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A study of enthalpic relaxation of a liquid crystal

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A liquid crystal, BL038, which was observed not to crystallize, has a glass transition at 215 K and a nematic to isotropic transition at 380 K. Samples aged below the glass transition at various temperatures T_a, exhibited an endotherm at the transition which developed with extent of ageing time, t_a. We attribute this endotherm to the relaxation of the glass towards the equilibrium liquid. The progress of the relaxation process was measured using differential scanning calorimetry. On subsequent reheating, the aged glass showed an apparent shift in the glass transition to higher temperatures. The endotherm was used to define the extent of enthalpic relaxation and the maximum value observed was found to increase initially then decrease, with the extent of undercooling from the glass transition temperature, ΔT, passing through a maximum for a $\Delta T = 15$ K. From the temperature dependence of the relaxation times, an apparent activation enthalpy for the relaxation process of $85 \pm 10\,\mathrm{kJ\,mol^{-1}}$ was determined. The small value of the activation enthalpy compared with that found in the ageing of polymers reflects differences in the molecular species involved in relaxation processes.

1. Introduction

Organic glasses are not in thermal equilibrium, but approach it over extended time periods in a limited temperature range close to but below the measured glass transition temperature. This process of change is called enthalpic relaxation [1–4] and has been studied in order to determine the underlying molecular dynamics. The nature of the glass transition as either a thermodynamic or kinetic process has been debated for many years; however, measurements of the enthalpic relaxation are consistent with the experimentally determined glass transition being a kinetic process. In this contribution we report the enthalpic relaxation of a low molecular mass nematic liquid crystal glass. The liquid crystal material used in this study is BL038 from EM Industries and is a blend of seven components, some of which are cyanobiphenyl derivatives. One of the components is 4-pentyl-4′-cyanobiphenyl, 5CB (alternatively known as K15). BL038 is an important technological liquid crystal (LC) material, because it has a wide operating temperature and a large refractive index anisotropy, Δn, of approximately 0.3 and is used in a number of electro-optic devices.

When a liquid is rapidly quenched from the melt, the molecular conformation of the liquid is frozen with the molecules in higher energy levels than the equilibrium conformation. However, the molecular conformations still retain some mobility and the molecules relax towards equilibrium with time in a process known as enthalpic relaxation or physical ageing. An endothermic process (with its associated energy change ΔH) arises as a result of the de-ageing on heating through the glass transition. The extent of this process can be followed by measuring ΔH.

As ageing develops, the properties of the glass change; density increases, and the dielectric constant and refractive index decrease. Physical ageing therefore has a considerable impact on the material properties in that they become time dependent. Unlike other ageing processes, the changes in properties are reversed on heating above the glass transition temperature. It is important to appreciate the extent of these changes as well as the underlying mechanisms involved, especially in such well defined materials as liquid crystals whose electrical properties are commercially exploited.

Ageing of organic glass-forming materials has been studied extensively using differential scanning calorimetry (DSC) [4, 5]. When held at a constant temperature (up to 50 K below the glass transition), enthalpic relaxation proceeds with time, t_a, and is observed as a progressive development of an endotherm on the step change of the specific heat at the glass transition. There is a corresponding enthalpy of relaxation $\Delta H(t)$ that has as a limit

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of ΔH_∞ as t tends to infinity. The limiting enthalpy ΔH_∞ is proportional to the under-cooling, $T_g - T_a$, and the change in specific heats between the liquid and the glass at T_g, i.e.

$$\Delta H_\infty = \Delta C_p(T_g)(T_g - T_a). \quad (1)$$

The extent of ageing $\phi(t)$ is defined as

$$1 - \phi(t) = \Delta H(t)/\Delta H_\infty. \quad (2)$$

The development of $\phi(t)$ with time was analysed using the Cowie–Ferguson method [5], assuming a spectrum of relaxations with their own characteristic relaxation times, such that

$$\phi(t) = \exp[-(t/\tau)^\beta] \quad (3)$$

where τ is an average relaxation time and β an inverse measure of the breadth of the relaxations involved in the ageing process. This analysis has previously been applied to the enthalpic relaxation of polymers [6–9].

