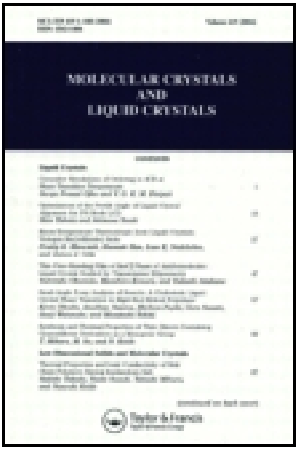


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase transition of liquid crystal carboxylate from crystalline state to smectic phase B investigated by low-frequency internal friction and DSC

Yongsong Liu [a] & Jiapeng Shui [a]

[a] Laboratory of Internal Friction and Defects in Solids, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031, P. R. China

Version of record first published: 27 Oct 2006

To cite this article: Yongsong Liu & Jiapeng Shui (2000): Phase transition of liquid crystal carboxylate from crystalline state to smectic phase B investigated by low-frequency internal friction and DSC, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 338:1, 151-157

To link to this article: http://dx.doi.org/10.1080/10587250008024426

Mol. Cryst. Liq. Cryst., Vol. 338, pp. 151-157
Reprints available directly from the publisher
Photocopying permitted by license only

Phase transition of liquid crystal carboxylate from crystalline state to smectic phase B investigated by low-frequency internal friction and DSC

YONGSONG LIU* and JIAPENG SHUI

Laboratory of Internal Friction and Defects in Solids, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, P. R. China

(Received December 14, 1998; In final form April 19, 1999)

Phase transition of liquid crystal carboxylate from crystalline state (K) to smectic phase B (S_B) is investigated by low-frequency internal friction (IF) and DSC method. The IF peak temperature increases with the increase of heating rate, but it has no clear dependence on vibration frequency. The experimental results agree with the characters of the low-frequency IF associated with first-order phase transition, and the change in the quantity of phase interface is responsible for the IF peak.

Keywords: internal friction; liquid crystal; phase transition; DSC; carboxylate

INTRODUCTION

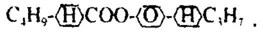
As an orientation-order fluid, liquid crystal is mesomophic phase between a complete ordering crystal and an anisotropic liquid. Because of their very wide application, there has been much research focused on these materials. The internal friction (IF) technique is useful for the study of structural transition in solids since it is structurally sensitive[1]. Since torsion braid analysis (TBA)[2] was put forward, the study range of the IF technique was expanded from solid materials to viscid liquids. Up to now, little IF study on the phase transition of liquid crystal has been done[3-5].

---

* Correspondence Author

On the origin of IF peak associated with phase transition, there are many different viewpoints. (a) In the explanation of the steady-state IF peak during martensitic transformation, a theory of soft modulus was presented[6]; (b) Ke, *et al.*[7]hold the viewpoint that the IF is related with movement of extended dislocations on the coherency interface; (c) Postnikov, *et al.*[8] suggested that the IF is concerned with the fluctuation during the phase transition; (d) Zhang, *et al.*[9] advanced an interface kinetic model and contributed the low-frequency IF to the movement of phase interface. In this work, compared with DSC results the phase transition of liquid crystal carboxylate from crystalline state (K) to smectic B (S_B) is studied by low-frequency IF method in forced-vibration mode and the mechanism of the IF peak is discussed.

EXPERIMENTAL PROCEDURE

In the experiments the liquid crystal material is *trans-4-(4'-propyleyclohexyl)phenyl trans-4-butylcyclohexane carboxylate*, which chemical formula of is  . It is prepared by Tsinghua Liquid Crystal Materials Company.

Low-frequency IF measurements were held on Multi-function Internal Friction Apparatus (MFIFA-I) and the measurement pattern is forced vibration. DSC experiments were carried out on Perkin-Elmer DSC-2C apparatus. The IF and DSC experiments were all measured with increasing temperature.

The samples used are composite of copper rod as substrate and a thin layer of liquid crystal covering it. The rod, made of commercial pure copper, is about 60 *mm* in length and about 1 *mm* in diameter. The layer thickness of liquid crystal is of the order of several micrometers.

