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ISOTROPIZATION OF NEMATIC LIQUID CRYSTALS BY TMDSC

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Abstract

Temperature-modulated differential scanning calorimetry (TMDSC) and traditional DSC are used to study the transition between the nematic liquid crystalline state and the isotropic liquid for two small molecules [4.4'-azoxyanisole and N,N'-bis(4-n-octyloxybenzal)-1,4-phenylenediamine] and one macromolecule (4,4'-dihydroxy-α-methylstilbene copolymerized with a 1:1 molar mixture of 1,7-dibromoheptane and 1,9-dibromononane). The DSC measurements with 4.4'-azoxyanisole were used for temperature calibration with varying heating and cooling rates. Quasi-isothermal TMDSC with small temperature amplitude and standard TMDSC with underlying heating and cooling rates were utilized to analyze the breadth of the transitions. It could be verified that the isotropization transition of a nematic liquid crystal is, indeed, reversible for all three molecules. The nature of the transition changes, however, from relatively sharp, for small, rigid molecules, to about three kelvins wide for the small molecule with flexible ends, to as broad as 20 K for the macromolecule. It was also demonstrated that quantitative heats of fusion of sharp transitions can be extracted from TMDSC, but only from the time-domain heat-flow signal.

Introduction

The transition from the nematic (N) liquid crystalline phase (LC) to the isotropic (I) melt is generally assumed to be a first-order, equilibrium transition [1]. In other words, the transition occurs at the same temperature on cooling and heating, and no nucleation is required for the I → N transition, in contrast to crystallization. Because of this reversibility, it has been demonstrated for the Perkin-Elmer power compensation DSC that the N → I transition can be used as standard for temperature calibration on heating and I → N for cooling [2,3]. In this paper a first investigation of these transitions is described using a heat-flux type, temperature-modulated differential scanning calorimeter (TMDSC). The transition is followed through the entire temperature range of the transition by using traditional DSC, quasi-isothermal TMDSC, and standard TMDSC with an underlying heating rate <q>. It will be shown that the transition from a nematic LC to the isotropic melt is, indeed, an equilibrium transition without need of nucleation. Dependent on the molecular character of the sample, the temperature range of the transition varies, however, from very narrow, to as much as 20 K, i.e. the nematic to isotropic transition has an intrinsic breadth. The selection of samples for temperature calibration becomes, thus, crucial since the width of the transition may cause confusion in data interpretation.

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In previous papers we have explored the advantages and limits of TMDSC [4-8]. Briefly, to modulate DSC, one adds a sinusoidal oscillation to the block temperature T_b that would have otherwise increased linearly for traditional DSC:

$$T_b = T_o + <q>t + A_{T_b} \sin(\omega t) \tag{1}$$

where T_o is the temperature at time t = 0; $<q>$, the underlying scanning rate; A_{T_b}, the amplitude of modulation at the block temperature; and ω, the modulation frequency in radians. The steady state temperature of the sample calorimeter is:

$$T_s = T_o + <q>t - \frac{<q>C_s}{K} + A\sin(\omega t - \varepsilon) \tag{2}$$

where A is the maximum modulation amplitude of T_s, fixed as a run parameter, and ε is the phase lag between the reference oscillation and the sample temperature. During isotropization of a liquid crystal, the latent heat is very small, therefore, the calorimeter is expected to stay close to steady-state (depending on the sharpness of the transition). Full descriptions of traditional DSC, quasi-isothermal TMDSC and standard TMDSC are given in refs. [8,9], [4,8], and [5,6,8], respectively.

