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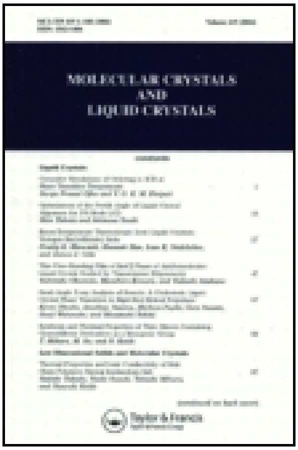

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TSD of Liquid Crystals in the Supercooled Nematic Phase

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MBBA and EBBA are used to apply the techniques of thermally stimulated depolarization (TSD) to liquid crystals in their glassy state. The orientational mobilities of the butyl and methoxy resp. ethoxy group show significant differences compared to the crystalline phases. A small TSD band in MBBA at 69.5 K and in EBBA at 64.5 K probably comes from relaxations of the butyl group. A ten times stronger TSD band at 117.5 K resp. at 124 K is due to relaxations of the methoxy respect to the ethoxy group. Using the partial heating technique and the thermal sampling technique a detailed analysis of this band allows more insight into the distribution of reorientation enthalpies and relaxation times.

§ 1. INTRODUCTION

The method of thermally stimulated depolarization (TSD) has become a valuable tool to study relaxation processes on atomic centres or molecular units containing an electric dipole moment whose orientation is altered during relaxation.[1] An undispensable condition is the possibility of freezing the orientation by cooling to low enough temperature which only in exceptional cases cannot be fulfilled.[2] Since we had successfully applied TSD methods to dipole centres in ionic crystals we became interested in applying TSD methods to the liquid crystals MBBA and EBBA in their glassy nematic state. To our knowledge this kind of experiment has not been done yet. There are high frequency dielectric loss measurements,[3] measurements of DSC,[4] thermal conductivity[5] and optical properties[6,7] as well as results of

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X-ray scattering[8] and optical microscopy,[5] performed over the range of LC phases and in metastable or stable crystalline phases. They already give some insight into the molecular dynamics and the phase transition of these substances.

While slow cooling with a rate $q < 0.5$ K/min only shows the reversible transition from the nematic phase into the stable crystalline phase—in MBBA at 295 K and in EBBA at 318 K—rapid cooling with $q \geq 10$ K/min keeps the probe in the nematic order and below 180 K we have the metastable glassy nematic state. Above 215 K in MBBA and 200 K in EBBA the probe will irreversibly transfer into metastable crystalline phase I and above 235 K in MBBA and 233 K in EBBA there is a second irreversible transfer into metastable crystalline phase II.[8-10] The irreversible transition into the stable crystalline state takes place around 259 K in MBBA and 253 K in EBBA. In this phase the mobility of the methoxy or ethoxy group as well as the butyl group is completely quenched and no contribution to dielectric loss can be observed. Theoretical considerations concerning the microdynamics of liquid crystal molecules lead to the following results. The rotations of the methoxy group around the OC-aromatic axis was studied on a simplified PAA model.[11] The enlarged COC angle of 118.7° (instead of 109.5°) indicates an influence of the H(benzene)-H(methyl) interaction on the barrier height. The methoxy group needs an activation enthalpy of about 0.2 eV. The analysis of the rotations of a butyl group has also been carried out on a simplified DB-PBB model. When all motions of the butyl group are separated into rotations of methyl, ethyl, propyl and butyl, activation enthalpies around 0.1 eV are obtained for all of these motions.[11] Other authors have calculated higher activation enthalpies for a rotation: 0.15 eV for the ethyl group and 0.35 eV for the propyl group.[12] These computational results demonstrate that the rotation of the end group of MBBA is more or less hindered by the molecule itself.

