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GLASSY TRANSITION IN LIQUID CRYSTAL EUTECTIC MIXTURES

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Abstract. Direct microscopic observation of liquid crystal eutectic mixtures during cooling in a differential thermal analyser (DTA) oven allows the identifications of peaks recorded on the DTA curve. The glassy transition observed at low temperature is "abnormal".

In order to fulfill the various requirements of liquid crystal displays the liquid crystals (L.C.) used are complex eutectic mixtures. Although melting point is a useful characteristic of these mixtures, it is difficult to determine because of large supercooling effects, and it is generally unknown or only an approximate value is given.

We report the freezing and subsequent melting of two commercial L.C. mixtures: a Schiff base mixture ROTN 200 from Hoffmann- La Roche (1) and a biphenyl mixture E 8 from BDH (2).

These transitions were studied using a Mettler ATD 2000 differential thermal analyser. Usually, closed cups of aluminium are used as sample containers in DTA measurement, but these cups degrade Schiff base, as was shown by the constant decrease of the nematic to isotropic transition temperature ($T_{N\rightarrow I}$) from one cycle to the next during repetitive temperature scanning.

With ROTN 200 ($T_{N\rightarrow I}$ = 65°C (1)), the first cycle from 25°C to 80°C gave, passing from the nematic to the isotropic state, a peak whose maximum was at 64,8°C (which is taken as $T_{N\rightarrow I}$). Cooling to - 170°C and reheating gave $T_{N\rightarrow I}$ =63,5°C, a third cycle giving 61,5°C.

In order to avoid this decomposition, the cups were treated with Silane A 1100 (3) which deactivates the superficial alumina layer.

The DTA curve of ROTN 200 recorded upon cooling from + 80°C (isotropic state) to - 170°C at a scan speed of 10°C/min is shown in Figure 1.

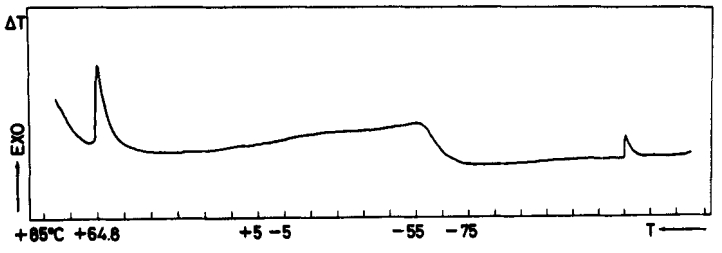

FIGURE 1. Differential thermogram of ROTN 200 L.C. on cooling. Reference Al_2O_3. Crucible Aluminium, silane treated. Atmosphere N_2. Scan speed 10°C/min. Range 50 μV/fsd. Sensitivity 63,5 μV/mcal/s.

Starting from the isotropic state (80°C), the isotropic to nematic transition appears as an exothermal peak at 64,8°C. On further cooling, the curve presents a step between - 55°C to - 65°C and then an exothermal peak with a steep rise at - 135°C.

Reheating from - 170°C gave the curve shown in Figure 2. Between - 60°C to - 55°C, a step is again observed, then a plurality of peaks and dips, the number and intensity of which varied from one recording to another. Such irreproducible behavior has already been reported on thermal investigation of MBBA (4). At 64,5°C a nematic to isotropic transition occurred.

Assignment of the thermal phenomena revealed by the DTA is speculative. Although the observed steps are indicative of glassy transition (5), which has already been observed in single liquid crystals (6), the identification of other peaks is not clear.

The oven of the Mettler ATD 2000 was modified in order to allow the observation of the L.C. through a polarising microscope during the temperature evolution.

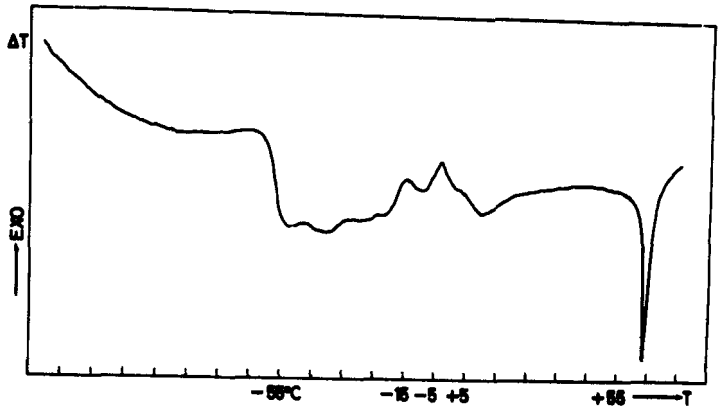

FIGURE 2. Differential thermogram of ROTN 200 L.C. on warming. Reference Al_2O_3. Crucible Aluminium, silane treated. Atmosphere N_2. Scan speed 10°C/min. Range 50 μV/fsd. Sensitivity 63,5 μV/mcal/s.

A drop of L.C. was placed in a glass cup which was lying on a piece of polariser inside the measuring cell; the reference was the same device. The cover of the oven was replaced by an anti-reflective glass and the inside illuminated with an optical fibre. The whole was kept under dry nitrogen. Under these conditions the DTA curves are the same as those obtained using Silane treated aluminium cups. Observing the L.C. drop through the microscope allows the following interpretation.

On cooling, at - 55°C the nematic L.C. turned into a pasty supercooled liquid, the thermal capacity C_p of which is near that of the solid, giving rise to a step due to the lower C_p of supercooled liquid as compared with that of the nematic phase (ΔC_p = 0,07 cal/g/°C). Although the DTA recording in this temperature range looked like that for a vitreous transition, it was only between - 100°C and - 145°C (- 136°C on Figure 1) that the L.C. drops froze suddenly and the internal energy of the supercooled liquid was released so quickly that sometimes the cups jumped in the oven.

The freezing was indicated by an exothermal peak with a steep rise in the range - 127°C to - 137°C. The solid which formed looked like a glass containing a lot of cracks.

On heating, the glass melted reproducibly between - 60°C and - 55°C giving a step similar to the one observed on cooling (ΔC_p = 0,09 ± 0,01 cal/g/°C); the glass transition temperature was T_g - 57°C.

The cracks present in the solid transformed into domain boundaries in the liquid. These boundaries migrated on further heating from - 50°C to - 15°C and disappeared either by the joining of two boundaries or by elimination at the edge of the drops. The disappearance of the boundaries gave rise to endothermal peaks when they fused or exothermal peaks when they disappeared. The intensity of the peaks depended on the length of the boundary which disappeared, corresponding to energy values from to 4,64 J/g. The peaks and dips observed on heating the glassy L.C. result from the migration of these cracks.

The L.C. behaviour was unchanged by the use of a lecithin aligning layer (homeotropic) or by the speed of cooling, whether the L.C. drop was quenched in liquid nitrogen or slowly cooled at 4°C/min. In every case, glass with cracks was formed.

E 8 and ROTN 200 gave similar DTA curves with glass transition temperatures (inflexion points) T_g = - 54,5°C and T_g = - 57,1°C respectively. These temperatures are reproducible and not as sensitive to impurities as the $T_{N \rightarrow I}$.

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