The Glassy Crystalline State —A Non-Equilibrium State of Plastic Crystals

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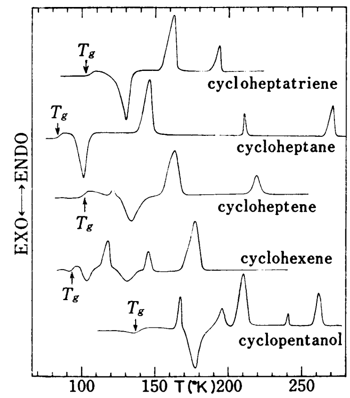
In a previous paper,[1] we reported that the supercooled crystal-I (plastic crystal) of cyclohexanol showed in its heat capacity curve an anomalous jump resembling that associated with ordinary glass transition. From heat capacity data we establsihed the existence of the residual entropy for this supercooled plastic crystalline phase and also found the relaxation effect at this anomalous region. Based upon these findings we have proposed a new term "**Glassy Crystal**" for this supercooled non-equilibrium state. In the present paper we should like to report several new examples of the glassy crystal found by using differential thermal analysis method. They are 2,3-dimethylbutane, cycloheptanol, cycloheptatriene, cycloheptane, cycloheptene, cyclohexene and cyclopentanol. Among them, 2,3-dimethylbutane and cycloheptanol have been investigated in detail by measuring their heat capacities, the results of which will be reported elsewhere.

Cycloheptatriene was synthesized by photochemical reaction of benzene with diazomethane. Its purification was carried out by fractional and vacuum distillation. Cycloheptane was prepared by the catalytic hydrogenation of cycloheptatriene with use of Raney nickel. Cycloheptene was synthesized by dehydration of cycloheptanol. Cyclopentanol was obtained from the Tokyo Kasei Co. LTD. Cyclohexene was obtained from the Nakarai Chemicals LTD. Both cyclopentanol and cyclohexene were purified by means of vacuum distillation. The apparatus employed was reported previously.[2] The specimens were transferred by vacuum distillation in the sample containers. The results are shown in the figure. Measurements were performed with heating rate about 1°K min^{-1} after the plastic phases of the specimens had been supercooled down to 77°K with cooling rate of about 3°K sec^{-1}. In the cases of cycloheptatriene and cycloheptane, direct irreversible transition was observed from the supercooled plastic crystalline phase to the most stable crystalline phase just above the glass transition temperature. Cyclopentanol and cyclohexene, however, transform irreversibly and indirectly to the most stable low temperature phase by passing through the intermediate metastable crystalline states. This phenomenon may be explained by the so-called Ostwalrd's step rule. The measurements of the heat capacities of cyclohexanol, 2,3-dimethylbutane and cycloheptanol also show a similar behavior.



D.T.A. curves of quenched plastic crystals

TABLE

Sample	T_g (°K)	T_t (°K)	T_g/T_t
Cycloheptatriene	106	153	0.69
Cycloheptane	84	135	0.61
Cycloheptene	100	153	0.65
Cyclohexene	92	140	0.65
Cycloheptanol	135	258	0.52
Cyclohexanol	150	265	0.57
Cyclopentanol	138	201	0.69
2,3-Dimethylbutane	76	136	0.55
cis-1,2-Dimethyl-cyclohexane[3]	94	173	0.54

All the glass transition points of glassy crystals known hitherto are listed in the accompanying table where the values of the ratio of T_g to T_t (transition point from the low-temperature phase to the plastic crystalline phase) are also given. It is found that the ratio has the value 0.5—0.7 and this fact corresponds to the empirical rule known for the ordinary glass where the ratio of T_g to T_m (melting point) amounts to 0.5—0.7.

1) K. Adachi, H. Suga and S. Seki, This Bulletin, **41**, 1073 (1968).

2) H. Suga, H. Chihara and S. Seki, *Nippon Kagaku Zasshi*, **82**, 24 (1961).

3) H. M. Huffman, S. S. Todd and G. D. Oliver, *J. Amer. Chem. Soc.*, **71**, 584 (1949).