§ 2. THE TSD MEASURING METHODS

The probe is positioned between two condenser plates. While an electric dc field E_p is applied, the probe is cooled to lower temperatures. Hereby molecular groups containing electric dipole moments may get a preferred orientation in the external field. In thermal equilibrium the resulting polarization P will increase with decreasing temperature following the Langevin equation

$$P = Np^2E_p/k_BT; \qquad (pE_p \ll k_BT) \tag{1}$$

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N is the dipole concentration, p the dipole moment, k_B the Boltzmann constant and T is the absolute temperature. Below a characteristic temperature T_m the reorientation of the special dipolar group may be quenched because the reorientation time follows the Arrhenius equation

$$\tau = \tau_0 \exp(H_a/k_B T) \tag{2}$$

(where H_a is the reorientation enthalpy and τ_0 the reciprocal frequency factor) and reaches values above say 10^5 s. Here the probe behaves like an electret. Now the electric field E_p is switched off and the condenser is connected to a sensitive ampere meter capable of measuring currents down to 1fA from high impedance sources. By increasing T with a constant rate $q = dT/dt$ the depolarization produces a current density

$$j(T) = \frac{P(T_p)}{\tau(T)} \exp\left[-\frac{1}{q} \int_{T_0}^{T} \tau(T')^{-1} \, dT' \right] \tag{3}$$

This 'glow' curve with a well defined activation enthalpy H_a is characteristic for isolated dipole centre depolarization in ionic crystals. In the undercooled nematic modifications we have to deal with similar short range order as in the nematic phase.[5,13] Below 180 K only relaxation of the end-group of the molecules is possible. Reorientation takes place in a plurality of different surroundings. Cooperative processes as formulated by Jonscher[14] cannot be excluded completely. But as long as we lack of an appropriate theory we apply the formulas known for isolated centres. Eq. (3) can be corrected for an inhomogeneous broadening due to variations in the reorientation enthalpy as van Weperen *et al.*[15] pointed out. For a gaussian distribution of H_a with halfwidth W one has to multiply the right side of Eq. (3) by the factor

$$\begin{aligned} F(H_a, \tau_0, W, T) = \frac{1}{W\pi^{1/2}} \int_0^\infty dH \Bigg[\exp\Bigg(&- \frac{H - H_a}{k_B T} - \frac{(H - H_a)^2}{W^2} \\ &- \frac{1}{b\tau_0} \int_0^T \left(\exp\left(-\frac{H_a}{k_B T'} \right) - \exp\left(-\frac{H_a}{k_B T'} \right) \right) dT' \Bigg) \Bigg] \end{aligned} \tag{4}$$

However, TSD bands of liquid crystals in their frozen glassy state are

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too broad to be analysed successfully by this way. So we have applied two different methods in order to reach a higher resolution.

The first method is known as the partial heating technique from which the activation energies are determined by the so-called initial rise (IR) method. After the sample has been polarized it is discharged by successively linear heating from a temperature T_0 to an elevated temperature T_m, ΔT higher than the previous T_m, always cooling to T_0 between the single steps. By plotting $\ln I$ vs. T^{-1} one derives the activation enthalpy as a function of T_m reached in each single run, as long as the exponent on the right side of Eq. (3) does not deviate substantially from unity. Consecutive temperatures T_m can be as small as $\Delta T = 4$ K.

The second method uses the 'thermal sampling (TS) technique'. The probe is kept in the polarizing field E_p at the constant polarization temperature T_p for the time t_p. Then, with the field still on, the temperature is decreased to $T_d = T_p - \Delta T$. Here the field E_p is switched off and a partial depolarization takes place during the time t_d. Finally the sample is cooled down to T_0, the starting temperature of a normal TSD run. By this procedure only those dipoles will contribute to the TSD peak which have been frozen in between T_p and T_d. In order to take account of the residual distribution in H_a we apply Eqs. (3) and (4) and make a computer fit to the experimental curve. Hereby the parameters H, τ_0, and W, obtained after each fitting procedure are independently varied in order to reach the absolute minimum of this least square fit. One obtains H_a and τ_0 as a function of the TSD peak temperature T_m, if one successively repeats this experiment with a constant ΔT and a T_p stepwise increasing over the temperature range of the broad TSD band.