Experimental

A commercial TMDSC, the Thermal Analyst 2910 system with liquid-nitrogen cooling-accessory (LNCA) from TA Instruments Inc. (MDSC^{TM}), was used in this study. Dry nitrogen gas with a flow rate of 20 mL/min was purged through the DSC cell. The temperature of the TMDSC equipment was initially calibrated in the standard DSC mode at 10 K min^{-1} by using the transition peaks for cyclohexane (186.09 and 297.7 K), octane (216.15 K), water (273.15 K), and indium (429.75 K). The transition temperatures of the standards are chosen at the extrapolated onsets [9]. Following the same procedure, the isotropization temperatures of the liquid crystals under investigation are determined on heating and cooling. The heat flow was calibrated with the heat of fusion of indium (28.45 J g^{-1}).
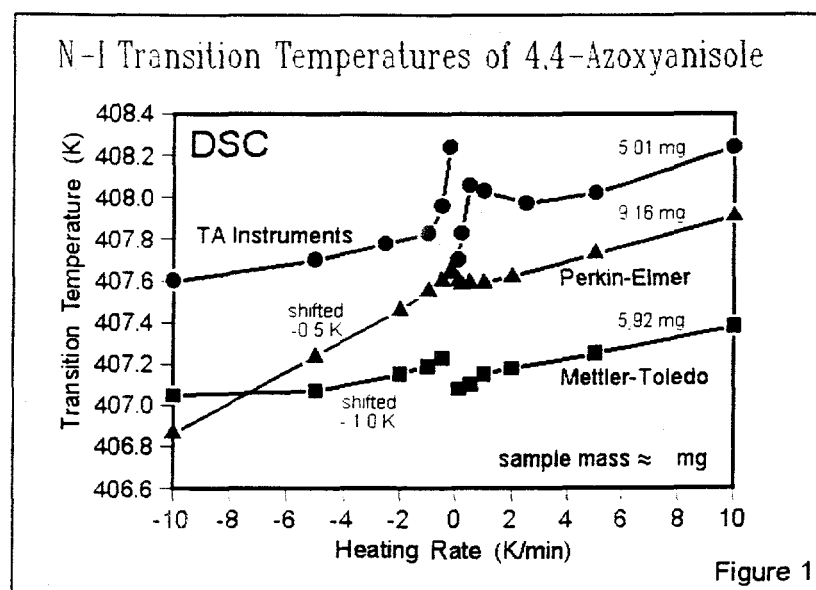
In this work, the following experiments were performed: (1) The transition temperatures were measured with traditional DSC as a function of scanning rate (from ±0.2 to ±20.0 K min^{-1} by the onset of isotropization and ordering). (2) Quasi-isothermal TMDSC was carried out with a modulation amplitude A = 0.1 K, coupled with a modulation period p = 60 s, and step-wise temperature-increments of 0.2 K. Except for cases specified, the quasi-isothermal runs lasted 20 minutes, each. The last 10 minutes were used for data collection. (3) Standard TMDSC runs were performed with underlying heating rates $<q>$ = ± 0.2 K min^{-1} and modulation parameters p = 60 s, A = 0.5 K. With these parameters the maximum heating and cooling rates q = dT/dt are 3.3 and 2.9 K min^{-1}, as calculated from Eq. (2).

The liquid crystal materials chosen for this study were: (1) 4,4'-azoxyanisole, obtained from Aldrich Chemical Co. (impurities <2%). It is a typical, small-molecule, nematic LC without major flexible appendages. The transition crystal → N occurs at T_d = 391 K (disordering), N →I at T_i = 408 K. ΔH = 2.56 J g^{-1}. (2) N,N'-bis(4-n-

octyloxybenzal)-1,4-phenylenediamine (abbreviated as OOBPD). It was synthesized following the method of ref. [10]. This sample shows multiple transitions on heating, characterized fully earlier [11,12]. In this study, attention will be focused on the isotropization at T = 501 K. This sample has flexible octyloxy-groups attached to its rigid center, the mesogen. (3) A main-chain, macromolecular LC-forming polyether was synthesized by coupling 4,4'-dihydroxy-α-methylstilbene (DHMS) with a 1:1 molar mixture of 1,7-dibromoheptane and 1,9-dibromononane. The name of this random copolymer is abbreviated as DHMS-7,9. The molar mass of DHMS-7,9 is 36,000 Da. It forms a nematic phase between 400 K and 470 K [13, 14].

