Journal of Thermal Analysis, Vol. 30 (1985) 61–64

THE HEIGHT OF DSC PHASE TRANSITION PEAKS APPLICATION TO LIQUID CRYSTALS

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A new method for differentiating first- and second-order transition in liquid crystalline systems is proposed. It is based on the use of the ratio $N = h/h_0$, where h_0 is the height of the transition peak recorded by DSC at a heating rate $\dot{T}_p$ with a mass m, and h is the height of the corresponding peak when the heating rate or the mass is doubled. The application of this new concept to phase transitions in octylcyanobiphenyl (8CB) is mentioned.

Differential scanning calorimetry (DSC) is a widely used technique, which gives reliable results quickly and requires only a small amount of material. Trouble may arise in certain cases, however, since what is measured is a differential heat power ΔP and a time t, while what is needed is a heat energy (or enthalpy) H and a temperature T. In most cases, the relationships between ΔP, t, H and T are known and a proper calibration gives the values of H and T.

In the case of liquid crystals, however, the situation is not so simple. Figures 1A and 1B illustrate two extreme cases. Figure 1A shows the enthalpy H versus temperature T curve for an isothermal first-order transition of a pure one-component material, and its DSC trace. It can readily be seen that there is not a linear correspondence between t and T in the DSC trace. The energy of the transition ΔH is represented by the hatched area, and it can be shown that it is about the same as the area of the peak between t_1 and t_3. Figure 1B is the enthalpy versus temperature plot and the DSC trace for a second-order transition (no isothermal enthalpy jump), of the type which is likely to occur in liquid crystalline phase transitions. In this case, there is a linear dependence of t and T. The hatched area between t_1 and t_3 in the DSC trace reflects the energy involved in heating the sample from T_1 to T_3. No latent heat is involved in this transition and the area under the peak represents the excess enthalpy H_E. The problem is even more complicated when strong pre- or post-transitional effects take place, as found in most liquid crystalline transitions and illustrated in Fig. 1C. It is very difficult to differentiate the DSC traces in cases B and C, and almost impossible to measure ΔH in case C (the hatched area in the DSC trace). Confusion between the area of the transition peak and the latent heat is frequently found in DSC studies of liquid crystalline materials.

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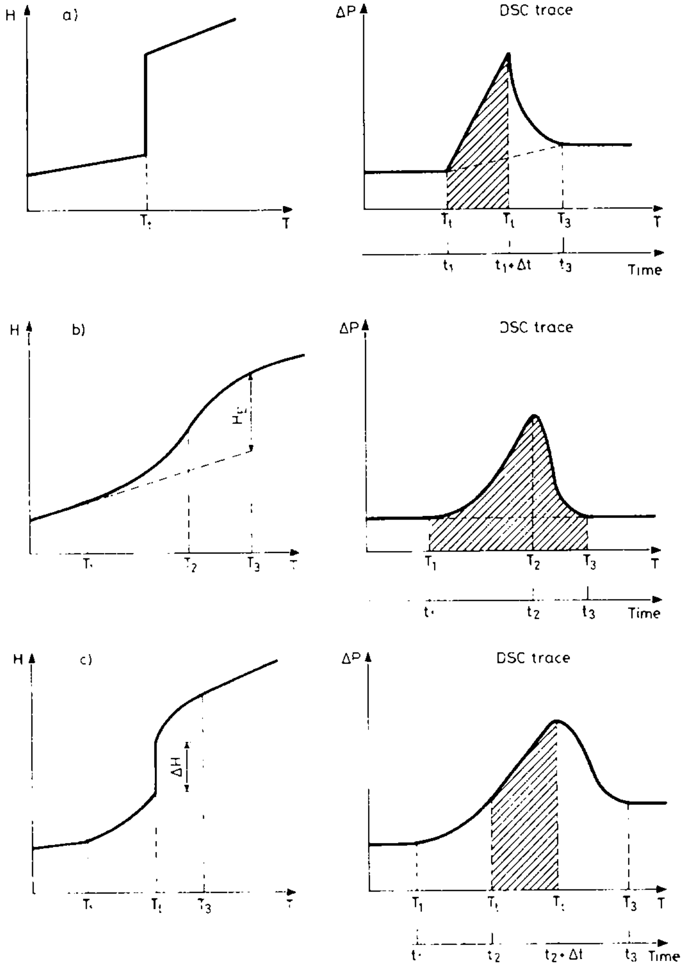

Fig. 1 a. Enthalpy H versus temperature T for a first-order transition and the corresponding DSC trace, where ΔP is the heat power and t the time. b. Second-order transition. c. First-order transition with pre- and post-transitional effects

In order to prevent this, a method for differentiating first- and second-order transitions in the case of a pure single-component material was recently proposed [1]. This method is based on the use of the ratio $N = h/h_0$, where h_0 is the height of the transition peak (at a heating rate $\dot{T}_p$ and with a mass m) and h the height of the corresponding peak when the heating rate or the mass is doubled.