§ 3. EXPERIMENTAL DETAILS

We use MBBA with a clearing point of 46 °C which has been synthesized and purified in our laboratory. EBBA (Riedel de Haen) is used without further purification. In order to obtain samples in the cylindrical shape of tablets (diameter 13 mm, thickness 0.5 mm) which can easily be mounted between circular plane electrodes, powder of potassium bromide (suprapur, Merck) is wetted with about 5% of the liquid crystal (EBBA needs $T \approx 60\,^\circ\mathrm{C}$) and pressed to a tablet (as used for IR techniques). Below 190 K pure KBr gives no detectable depolarization current and up to 300 K its contribution to the TSD current is negligible compared to that of the liquid crystals. Vapor

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pressure of the liquid crystals below 190 K is low enough so that no material loss is observed during most of the measurements and also at 300 K losses by evaporation remain small enough. In order to transfer the probe from the liquid crystalline into the glassy state we cool it with a rate $q \geq 50$ K/min starting from the stable nematic phase.

For the TSD measurements we use the same equipment as described.[16] The condenser, containing the probe has good thermal contacts to the inner tank of a He cryostat. One electrode highly insulated by sapphire plates ($R \geq 10^{16}$ Ω) can be connected to a vibrating capacitor electrometer (Keithley 640). Its time constant of 20 seconds has no noticeable effect upon the TSD curves obtained with a heating rate up to $q = 2 \times 10^{-2}$ K/s. Temperature differences within the probe are negligibly small and do not disturb the TSD curves. Temperatures are measured with an iron vs. constantan thermocouple. The resolution of the temperature measurement is better than 0.1 K for $T > 70$ K.

§ 4. RESULTS AND DISCUSSION

a) Survey of the TSD spectra

An example of the complete TSD spectrum of EBBA is given in Figure 1. The probe has been cooled from 330 K with a cooling rate of $q \approx 50$ K/min. At about 273 K an electric field of $E_p = 30$ kV/cm has been applied down to 15 K. The TSD current is measured from He temperature up to room temperature with a heating rate of $q = 1$ K/min. One observes three distinct broad bands with maxima T_m at 64.5 K, 124.7 K, and 254 K. Similar results are obtained from MBBA with the two lower bands shifted to 69.5 and 117.5 K.

The high temperature band observed in both materials is strongly influenced by their d.c. conductivity. Because it is one hundred times higher than the middle band the contributions due to molecular dipole orientation seemed to be negligibly small to space charge and interfacial polarization. From the special preparation of our probes we have to deal with areas of LC material of different sizes and shapes, isolated within the KBr matrix. This band would be a kind of interfacial Maxwell-Wagner-Sillar polarization.[1] At the moment we are not further interested in it.

The lowest band has a very small area, about 1/10 of the middle band. Therefore and because of the experimental expenditures for cooling to He temperatures we have not further analysed it yet. Dipole

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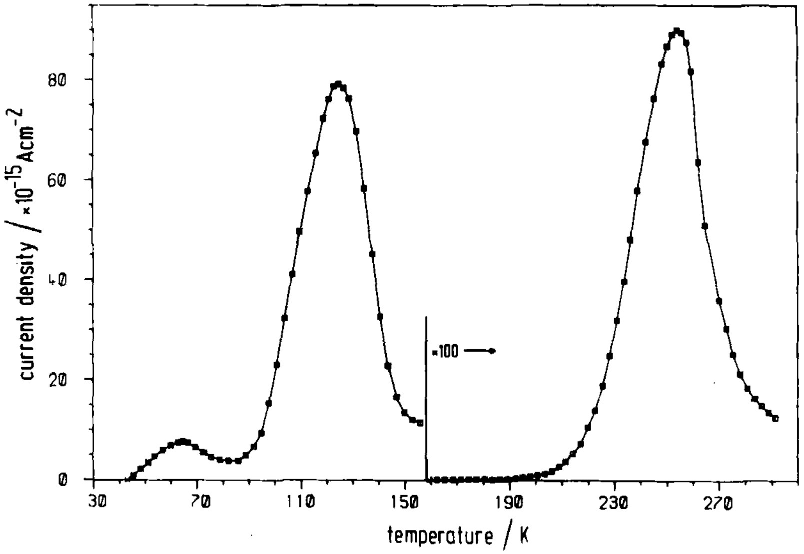

