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THE HEIGHT OF DSC PHASE TRANSITION PEAKS
II. Some applications to liquid crystals

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Liquid crystal → liquid crystal and liquid crystal → isotropic liquid transitions of several materials are studied using a number N, where N is defined as the ratio h'/h, h and h' being the heights of the transition peaks at heating rates $\dot{T}_p$ and $2\dot{T}_p$ respectively. N is found close to two, which shows that a heat capacity increase occurs near the transition temperature, in agreement with the current theories describing these transitions.

In Part I of this paper [1], theoretical expressions are derived for a number N, defined as $N = h'/h$, where h is the height of a transition peak for a mass of sample m and a heating rate $\dot{T}_p$ and h' is the height of the same peak for a mass $2m$ or a heating rate $2\dot{T}_p$. Values of N are given for different types of transition. Two main pieces of information can be deduced from the measurement of N. The first one is connected with anomalous values of N and the other one with an estimate of the relative importance of the first and the second order components in a phase transition. The transition between a nematic (or cholesteric) phase and an isotropic liquid phase is of first order, but is usually described as "a weakly first order" transition [2]. The purpose of this paper is to apply the measurement of N to several low molar mass or polymer liquid crystalline systems.

Phase transitions in liquid crystals

Liquid crystals are one of the sub-classes of mesomorphic materials (materials having properties and structures intermediate between a true crystal and a true liquid). Liquid crystals can be roughly described as sets of molecules having no long range positional order but only a long range orientational order. There are several possibilities for such a molecular arrangement, called nematics, cholesterics or smectics (see for example ref. [2]). Low molar mass liquid crystals are the most well known, but it is also possible to obtain liquid crystalline phases with polymers, either in the bulk or in solution.

The liquid crystal to isotropic liquid (LC → L) transition has been studied mainly in two ways. The first one is to consider the isotropic liquid, and the second the liquid crystal phase.

The isotropic liquid was studied by De Gennes [3] who used a Landau type theory. This theory involves a power series expansion of the Helmholtz free energy F near the transition in terms of an order parameter S. The deductions which can be made concerning magnetic birefringence, flow birefringence, light scattering intensity and shear viscosity are all consistent with experiments. The transition is of first order, with a strong second order component.

Numerous theories describe the liquid crystalline phase, and it is beyond the scope of this paper to review them (see for instance the review paper of Smith [4]). Most of the theories are more or less based on the original work of Maier and Saupe. These authors used a mean field theory with a quadratic S dependence of the interaction energy between molecules. The main features of this theory and its derivatives are in agreement with experimental evidence. The theory predicts a first order liquid crystal-isotropic liquid transition. This result was criticized by some authors who discussed whether this first order transition could be due to the mean field approximation and found, by other methods, a second order transition [4]. The results are less certain when smectic phases are involved since their description is not fully established.

As seen above, the exact nature of phase transitions involving liquid crystalline phases is not well known. From an experimental point of view, the easiest way to study these phase transitions is to use a calorimetric tool. As seen in Part I, the problem is that the recorded heat power (for DSC) is a mixture of the enthalpy and the specific heat capacity contributions. This can be illustrated in the following manner: due to long range fluctuations of the order parameter near the transition, the specific heat capacity is supposed to increase a lot up to the transition point, as drawn in Fig. 1. At the transition temperature, a first order phase transition takes place with a transition enthalpy ΔH (Fig. 1). The recorded DSC peak will be the mixture of these two contributions, and N will strongly depend on the relative importance of the specific heat capacity and the height of the peak. If the specific heat capacity is small, even its strong increase at the transition will not affect N, which will be a first order phase transition (Fig. 2.a). In the opposite case, N will reflect the increase of the specific heat capacity, and should be near 2 (Fig. 2.b).

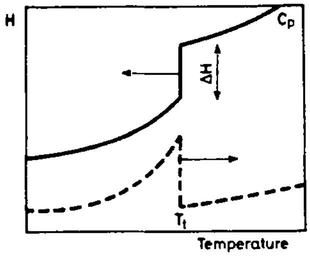

Fig. 1 Schematic liquid crystal → isotropic liquid transition. T_t: transition temperature, H: enthalpy, C_p: heat capacity

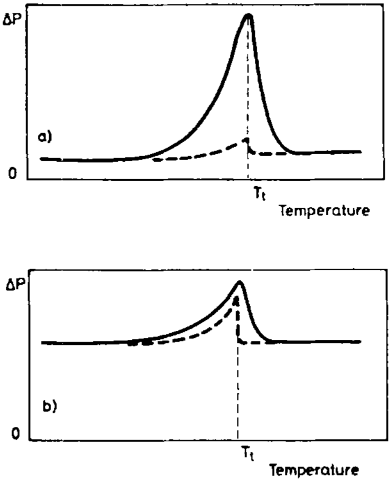

Fig. 2 Schematic DSC trace for a liquid crystal → isotropic liquid transition. a: heat capacity small compared to the height of the peak, b: heat capacity large compared to the height of the peak

Several liquid crystalline materials will be studied, and the number N measured. Its value will be discussed in the light of the theoretical results exposed above.

