New Finding of Glassy Liquid Crystal – a Non-equilibrium State of Cholesteryl Hydrogen Phthalate

Kazuhiro Tsuji, Michio Sorai, and Syûzô Seki
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

(Received March 25, 1971)

The ordinary glassy state is realized for many liquids when they are supercooled below their glass transition points without crystallization. This type of glassy state, however, can be established by other procedures, *e.g.* condensation of vapor,[1] precipitation process,[2] or thermal decomposition.[3] Recently we reported also the possible existence of glassy state of crystalline materials as a non-equilibrium state of many plastic crystals.[4] In this communication, we should like to report the new finding of the glassy state for liquid crystal of cholesteryl hydrogen phthalate (abbrebiated as CHP).

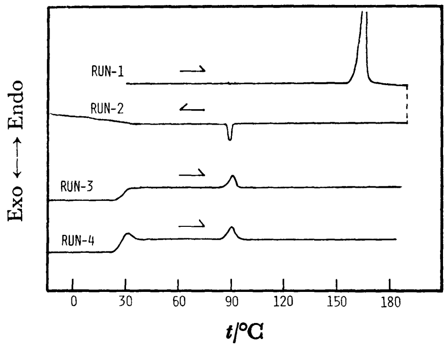

Fig. 1. DSC curves of cholesteryl hydrogen phthalate.

CHP obtained from Tokyo Kasei Kogyo Co., was recrystallized twice from ethanol. Thermal analysis was carried out for this specimen with a differential scanning calorimeter (Perkin-Elmer DSC-1B) as shown in Fig. 1. Run-1 shows a heating curve of crystalline CHP from room temperature to 190°C with the heating rate of 5°C/min. The crystalline CHP melted directly into an isotropic liquid at 160°C. Run-2 shows a cooling curve of the isotropic liquid with cooling rate of −5°C/min. The isotropic liquid was transformed into a liquid crystalline state at 90°C and no other thermal anomaly was observed between 90 and −100°C except for a slight baseline shift around 27°C. This implies that there exists only one liquid crystalline phase for CHP in contrast to the results by Barrall II *et al.*,[5] who reported two liquid crystalline states obtainable through monotropic transitions on cooling the isotropic liquid. Observation under polarizing microscope revealed a focal-conic texture for the present liquid crystal, but identification of its type has not been made. Run-3 shows a heating curve of the supercooled liquid crystal thus obtained. The DSC curve showed two thermal anomalies; a conspicuous stepwise anomaly at *ca.* 27°C which bears close resemblance to usual glass transition, and a phase transition at 90°C from liquid crystal to isotropic liquid.

Run-4 shows a heating curve of the supercooled liquid crystal annealed for 2 hr at 23°C just below the apparent glass transition point and then cooled down to −20°C before heating. It gave a stepwise curve with a small peak which corresponds to the enthalpy relaxation usually observed in an ordinary glass transition phenomenon. These facts confirm the view that the thermal anomaly at about 27°C might be considered to be a glass transition of the liquid crystalline state in CHP.

In order to examine more precisely the nature of this glass transition, activation enthalpy was determined according to McMillan's method.[6] Figure 2 shows the activation plot, from which the activation enthalpy was found to be 76.6±3 KJ mol^{-1}.

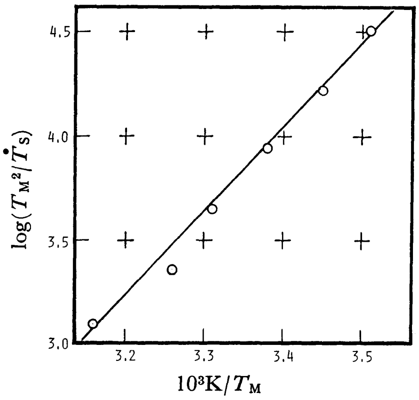

Fig. 2. Activation plot for glass transition of cholesteryl hydrogen phthalate ($\dot{T}_M$, Inflection point; $\dot{T}_S$, Heating rate).

The glass transition temperature (T_g) was determined to be 22°C from the heat capacity measurements by use of an adiabatic calorimeter and the characteristic heat capacity jump at T_g, ΔC_p, was found to be 180 J K^{-1} mol^{-1}. The details of the present results of the heat capacity measurements will be given in due course.

From these results it can be concluded that the glassy state of liquid crystal has been established for the first time in the present study and we propose to designate this state as "**glassy liquid crystal**".

---

[1] M. Sugisaki, H. Suga, and S. Seki, This Bulletin, **41**, 2581, 2591 (1968).

[2] N. Onodera, H. Suga, and S. Seki, *J. Non-Cryst. Solids*, **1**, 331 (1969).

[3] N. Onodera, H. Suga, and S. Seki, This Bulletin, **41**, 2222 (1968).

[4] K. Adachi, H. Suga, and S. Seki, This Bulletin, **41**, 1073 (1968); **43**, 1916 (1970); **44**, 78 (1971).

[5] E. M. Barrall II, J. S. Porter, and J. F. Johnson, *Mol. Cryst. and Liq. Cryst.*, **8**, 27 (1969).

[6] J. A. McMillan, *J. Chem. Phys.*, **42**, 3497 (1965).