While there has been a study of the enthalpic relaxation of a liquid crystal polymer glass [10], to our knowledge there are no reported studies on low molar mass liquid crystals. A comparison of the molecular dynamics as well as the β values of different organic glasses, especially of a low molar mass liquid crystal, should be useful in elucidating the molecular nature and the distribution of molecular relaxation processes involved.

2. Experimental

DSC measurements were made on a power-compensation Perkin-Elmer model DSC-2, interfaced to a PC. The calorimeter was cooled with liquid nitrogen.

Liquid samples, 13.84 ± 0.01 mg, were sealed in aluminium pans with an empty pan as reference. The DSC temperature was calibrated from the melting temperatures of indium, stearic acid, water and *n*-dodecanane; and the thermal response from the enthalpy of fusion of indium ($28.42\,\mathrm{J\,g^{-1}}$), and the heat capacity of sapphire.

The sample was heated initially to 410 K so that it was in the isotropic phase and then cooled at $320\,\mathrm{K\,min^{-1}}$ through the glass transition to produce a standard glass. The glass transition temperature was taken to be the midpoint of the step change and measured at heating rates from 40 to $2.5\,\mathrm{K\,min^{-1}}$. The value of T_g was determined by extrapolation to zero heating rate to correct for thermal lag. This value of 213.3 K for the T_g corresponds to that of the standard glass.

Samples were aged in the DSC at under-coolings of 5, 10, 15 and 20 degrees from 15 to 960 min. This was the maximum possible ageing time for the experimental set-up adopted.

3. Results

The LC sample was initially quenched from room temperature at $320\,\mathrm{K\,min^{-1}}$ to 190 K. On subsequent reheating a glass transition was observed at 215 K and a nematic to isotropic transition at about 380 K, see figure 1. The step change in the heat capacity was $0.41\,\mathrm{J\,g^{-1}\,K}$ which is similar to that observed for most organic glasses and consistent with the increase in rotational modes conventionally associated with heating the glass through the transition.

Samples immediately reheated following quenching exhibited a small endotherm superimposed on the glass transition. This is a measure of the asymmetry in cooling at 320 and heating the glass at $20\,\mathrm{K\,min^{-1}}$.

On ageing at a fixed temperature, the extent of enthalpic relaxation was measured by heating the sample through the T_g at an underlying heating rate of $20\,\mathrm{K\,min^{-1}}$. The sample was then quenched at $320\,\mathrm{K\,min^{-1}}$ through the glass transition to 190 K and immediately reheated at $20\,\mathrm{K\,min^{-1}}$, see figure 2. The enthalpy relaxation endotherm superimposed on the heat capacity step-change at

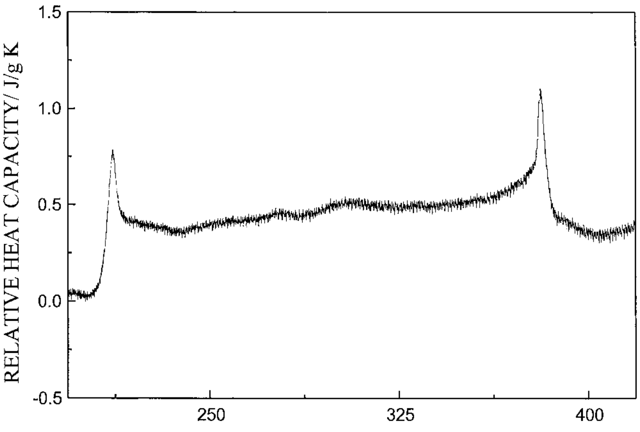

Figure 1. Thermal transitions for BL038 by conventional DSC (heating rate = $20\,\mathrm{K\,min^{-1}}$).