FIGURE 1 TSD current density as a function of temperature for EBBA (polarized from T_p = 273 to T_0 = 15 K).

moments belonging to this band should be small compared to those of the middle band. A small dipole moment can be expected for the butyl group. We estimate for the activation enthalpy H_a a range between 0.13 eV and 0.18 eV. This is the same order as calculated for the rotation of the ethene group at the end of the buthene chain.[11,12] From the difference in T_m we estimate the reorientation enthalpy in MBBA about 0.15 meV higher than in EBBA. It can be a consequence of the larger portion of rigidity in MBBA compared to EBBA at about the same density for both.

The middle band appears at temperatures where the mobility of the molecules is still quenched with regard to translation or reorientation of their long axes. From the average reorientation enthalpies analyzed for this band (see Figure 4) namely 0.28 eV for MBBA and 0.31 eV for EBBA, and from the fact that changes of the polarization of dipole moments connected to the possible motion of the methoxy or ethoxy group are considerably higher than for the butyl group, we associate this band with those groups which distinguish MBBA from EBBA.[17,18] Because of its sufficient intensity this TSD band will be studied more thoroughly in *b*) and *c*). However before we do that let us report

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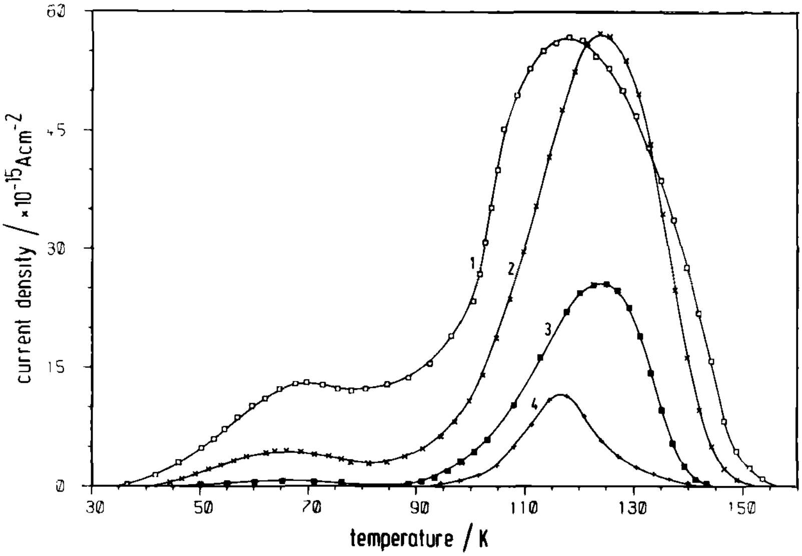

FIGURE 2 TSD-spectra of MBBA obtained by annealing the sample. 1) After rapid cooling to the supercooled nematic phase. 2) After annealing at 230 K for 3 minutes. 3) After annealing at 230 K for 180 minutes. 4) After annealing at 278 K for 300 minutes.

experimental results about the annealing behaviour of the two low temperature bands in the case of MBBA.

Figure 2 shows 4 TSD runs between 30 K and 160 K. First the probe is cooled down with a rate of q = 70 K/min from 305 K to 78 K. The polarizing steps are the same for each curve. At 137.5 K a polarizing field of E_p = 30 kV/cm is applied for t_p = 4 min. With the field still on, the probe is cooled down to the temperature of liquid helium. Then the TSD current is measured using a heating rate of q = 1.0 K/min. No difference to curve 1, which belongs to the freshly quenched probe, can be observed, after keeping the probe for 3 h at 180 K. Curve 2 is obtained after the probe has seen 230 K. Curve 3 is the result after annealing the probe at 230 K for 3 hours. Finally the probe is annealed at 178 K for 6 h and curve 4 is found.