Results

Figure 1 shows the onset temperatures for the isotropization and ordering of 4,4'-azoxyanisole as a function of scanning rates on both, heating and cooling (solid circles) measured by traditional DSC. The transition temperatures change linearly
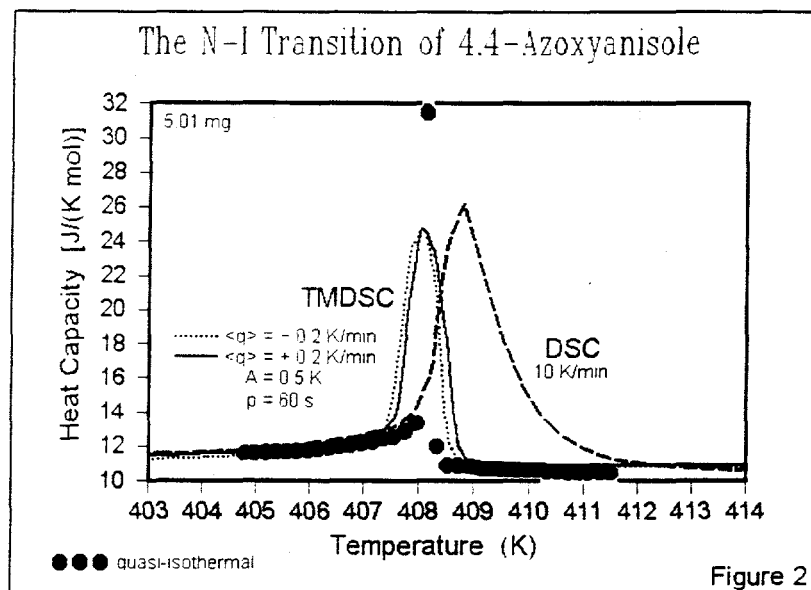

Figure 1

with heating/cooling rates. A linear equation can be used to represent the temperature dependence of the onset temperatures with heating rate q (data represented by the upper curve, solid circles):

$$T_i = 0.030 \times q + 407.93 \qquad (3)$$

The equilibrium T_i of 4,4'-Azoxyanisole is, thus, 407.93 K (q = 0).

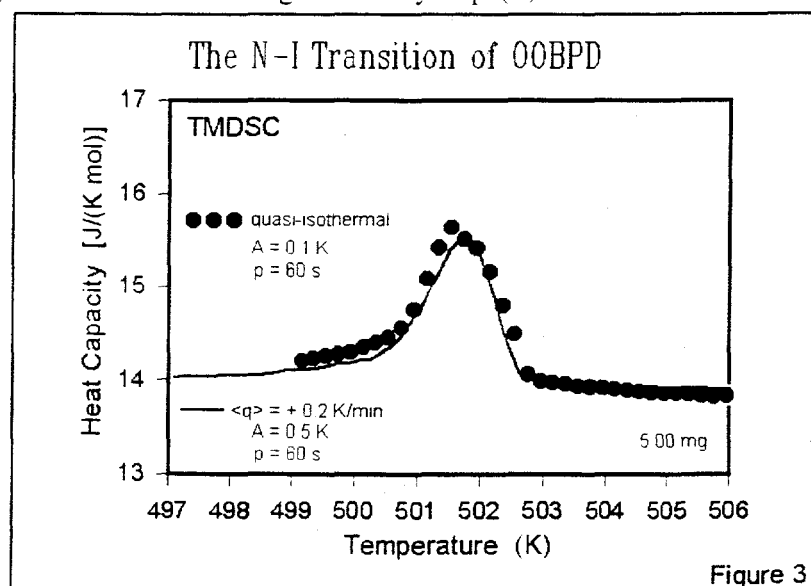It is of interest to note that a systematic deviation from the linear dependence of T_i occurs as q approaches zero. This deviation is considered to be an instrument effect. To elucidate this effect, the experiments were repeated on the different DSCs of Perkin-Elmer (solid triangles) and Mettler-Toledo DSC (solid squares). For clarity, these two data sets are shifted by 0.5 and 1.0 K to lower temperature.
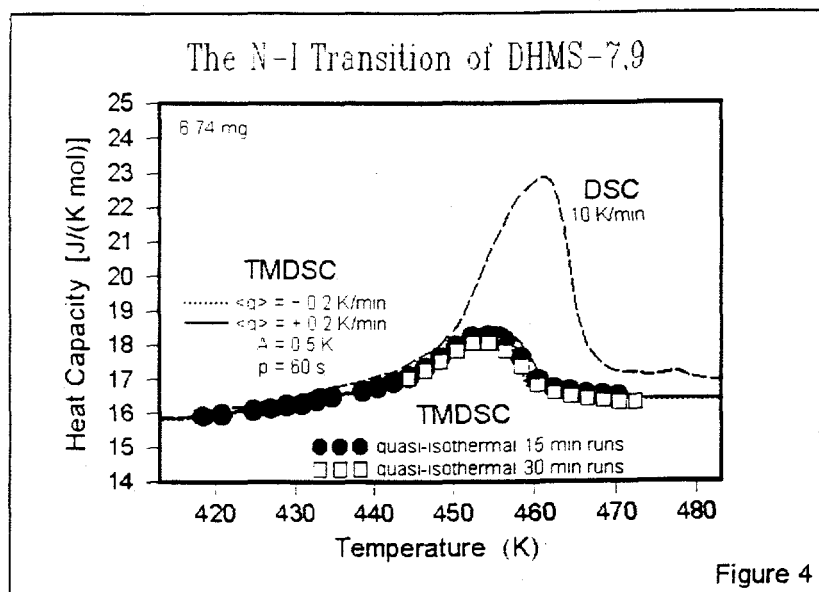
Figure 2