RESULTS

In Fig.1, Curve (i), the IF verus temperature (Q^{-1}-T) curve of pure copper rod shows that the IF value (Q^{-1}) increases slowly with increasing temperature, as the background value in our experiments, and Curve (ii) shows the Q^{-1}~T curve of composite of liquid crystal and copper rod in the temperature range from 30 °*C* to 80 °*C*. It is seen that there is one IF peak at about 54 °*C*. So the peak is contribute to the internal structure transition of liquid crystal.

Fig.2 shows DSC scanning spectrum of liquid crystal during heating process. There is one endothermal peak at about 52 °*C* in the temperature range from 30 °*C* to 80 °*C*, corresponding with the phase transition from K to S_B.

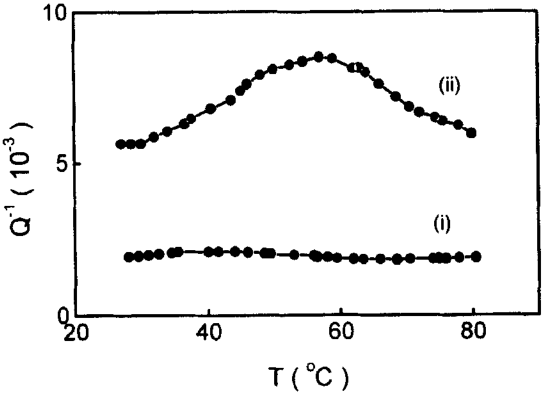


FIGURE 1 The temperature-dependence of IF (Q^{-1}) (i) the pure copper rod, (ii) the composite of liquid crystal carboxylate and copper rod

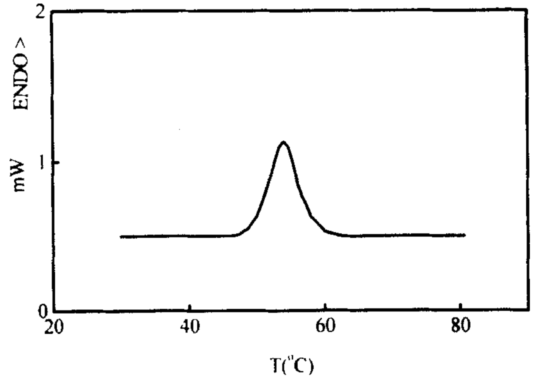


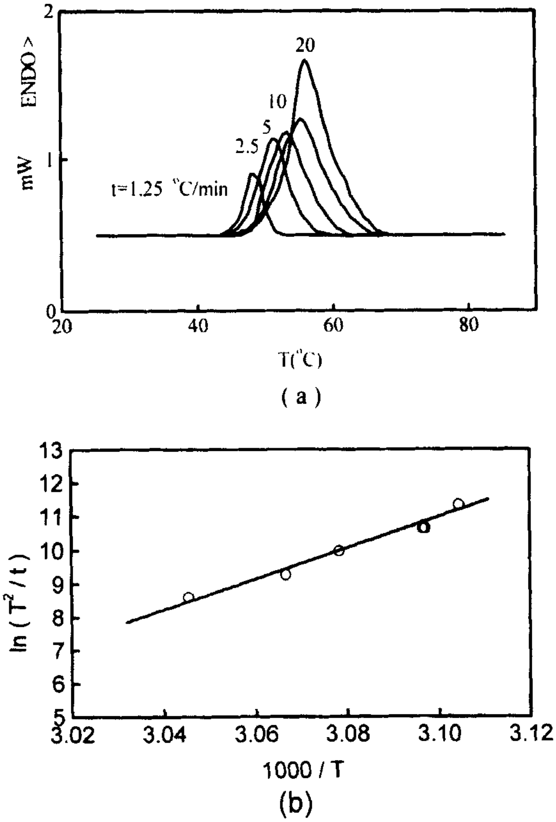
FIGURE 2 DSC scanning spectrum of liquid crystal carboxylate during heating process (heating rate: 5 °C/min

In order to calculate the activation energy of the phase transition of liquid crystal carboxylate from K to S_B, a series of DSC experiments were carried out during heating process at five different scanning rates (1.25, 2.5, 5, 10 and 20 °*C/min*), see Fig. 3(a). It can be seen that the peak temperature (*T*) and height all become higher with the increase of scanning rate (*t*). The relationship can be described with Kissinger Equation[10],

$$\ln\left(\frac{T^2}{t}\right) = A + \frac{E}{KT}$$

where A is a constant, E is the apparent activation energy, T is peak temperature, t is heating rate, and K is the Boltzmann constant. Using the formula, we can get the relationship curve in Fig. 3(b) and the apparent activation energy of the endothermal peak is the slope of the straight line, $E_{DSC}=(3.80\pm0.45)eV$.