As explained in the introduction the glassy nematic phase is converted into metastable phase I around 215 K and then into the metastable phase II around 235 K. Finally around 265 K one observes another transition into the stable crystalline state. From our few data we suggest that curves 2 and 3 already belong to metastable phase I in which the part of mobile butyl and methoxy groups is steadily decreased. Especially this holds for the low temperature band of the

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butyl group which is nearly lost in curve 3. Here transition into metastable phase II can be supposed. In curve 4 the small band at $T_m = 113$ K could be due to residual mobility of the methoxy group within grain boundaries of the otherwise crystalline probe.

Such TSD measurements on stepwise annealed probes appear as a sensitive method for studying structural changes from the metastable glassy to the crystalline state. However if we restrict us to the glassy nematic state we find the bands much broader than can be described by Eq. (3) using a definite H_a and τ_0 value. So the width of the middle band of curve 1 in Figure 2 is more than four times as broad as the ideal TSD band using parameters as finally found for this band. Therefore now this band is studied in more detail by applying the partial heating and the thermal sampling technique.

b) The initial rise (IR) method (partial heating technique)

The detailed analysis of the middle band takes the following steps. After fast cooling the probe into the glassy nematic phase we apply a polarizing field $E_p = 30$ kV/cm at $T_p = 137.5$ K and wait 4 min until we cool the probe down to 78 K. After the field is switched off, we temporary warm up to 90 K in order to get rid of the low temperature part of the band. Then the probe is heated from a low enough temperature with a constant rate of $q = 1$ K/min so that the initial rise of the depolarization current can be measured. The maximal temperature T_m at which the probe is rapidly cooled down again is stepwise increased by 4 K. From a logarithmic plot of the current versus reciprocal temperature we obtain sufficiently good straight lines. Their slope determines the activation enthalpy belonging to T_m. These data are collected in Figure 4 for MBBA and for EBBA as dashed lines. The vertical error bars are estimated to ± 10 meV. Here we have taken into account some uncertainty in the background current and in the way to adapt the straight line to the measuring points. For MBBA we find a steady increase of H_a from 0.26 eV at 94 K to 0.32 eV at 122 K. For EBBA the increase of H_a goes from 0.23 eV at 74 K to 0.33 eV at 130 K. The IR method does not allow to get τ_0 values, which normally are a good control if the data agree with common models.

c) The thermal sampling (TS) method

Following the steps described in § 2 we have used $T_p - T_d = \Delta T = 2$ K, $t_p = 120$ s and $t_d = 30$ s before rapid cooling down to LNT. The

TSD bands obtained from each run while stepwise increasing T_p by 2 K show monotonically increasing areas. To each band a theoretical TSD curve is fitted as described in § 2. Figure 3 gives an example for EBBA with $T_p = 120$ K and $T_d = 118$ which is typical for all TSD curves analysed. The parameters for this curve are $T_m = (117.9 \pm 0.2)$ K, $H_a = (0.342 \pm 0.004)$ eV, $\lg(\tau_0/\mathrm{s}) = -12.1$, and $W = (15.6 \pm 1.0)$ meV.

There is one important experimental fact which holds for MBBA as well as for EBBA: The maximum temperature T_m of the TSD bands comes out to be, within narrow limits, directly proportional to T_p. Only at the upper end of the temperature range investigated, the straight line correlating T_m with T_p values shows small deviations in a way that T_m is about 2 degrees smaller than T_p. In case the broad middle band would consist of a number of discrete single TSD bands one would expect steps with nearly constant T_m values. Because this is not so we may conclude that the middle band belongs to a single relaxation mechanism. The new data of $H_a(T_m)$ are plotted in Figure