Experimental section

p-Azoxyanisole (PAA) was supplied by Fluka. A smectic and cholesteric sample for thermometry, labelled TM75A, was used as received from BDH. Hydroxypropylcellulose (HPC), $M_w = 60.000$, from Hercules, was dehydrated at 100°C prior to use. Cellulose triacetate (CTA), supplied by Fluka was mixed with trifluoroacetic acid (TFA) at room temperature for several hours and studied in the following three days. Measurements were performed with a Perkin–Elmer DSC 2 calorimeter.

Results and discussion

p-Azoxyanisole

Figure 3 shows a DSC trace of p-azoxyanisole: the first peak at 117° is the crystal → nematic transition peak. Its N value is 1.4 (measured with $\dot{T}_p = 2.5$, 5 and 10 deg min^{-1}). The second peak at 135° is the nematic → isotropic liquid transition peak. Its N value is 1.3 (same heating rates). These two N values are typical of first order phase transitions (see Part I).

The heat capacity of PAA is small compared to the height of the peak. Even if an anomalous second order phenomenon occurs, increasing the heat capacity jump under

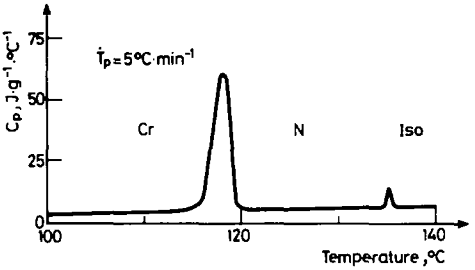

Fig. 3 Experimental DSC trace of *p*-azoxyanisole. Cr: crystal, N: nematic phase, Iso: isotropic liquid

the nematic → isotropic liquid peak by 100% or 200%, it cannot shift *N* towards two in a detectable way. It is the case shown in Fig. 2.a.

TM75A

Figure 4 shows a DSC trace for this material. The two peaks at 41° and 53° correspond respectively to the smectic → cholesteric and cholesteric → isotropic liquid transitions. The *N* values were measured for low heating rates (0.62, 1.25 and 2.5 deg/min) since the peaks are close together, and found to be 1.9 for the first peak and 1.8 for the second one. TM75A is a favorable case since its heat capacity is large compared to the height of the peaks. The smectic → cholesteric peak is enlarged in Fig. 5. Even by taking into account the variation of heat capacity between the two

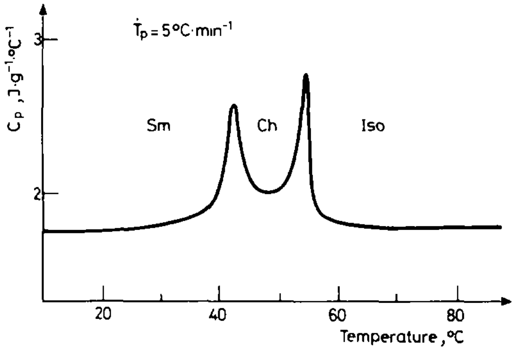

Fig. 4 Experimental DSC trace of TM75A. Sm: smectic phase, Ch: cholesteric phase, Iso: isotropic liquid

phases under the peak, it is impossible to find a *N* value so close to two. The only way is to suppose that a second order component plays an important role, as in Fig. 2.b. This is what is theoretically predicted.

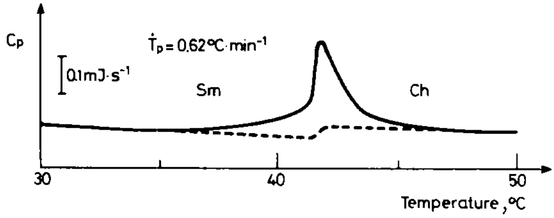

Fig. 5 TM75A: the smectic A → cholesteric transition. Sm: smectic phase, Ch: cholesteric phase

Cellulose triacetate – trifluoroacetic acid cholesteric solutions

This kind of lyotropic liquid crystal polymer undergoes a mesomorphic-isotropic solution transition upon heating [5]. The peak is well defined, but very small. No precise explanation is available for describing the transition since several theories exist [6]. The determination of *N* for this transition gives 1.85 (concentration of polymer: 26% by weight). The number *N* is very close to 2 and this can be explained if it is the melting of an impure solution, or the end of a dissolution process or if there is a strong second order component in the transition. The materials used are pure, and the second hypothesis is not valid [6]. So, this high value of *N* probably reflects that a liquid crystal (nematic) – isotropic solution transition is only weakly first order. This result is close to the case of TM75A. This is consistent with new theories of semi-flexible mesomorphic polymers [7, 8] using Landau and Maier–Saupe type theories.