Compared with the DSC results, the Q^{-1}~T curves at five different heating rates (1, 2, 4, 6 and 8 °*C/min*) show that the peak temperature (T) and height of the IF peak also become higher with the increase of the heating rate (t) (see Fig. 4(a)), a same variation tendency with that in Fig. 3(a). According to the Kissinger Equation, the relationship curve is plotted in Fig. 4(b) and the apparent activation energy of the IF peak is: $E_{IF}=(3.87\pm0.62)eV$. The two values of activation energy are equal within the effective error range. Hence, the IF peak is due to the phase transition from K to S_B.



(a)

(b)

FIGURE 3 (a) The endothermal curves of DSC at different scanning rates. (1.25, 2.5, 5, 10 and 20 °*C/min*). (b) The relationship curve between the peak temperature of endothermal peak (T) and scanning rate (t)

Simultaneously, in order to study the frequency dependence of IF peak, the Q^{-1}~T curves at different vibration frequencies are plotted as Fig.5. The vibration frequencies are 0.1, 0.5, 1 and 2.5 *Hz*. They show that the peak temperature hardly changes with vibration frequency. The results are corresponding with the general characters of the low-frequency IF associated with first-order phase transition.

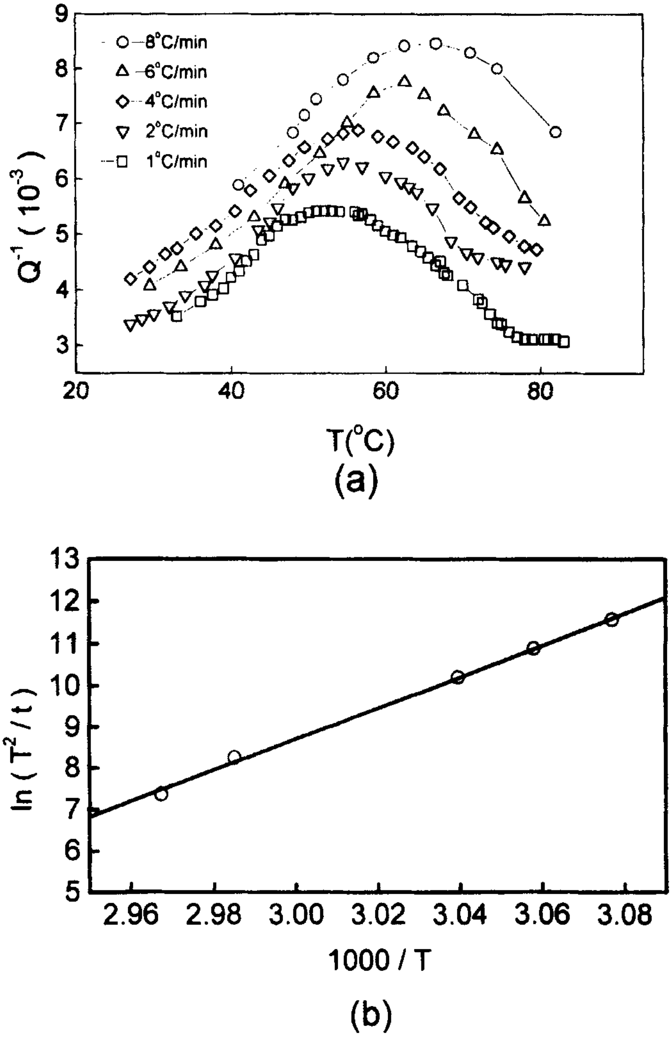


FIGURE 4 (a) The low-frequency IF-temperature curve at different heating rates (1, 2, 4, 6 and 8 *°C/min*). (b) The relationship curve between the peak temperature of IF peak (*T*) and the heating rate (*t*)

DISCUSSION

The transition from crystalline state to liquid crystal is a reversible endothermal phase transition, called as first-order phase transition in thermodynamics, verified by DSC experimental results. Phase transition happens at a curtain temperature, called temperature of phase transition, and also called chain-melting temperature (T_{cm}) for liquid crystal. The experimental results have showed that the IF peak is due to phase transition from K to S_B.