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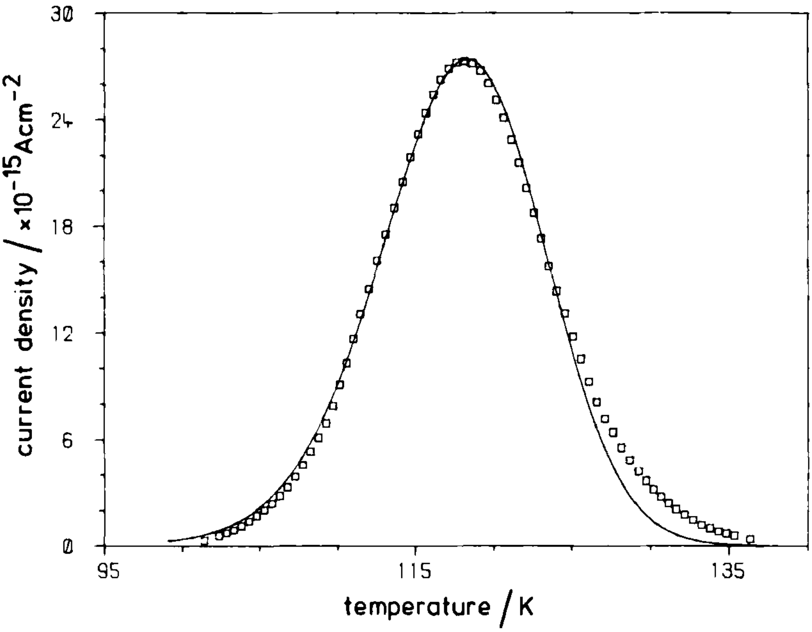

FIGURE 3 Typical thermal sampling measurement of EBBA with polarization interval from $T_p = 120$ K to $T_d = 118$ K. The full line is the least-squares fit to the data points (applying Eq. (3) and (4)).

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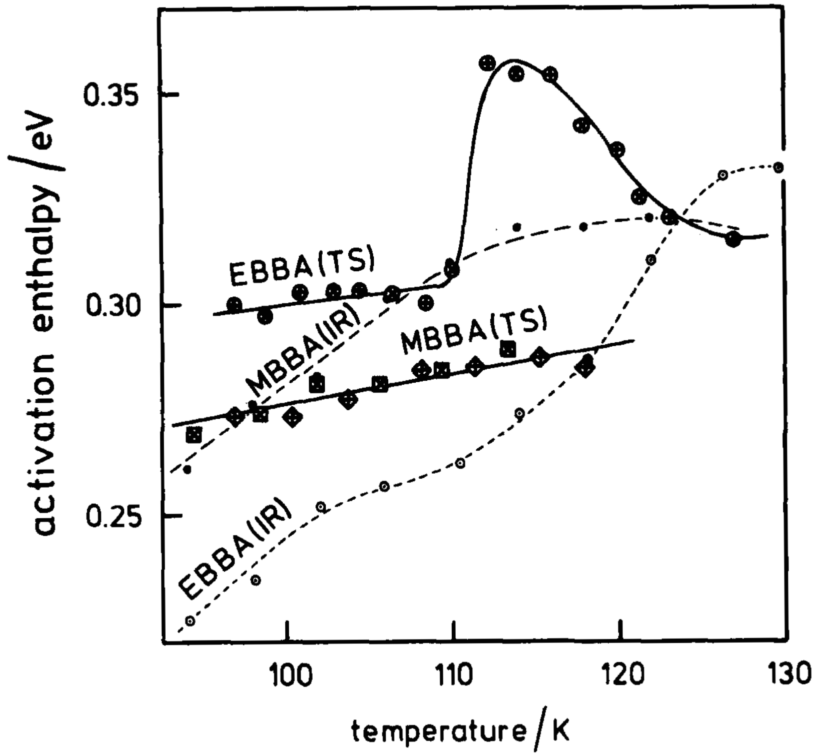

FIGURE 4 Activation enthalpy as a function of temperature T_m for MBBA and EBBA. IR (dashed lines): initial rise of partial heating (T_m = maximum temperature of single heating step). TS (full lines): thermal sampling (T_m = temperature of maximum of TSD band).

4. They are connected by a smooth full curve in order to distinguish the TS data from the IR data.

If we first restrict to MBBA we recognize that TS gives less variation in $H(T_m)$ than IR. On the other hand if we look at the logarithmic plot of τ_0 vs. T_m (Figure 5) we observe a steady increase of τ_0 with T_m.