Plots of the N → I transitions of 4,4'-Azoxyanisole. OOBPD and DHMS-7.9 measured under different DSC modes are illustrated in Figs. 2-4. respectively. The dashed lines represent the traditional DSC measurements with a heating rate of 10 K min [1]. The solid and dotted lines represent the standard TMDSC traces with an underlying heating and cooling rate. respectively. The solid circles mark the quasi-isothermal TMDSC runs. For DHMS-7.9, the quasi-isothermal TMDSC was performed with runs of 15 min (circles) and 30 min (squares) at each temperature.

Discussion

The onset temperatures for the 4.4'-Azoxyanisole by traditional DSC depend on scanning rate. as shown in Fig. 1 and by Eq. (3). The cause of this shift is the

Figure 3

Figure 4

changing temperature difference between sample and sensor (sample thermocouple). Its magnitude is identical to that found with the same DSC for indium [15]. No supercooling is observed in Fig. 1. showing that no nucleation of the nematic phase is necessary. Crystallization of In. in contrast. needs a supercooling of 1.0 K [15]. For the different instruments of Fig. 1. the slopes are similar. The small changes of slope for heating and cooling differ for the various instruments and also for different measuring conditions with the same instrument (cooling device. N_2-flow. etc.) [15].
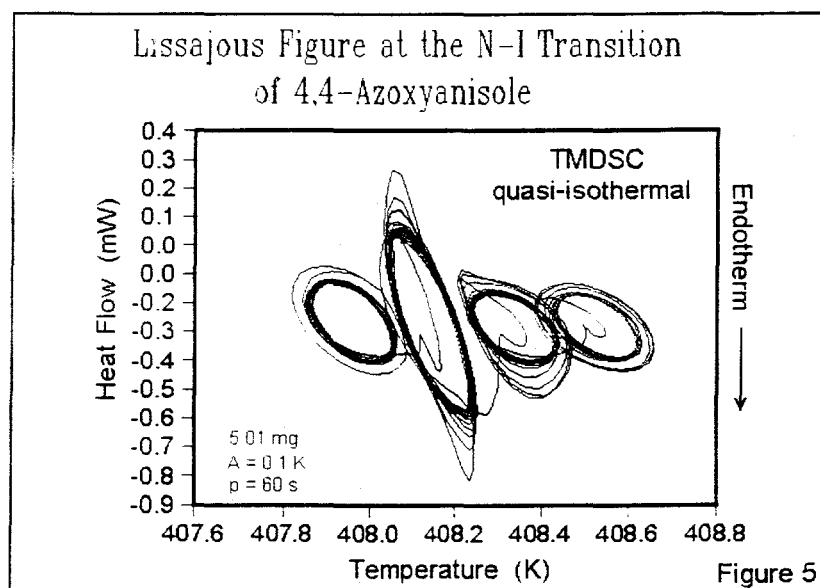
Bigger deviations from Eq. (3) near zero heating rate are common for all instruments. This was first discovered on calibration with In [15]. The cause seems to be that the transition starts at the bottom of the sample, close to the sensor. and fixes the sample temperature. The heat flow is governed. however. by the changing heater temperature to attain a fixed q. regardless of the sample temperature. As a result. the (small) temperature difference between sample and sensor changes. This changed temperature difference sets up a small. additional heat flow between sample and sensor. resulting in the lower than expected temperature of Eq. (3) on heating, and a higher on cooling. For larger q. this effect becomes negligible. There is not sufficient time to hold the bottom sample layer at the constant transition temperature. Obviously this temperature deviation around zero scanning rate is dependent on the sample mass. placement and geometry of the pan. as well as the overall DSC construction and running conditions. In the present cases the maximum effects are about ±0.3 K . ±0.1 K. and ± 0.05 K for the TA Instruments. Mettler-Toledo and Perkin-Elmer DSC. respectively.