Hydroxypropylcellulose

Hydroxypropylcellulose was found to be a thermotropic liquid crystal between 160° and 205° [9]. Upon heating, a DSC trace shows only one peak, which corresponds to two transitions, the crystal – liquid crystal and the liquid crystal – isotropic liquid ones (Fig. 6). The *N* value is 2.6. This anomalous value reflects a two-transition phenomenon, as in the case of *N*-methylmorpholine *N*-oxide (see Part I). Indeed, these two peaks can be detected upon cooling, as is usual for monotropic liquid crystals (Fig. 6). The first use of the *N* number, i.e. the detection of anomalous transition, finds here another application.

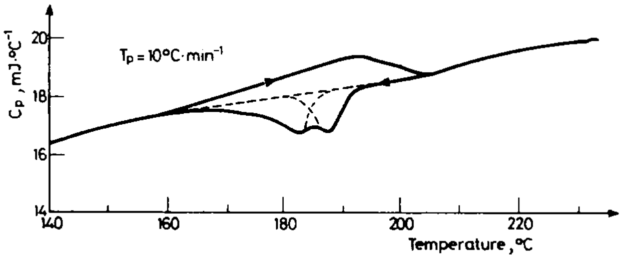

Fig. 6 Experimental DSC trace of hydroxypropylcellulose

Conclusion

The use of the number N for studying the liquid crystal → isotropic liquid transition gives the following results: liquid crystals with a small heat capacity compared to the height of the peak show the first order component of the transition. On the contrary, liquid crystals with a large heat capacity have a N number close to two, which cannot be understood without involving a large increase of heat capacity at the clearing point, in agreement with the theoretical predictions. A liquid crystal → liquid crystal (smectic A → cholesteric) transition gives the same result. All these results imply that the measurement of enthalpies of these transitions should be carried out with care. If N is close to 1.4, measured enthalpies reflect the enthalpy of the first order component of the transition, and it is correct. If N is close to 2, the area of the peak is not directly connected with the enthalpy of the transition since the baseline line under the peak is not flat.

In conclusion, the number N seems to be a very useful tool to characterize the liquid crystal → isotropic liquid and liquid crystal → liquid crystal transitions. A lot of work has now to be performed to check that it is applicable to all the transitions found for liquid crystal materials. It is, of course, beyond the scope of this paper to consider all the types of mesomorphic phases and all the transitions they can undergo. The main purpose of the present paper is to give preliminary results showing that the use of the number N is likely to provide valuable information on phase transitions in liquid crystalline materials. In the near future, this new concept could be applied with benefit to other low molar mass liquid crystalline systems, such as alkylcyanobiphenyls. This could explain, in particular, considerable discrepancies between the different transition enthalpy measurements [10, 11]. It is also planned to use the number N in the study of phase transitions in lithium stearate, which are currently under investigation in our laboratory [12].

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Zusammenfassung — Für verschiedene Materialien wurden die Übergänge Flüssigkeitskristall → Flüssigkeitskristall und Flüssigkeitskristall → isotrope Flüssigkeit untersucht, wobei eine Zahl N eingeführt wurde, die als das Verhältnis h'/h der Höhen der Übergangspeaks bei den Aufheizgeschwindigkeiten $\dot{T}_p$ bzw. $2\dot{T}_p$ definiert ist. Es wurde festgestellt, daß N nahe 2 ist, was zeigt, daß in Übereinstimmung mit den diese Übergänge beschreibenden aktuellen Theorien die Wärmekapazität in der Nähe der Übergangstemperatur ansteigt.

Резюме — Изучены для некоторых веществ переходы типа жидкий кристалл-жидкий кристалл и жидкий кристалл-изотропная жидкость, используя параметр N, определяемый отношением h'/h, где h и h'-высота пиков перехода при скоростях нагрева, соответственно, $\dot{T}_{\text{п}}$ и $2\dot{T}_{\text{п}}$. Найденный параметр N близок к значению 2, что свидетельствует об увеличении теплоемкости около температуры перехода. Это явление согласуется с теориями, принятыми для описания таких переходов.