The data of EBBA reveal an additional phenomenon which can only be recovered from the TS technique and is not seen with the IR technique. Between 112 K and 122 K one observes a deviation from the more linear behaviour seen in EBBA below 110 K and in MBBA over the full range. Extrapolation of this straight line in EBBA to

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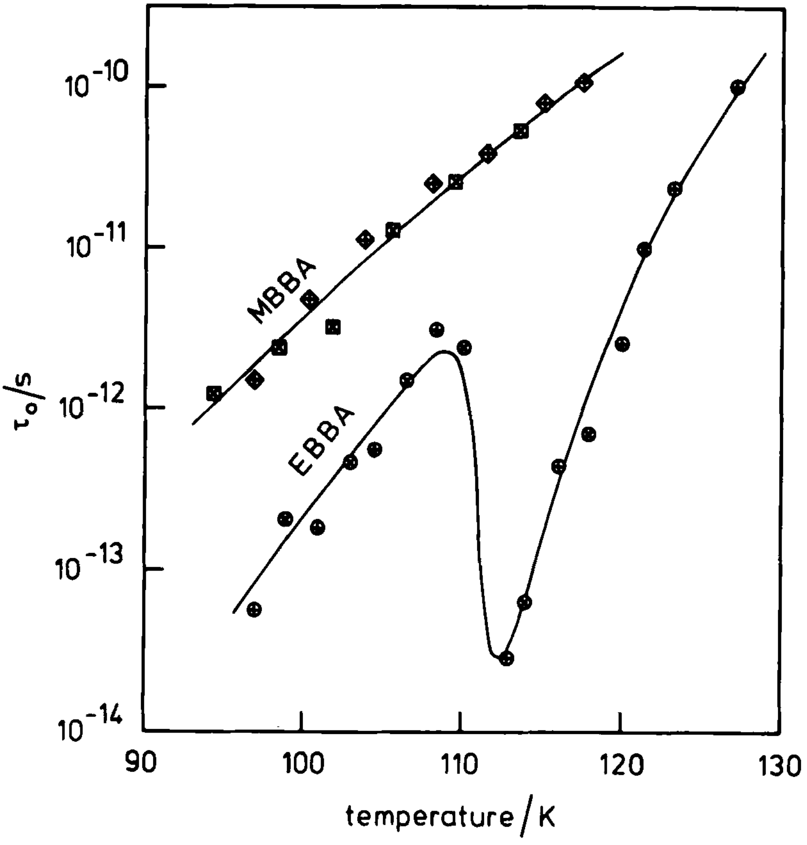

FIGURE 5 Reciprocal frequency factor as a function of temperature T_m for MBBA and EBBA, obtained from TS technique.

higher T_m meets again the measured points at 127 K. In this range of deviation H_a is increased by up to 50 meV and τ_0 is decreased by up to two orders of magnitude measured from the extrapolated straight line. The different signs used in Figure 4 and Figure 5 belong to different probes which confirm the reproducibility of these data.

The gaussian broadening W obtained from fitting the TSD bands is pretty constant over the whole T_m range except the upper two runs where a tendency to smaller values is indicated. In the average we find $W = 11.8$ meV for MBBA and $W = 14.1$ meV for EBBA, without any notable deviation between 112 and 122 K.

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d) Discussion of the IR and TS results

The activation enthalpy for reorientation of the methoxy group in MBBA and the ethoxy group in EBBA, determined by the IR and the TS method and presented in Figure 4, show certain similarities, concerning their temperature dependence, if one compares curves obtained with the same method. Otherwise they show remarkable differences, if one compares the IR and the TS curve of the same substance. While TS recovers features in $H_a(T_m)$ and $\tau_0(T_m)$ (see Figure 4 and Figure 5), the IR method presents a much larger dependence of H_a with T_m. It seems to us that the IR method averages over a larger ensemble of molecular surroundings than the TS method. If τ_0 is more influenced than H_a by different surroundings, a result obtained by the TS method, then the IR method wrongly interprets this fact as a stronger variation in $H_a(T_m)$. Therefore we shall base our discussion more upon the TS results.