It is known that liquid crystal is composed of rod-like molecules. The alignment of rod-like molecules will change when the phase transition takes place. The position shift of rod-like molecules usually is behind the external force, *i.e.*, there is a lag in phase between external force and strain produced by the movement of molecules, due to its mass and long chain structure. It is the origin of IF associated with phase transition of liquid crystal.

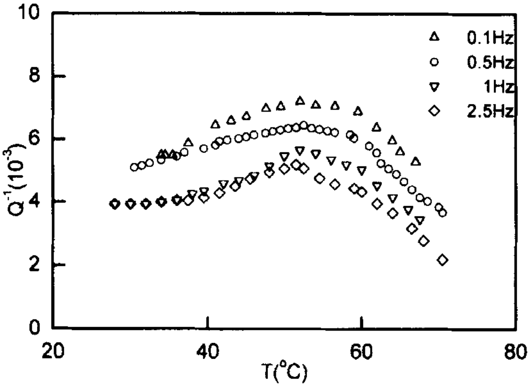


FIGURE 5 Q^{-1}-T curves at different vibration frequencies: 0.1, 0.5, 1 and 2.5 *Hz*

The IF peak is due to the change in the quantity of phase interface. When the temperature reaches T_{cm}, the liquid crystal sample begins phase transition from K to S_B, and the phase interface forms. Phase interface is viscoelasticity, so at this time viscoelasticity internal friction shows majority role. With temperature increasing the quantity of phase transition increases much, and the quantity of phase interface also increase, so the IF value increases rapidly; when the quantity of phase interface amounts to the maximum, the IF value reaches the maximum; with the continuous increase of quantity of phase transition due to the increase of temperature, the quantity of phase interface begins to decrease because the volume fraction of the new phase is bigger than that of the parent phase, so the IF value also begins to decrease: when the parent phase all changes into the new phase, the phase interface disappears, so the IF value of the new phase increases with increasing temperature.

The peak temperature of IF peak increases with the increase of heating rate. When the heating rate increases, the phase transition of liquid crystal delays due to the kinetic reason, hence the temperature of phase transition increases.

With the same heating rate, the change of the vibration frequency does not affect the begin temperature of phase transition, *i.e.*, the temperature of IF peak has not clear dependence on the vibration frequency. So the temperature of IF peak hardly change with vibration frequency.

CONCLUSIONS

The phase transition of liquid crystal carboxylate from K to S_B is investigated by low-frequency IF and DSC technique. From the experimental results and discussion, the following conclusions are obtained,

(1) The peak temperature increases with the increase of heating rate; it has no clear dependence on vibration frequency, but the IF peak height decreases with the increase of vibration frequency. The results agree with the characters of the low-frequency IF associated with first-order phase transition.

(2) The IF peak is due to the change in the quantity of phase interface.

(3) The IF technique can be effectively used to study the phase transition of liquid crystal.

Acknowledgements

Liquid crystal carboxylate taken by TsingHua Liquid Crystal Material Company is gratefully acknowleged. Authors thank Dr. G. T. Fei and Dr. G. S. Cheng for the valuable suggestions.

References

(1) D. C. Wu, X. G. Xie and J. J. Xu, *Polymocular Liquid Crystals* (in Chinese) (Sichuan Education Press, Chengdu, China, 1988) 1st ed..
(2) J. K. Gillham and M. B. Roller, *Polym. Eng Sci.*, **11**, 295 (1971).
(3) D. Samatowicz, *J. de Phys. Colloque*, **48**, C8–525 (1987).
(4) W. Brostow and D. Samatowicz, *Poly. Eng. Sci.*, **33**, 581 (1993).
(5) J. S. Zhu, M. Gu, Z. M. Sun, Z. F. Zhang, *Phy Stat. Sol. (a)*, **125**, K53 (1991).
(6) Y. N. Wang, Z. J. Yang, H. Zhu and J. C. Ma, *Acta Nanjing University* (in Chinese), **7**, 1(1963).
(7) Y. L. Ma and T.S. Ke, *Acta Chin. Phys.*(in Chinese), **20**, 910 (1964).
(8) V. S. Postnikov et al, *Nuova Cinento*, **B33**, 1125 (1976).
(9) J. X. Zhang, P. C. W. Fung and W. G. Zeng, *Phys. Rev.* **B52**, 258 (1995).
(10) H. E. Kissinger, *Anal. Chem.*, **30**, 2129 (1982).