of the unique characteristics associated with the diffusion of oriented low molar mass liquid crystals.

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