The methoxy group is most favorably oriented normal to the plane of the neighbour benzene ring. For an 180° reorientational jump the benzene ring presents the potential barrier. This intramolecular part of the activation enthalpy dominates over the intermolecular contributions. So the activation enthalpy is only spread from 0.27 eV to 0.29 eV. In agreement with that is the gaussian width $W = 11.9$ meV of the single TSD bands. So the main broadening effect to the complete methoxy band comes from the differences of more than two orders in the τ_0 values. This is common to other organic molecular compounds, especially to polymers.[19] As already pointed out in the case of the ethoxy band in EBBA one has a more complicated situation. Leaving aside this deviation from a straight run between 112 K and 122 K then we can find the same argument as given for the methoxy reorientation. Again the ethoxy group is more favorably oriented normal to the plane of the adjacent benzene ring. Hereby the ethoxy group has the stretched trans-position. However, also, the cis-position can be expected. While in the transposition of the ethoxy group the intermolecular interaction will be higher than in the cis-position, we expect a higher intra-molecular activation enthalpy and a shorter relaxation time for this cis-position. This could be the reason why between 112 K and 122 K we observe the deviation in H_a and τ_0. However, it must not be the simple superposition of the action of two independent sets of molecules. Otherwise we would not have observed the nearly perfect identity of T_m and T_p over the whole temperature range, and we would not observe the smooth broad middle band in Figures 1 and 2. So we have further to suppose that trans- and cis-position of the ethoxy group are in thermal equilibrium with one another.

References

1. C. Bucci, R. Fieschi and G. Guidi, *Phys. Rev.*, **148**, 816 (1966); J. Vanderschueren and J. Gasiot, Thermally Stimulated Relaxation in Solids, Ed. by P. Bräunlich (Springer, Berlin, Heidelberg, New York, 1979), Chap. 4, pp. 135–223.
2. H. S. Sack and M. C. Moriarty, *Solid State Commun.*, **3**, 93 (1965).
3. J. M. Moscicki, *Solid State Commun.*, **20**, 481 (1976).
4. T. Shinoda, Y. Maeda and H. Enokido, *J. Chem. Thermodynamics*, **6**, 921 (1974).
5. J. O. Kessler and J. E. Lydon, Liquid Crystals and Ordered Fluids, Vol. 2, Ed. by J. F. Johnson and R. S. Porter (Plenum Press, New York, London, 1974), pp. 331–339.
6. W. Witko and J. M. Janik, *Acta Phys. Pol.*, **A54**, 521 (1978).
7. P. Arendt, H. D. Koswig, P. Reich and W. Pilz, *Mol. Cryst. Liq. Cryst.*, **70**, 295 (1981).
8. J. E. Lydon and J. O. Kessler, *J. de Phys.*, **36**, C1-153 (1975).
9. J. Mayer, P. Waluga and J. A. Janik, *Phys. Lett.*, **41A**, 102 (1972).
10. V. Rochev, O. P. Kevdin, V. G. Nikolskii, A. M. Kaplan, R. Detjen and M. Stryrikovich, *Acta Phys. Pol.*, **A56**, 709 (1979).
11. S. Kugler and G. Naray-Szabo, *Acta Phys. Acad. Sci. Hung.*, **46**, 69 (1979).
12. M. Mizuno and T. Shinoda, *Mol. Cryst. Liq. Cryst.*, **69**, 103 (1981).
13. M. Kirov and M. P. Fontana, *Mol. Cryst. Liq. Cryst.*, **56**, 195 (1980).
14. A. K. Jonscher, *J. Mater. Sci.*, **16**, 2037 (1981).
15. W. van Weperen, B. P. M. Lenting, E. J. Bijvank and H. W. den Hartog, *Phys. Rev. B*, **16**, 2953 (1977).
16. A. Wilbrand and F. Fischer, *Phys. Stat. Sol. B*, **101**, 209 (1980).
17. V. K. Agarwal and V. P. Arora, *J. Chem. Phys.*, **66**, 2817 (1977).
18. V. K. Agarwal and V. P. Arora, *Mol. Cryst. Liq. Cryst.*, **43**, 117 (1978).
19. J. van Turnhout, Thermally Stimulated Discharge of Polymer Electrets (Elsevier, Amsterdam, 1975).

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