The details of the N=I transition are revealed by TMDSC. Figure 2 shows with the quasi-isothermal results (circles) that the heat capacity of the 4.4'-azoxyanisole gradually increases on approaching the transition temperature from the

low-temperature side. as is common for LCs [1]. A larger upturn, that may be considered a pre-transition effect. starts at ≈407 K. Close to the onset of isotropization measured with traditional DSC [407.93 K. see Figs. 1 and 2 and Eq. (3)]. a large jump occurs in the quasi-isothermal TMDSC. as expected for a sharp first-order transition. The occurrence of the transition can be illustrated more clearly in the time domain. using the Lissajous traces shown in Fig. 5 (modulated heat flow vs. temperature plots). Starting from the left. the second set of Lissajous traces indicates that the major part of the transition occurs between 408.05 and 408.25 K. The initial onsets of endotherms and exotherms are at ≈408.15 K. The small difference from Eq. (3) can easily be accounted for by the uncertainty of the sample temperature at low q. The third set of Lissajous traces indicates some residual N⇌I transition in the sample. It is interesting to note that the initial sharp transition peaks disappear with time. reaching a new steady state of temperature gradients (compare to Fig. 6. for standard TMDSC).

Taking the beginning of the transition at the stronger upturn of heat capacity at 407 K and the end at 408.5 K. as suggested by Figs. 2 and 5. the actual transition has a temperature range of about 1.5 K. even though the main transition is much narrower (<0.2 K). The reversible. apparent heat capacity of the standard TMDSC is much broader when compared to the quasi-isothermal measurement. The reason for this peak broadening is the larger modulation amplitude (A = 0.5 K) and the multiple averaging used in the evaluation of the reversing heat-flow amplitude [5] (3/2 cycles = ±0.3 K). With an underlying cooling rate (dotted curve of Fig. 2) practically identical curves to heating result. supporting the fact that the transition is an equilibrium transition. The small shift is in agreement with Eq. (3).