Application of number N to phase transitions in liquid crystals

For a first-order transition (as in Fig. 1A):

$$N = \frac{2\left[-1 + \left(1 + \frac{\Delta h}{mC_p^2 R_0 \dot{T}_p}\right)^{\frac{1}{2}}\right]}{-1 + \left(1 + \frac{2\Delta h}{mC_p^2 R_0 \dot{T}_p}\right)^{\frac{1}{2}}} \tag{1}$$

and so

$$1 \leqslant N \leqslant \sqrt{2}$$

where Δh is the specific enthalpy of the transition, m is the mass of the sample, C_p is the specific heat capacity of the sample below the transition, R_0 is the thermal resistance between the sample and the oven, and $\dot{T}_p$ is the heating rate.

For a second-order transition (as in Fig. 1B):

$$N = 2 \tag{2}$$

Thus, a simple measurement of the height of the peak allows the determination of a latent heat, if one exists. One of the main uses of this method is its application to liquid crystals, where some transitions are known to be of the types shown in Fig. 1B and 1C. The measurement of N was first carried out for several mesomorphic materials [2], and the values were found to range from 1.4 to 1.9, indicating that either pre- or post-transitional effects or second-order transitions are present and can be detected. When the material in question is not pure or is a mixture, the use of this theory is problematical, and this cannot readily be resolved.

We recently overcame this difficulty by studying materials which have several transitions, at least one of which is known to be first-order with no pre-transitional effects [3]. One can easily check the validity of the theory by measuring N for this known peak ($N \leqslant 1.4$). The results have shown that octylcyanobiphenyl (8CB) has first-order crystal-smectic and nematic-liquid transitions, with N being 1.3 for these two transitions, while N is 2.0 for the smectic-nematic transition [3]. Several studies [4, 5] have shown that the tricritical point, at which the smectic-nematic transition changes from second-order to first-order, is at 9 carbon atoms in the alkyl chain, and that 8CB has a second-order smectic-nematic transition. All the previous DSC studies have assigned a first-order character to this smectic-nematic transition. The measurement of N is thus a way to prevent confusion between the existence of a DSC peak and the first-order character of a transition. It eliminates the possibility of a latent heat when the transition shows strong pre- and/or post-transitional effects. This method has also bridged a gap between high-resolution adiabatic calorimetry and DSC and allows the determination of the order of a transition by DSC.

References

1 P. Navard and J. M. Haudin, J. Thermal Anal., 29 (1984) 405.

2 P. Navard and J. M. Haudin, J. Thermal Anal., 29 (1984) 415.

3 P. Navard and R. J. Cox, Mol. Cryst. Liq. Crist., 102 (1984) 261.

4 J. Thoen, H. Marynissen and W. Van Dael, Phys. Rev. Lett., 52 (1984) 204.

5 B. M. Ocko, R. J. Birgeneau, J. D. Litster and M. E. Neubert, Phys. Rev. Lett., 52 (1984) 208.

Zusammenfassung — Eine neue Methode zur Unterscheidung von Umwandlungen erster und zweiter Art in flüssigen Kristallen wird vorgeschlagen, die auf Anwendung des Verhältnisses $N = h/h_0$ basiert, wobei h_0 die Höhe des durch DSC bei einer Aufheizgeschwindigkeit $\dot{T}_p$ und für die Masse m registrierten Umwandlungspeaks und h die Höhe des entsprechenden Peaks bei Verdoppelung der Aufheizgeschwindigkeit oder der Masse bedeuten. Auf die Anwendung dieses neuen Konzepts auf Phasenübergänge in Octylcyanobiphenyl (8CB) wird eingegangen.

Резюме — Предложен новый метод дифференциации переходов первого и второго порядков в жидких кристаллических системах. Метод основан на использовании соотношения $N = h/h_0$, где h_0-высота температурного пика, измеренного методом ДСК при скорости нагрева $\dot{T}_p$ и с массой m, а h-высота соответствующего пика при двойной скорости нагрева и массе. Показано применение новой концепции к фазовым переходам в октилцианобифениле.