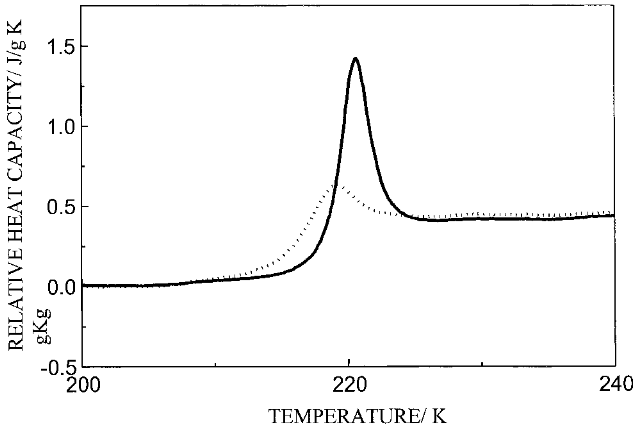

Figure 2. Aged (solid line) and quenched (dotted line) BL038.

the glass transition increased progressively with storage time. This was accompanied by an apparent shift in the glass transition to higher temperatures, see figure 3. Outside the temperature range of the transition and the endotherm, the specific heats of the glass and liquid were independent of storage time and returned to the liquid values following the enthalpy relaxation endotherm.

Due to the asymmetry in heating and cooling the glass, a baseline for un-aged material was subtracted from the specific heat–temperature dependence of the aged samples and the areas under the endotherms integrated to determine ΔH_t, the enthalpy of relaxation at time, t, see figure 4. Equilibrium was considered to have been achieved once the value of $\Delta H(t)$ attained a limiting value as determined from a plot of $\Delta H(t)$ against $\ln(t)$, see figure 5. This was the case for $\Delta T = 5$ K only. At higher ΔT values, equilibrium was not achieved in the time available and this method was considered to underestimate the values of ΔH_∞.

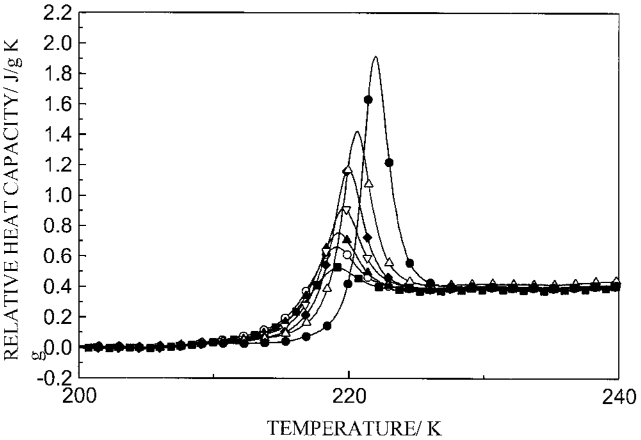

Figure 3. Enthalpic relaxation peak superimposed on T_g of BL038 for ageing time of 0 (solid square), 15 (open circle), 30 (solid up-triangle), 60 (open down-triangle), 120 (solid diamond), 240 (open up-triangle), and 960 (solid circle) min.

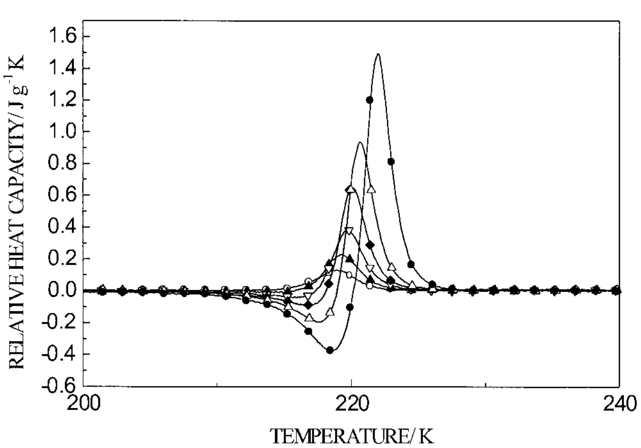

Figure 4. Development of enthalpic peak with time for ageing times of 15 (open circle), 30 (solid up-triangle), 60 (open down-triangle), 120 (solid diamond), 240 (open up-triangle), and 960 (solid circle) min.