From the reversing heat capacity of the standard TMDSC in Fig. 2 (solid and doted lines) one may be tempted to evaluate a heat of transition. It must be pointed
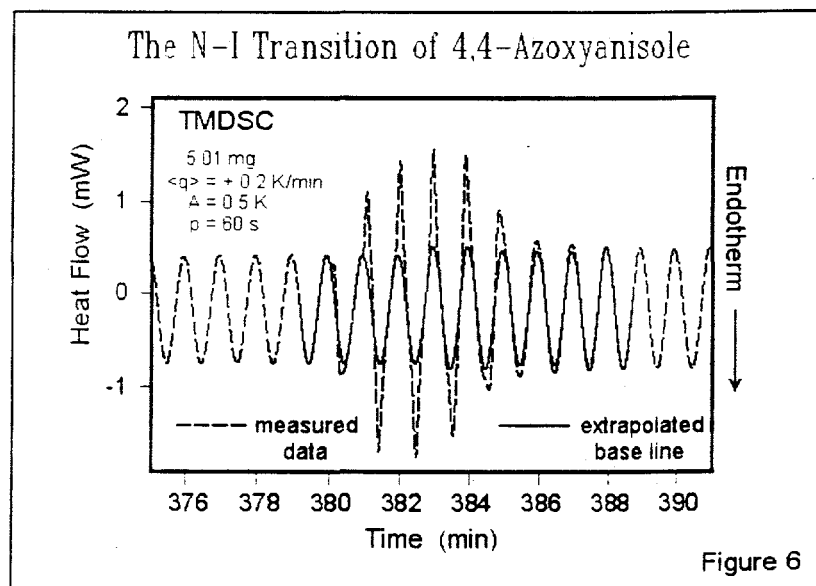

Figure 5

out, however, that the reversible heat flow represents only the first harmonic of a Fourier series used to fit the time-dependent heat flow [5,6]. As shown in Fig.6, the heat flow signal in the transition range (dashed line) no longer follows a sinusoidal pattern, the line shape becomes sharper and shifts its peaks from cycle to cycle as the underlying temperature increases. Therefore, in the transition range, higher harmonics of the Fourier series need to be added to describe the heat flow fully. One can, however, carry out the integration of the heat flow due to the transition in the time domain. From the plot of heat flow *vs.* time in Fig.6, at high and low temperatures one can establish a base line in the transition range (solid line in Fig. 6). The difference between the actual heat flow and the base line can then be related to the heats of transition. The heat of isotropization of the nematic phase for 4,4'-Azoxyanisole determined by this method is 2.56 J g^{-1}, which agrees well with the value obtained from traditional DSC (2.52 J g^{-1}).

For OOBPD, shown in Fig. 3, only quasi-isothermal and standard TMDSC on heating were performed. Both measurements coincide and indicate that isotropization of the nematic phase of OOBPD occurs more gradually, covering a temperature range of ≈ 3.0 K. The identical data for both measurement methods are due to the fact that the modulation amplitudes (A = 0.1 and 0.5 K, respectively) are much smaller than the intrinsic transition width (3.0 K) so that the peak broadening effects, seen in the case of 4,4'-Azoxyanisole, do not occur. Since the sample is known from NMR to be relatively pure [12], the molecules must actually have a continuous series of states of intermediate order.

For the polymer sample DHMS-7,9 (Fig. 4), the breadth of the N⇌I transition is ≈ 20 K. The most likely explanation rests with the polydispersity of the macro-molecule and local variation in chemical structure of the copolymer, *i.e.*, the different molecules or segments have transitions at different temperatures. It is reported in the

The N-I Transition of 4,4-Azoxyanisole

TMDSC

5.01 mg
$<q> = + 0.2$ K/min
A = 0.5 K
p = 60 s

Heat Flow (mW)

Endotherm

----- measured data
——— extrapolated base line

Time (min)

Figure 6

literature and seen by optical microscopy in our laboratory that at the $N \leftrightarrow I$ transition there is a temperature interval where the nematic and isotropic phases coexist.[13].

Finally. it should be pointed out that . like in the case of 4.4'-Azoxyanisole, an "excess" heat-capacity increase below the onset isotropization temperature was also observed for OOBPD and DHMS-7.9 (see Figs. 3 and 4). This excess heat capacity is very much less above the $N \leftrightarrow I$ transition. It seems to lead to the conclusion that a certain "pre-transition" occurs in the nematic phase. Detailed investigations of this pre-transition that occurs also before melting is in progress.

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