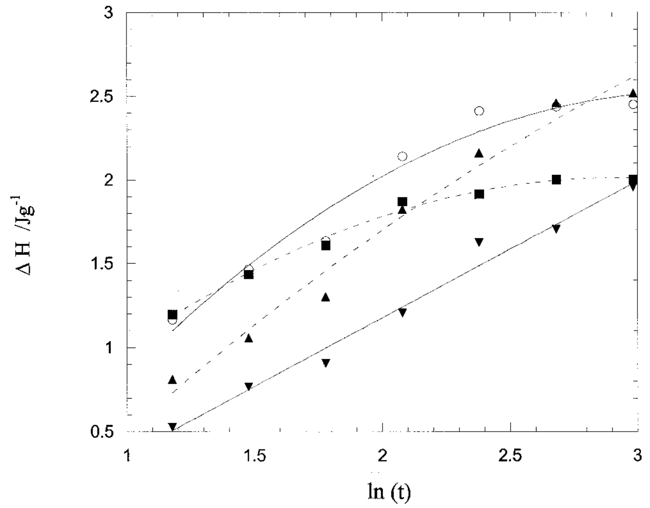

Figure 5. The extent of ageing with ln time (min) for ΔT of 5 (solid square), 10 (open circle), 15 (solid up-triangle) and 20 (solid down-triangle).

The extent of enthalpic relaxation with time was fitted to the Cowie–Ferguson relationship using a non-linear least squares fit. ΔH_∞, τ and β were used as adjustable parameters and best fit values determined for each rate curve, see table 1 and figure 6. The value of β was found to be constant at about 0.47 ± 0.03 and independent of temperature. The temperature dependence of the relaxation time, τ_a, gave an activation enthalpy of $85 \pm 10\,\mathrm{kJ\,mol^{-1}}$. These values of the equilibrium enthalpy of ageing increased non-linearly up to a ΔT of 15 K, see figure 7. The initial gradient was $0.40 \pm 0.02\,\mathrm{J\,g^{-1}\,K^{-1}}$ which is the change in heat capacity at the step change of the glass transition. Equation (1) appears only to be valid at low degrees of under-cooling and ΔH_∞ has been grossly underestimated at the higher ΔT values, see table 1.

Alternatively non-linearity may be present in the enthalpic relaxation. A second procedure was adopted to determine the rate parameters. ΔH_∞ was calculated from equation (1) using a ΔC_p value of $0.41\,\mathrm{J\,g^{-1}\,K^{-1}}$ and the extent of enthalpic relaxation analysed from

Table 1. Enthalpic relaxation kinetic analysis by curve fitting to the Cowie–Ferguson equation.

ΔT/K	ΔH_∞ /J g^{-1}	τ/min	β	$\Delta H_\infty/\Delta T$ /J g^{-1} K^{-1}	ΔH_∞ /$\Delta C_p \Delta T$
5	2.00	18.6	0.48	0.40	0.98
10	2.50	37.1	0.49	0.25	0.61
15	3.00	129	0.49	0.20	0.49
20	2.55	343	0.44	0.13	0.31

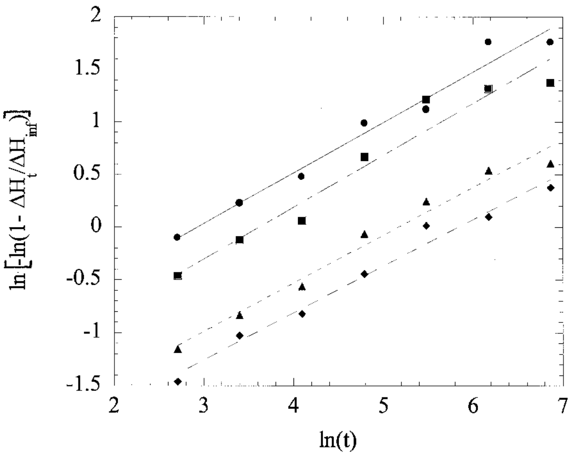

Figure 6. Data fitted to the Cowie–Ferguson relationship to determine ΔH_∞, τ and β. ΔT in degrees = 5 (solid circle), 10 (solid square), 15 (solid up-triangle), 20 (solid diamond).

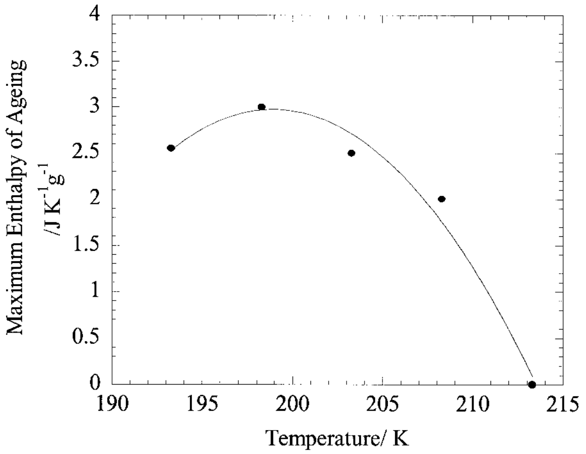

Figure 7. Maximum enthalpy of relaxation versus temperature.

plots of $\ln[-\ln(1-\Delta H_t/\Delta H_\infty)]$ against $\ln(t)$. The β and τ values were determined from the slopes and intercepts and are listed in table 2. There is an overall decrease in β to 0.35 ± 0.5 but more significantly a large increase in τ, especially at higher values of ΔT, and a corresponding increase in the activation enthalpy to 160 kJ mol^{-1}.

Table 2. Enthalpic relaxation kinetic analysis using $\Delta H_\infty = \Delta C_p \Delta T$.

ΔT/K	ΔH_∞/J g^{-1}	τ/min	β
5	2.05	17.5	0.37
10	4.10	643	0.27
15	6.15	3650	0.34
20	8.20	31600	0.34

4. Discussion

The kinetics of enthalpic relaxation appear to follow the Cowie–Ferguson relationship which was derived for polymeric glasses and to have a similar breadth to the relaxation spectrum, i.e. β values of 0.37, which compare well with values observed in other systems. In the case of low molar mass liquid crystals, this low value for β arises from the molecular relaxation of the number of molecular species in the glass, each with their own characteristic relaxation times, rather than the involvement of a number of different chain segments as postulated in the relaxation of a polymer glass [4]. This would be confirmed by a similar study of glass-forming low molar mass liquid crystals containing a single molecular species.

The development of the process in the low molar mass liquid occurred over extended storage times, particularly at the higher degrees of super-cooling and it was not possible to follow it to completion due to experimental limitations in maintaining the temperature below 200 K for more than 1000 h. Since the extent of enthalpic relaxation was not followed to a high enough conversion, 60–30%, see table 1, the curve-fitting analysis greatly underestimated ΔH_∞, and the average relaxation time, τ.

The activation enthalpy determined, 160 kJ mol^{-1}, is less than that normally observed for organic polymers, but is consistent with the lower glass transition temperature, 210 K, and the comparative flexibility of the liquid crystal segments.

Small molar mass liquid crystals should readily crystallize on cooling. One of the components of the blend, 4-pentyl-4′-cyanobiphenyl, 5CB, (also known as K15) exhibits a crystalline–nematic transition at 297.2 K and a nematic–isotropic transition at 308.2 K [11]. However, its crystallization behaviour was irreproducible and strongly dependent on thermal history. It was prone to supercooling and crystallized up to 60 K below the m.p. Blended with other low molar mass liquid crystals, it is possible that the crystallization rate was further depressed.

It is interesting to note that the T_g/T_m ratio is approximately 2/3 which is widely observed in many glass-forming systems.

5. Conclusions

The low molar mass liquid crystal undergoes enthalpic relaxation at rates that depend on the extent of undercooling from the glass transition temperature and is apparent as an endotherm superimposed on the glass transition. The process is interpreted as an extension of the relaxation of the liquid to equilibrium conformations of the molecules whose formation has been prevented by the onset of the glass formation.

This confirms the general conclusions that the glass transition is kinetic in nature.

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