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# NEW FINDING OF THREE KINDS OF GLASSY STATE FOR CYCLOHEXENE AS A SINGLE COMPOUND

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Three kinds of glassy state of cyclohexene were discovered. Two of them are of crystalline phase, and were prepared *in situ* in calorimeter cell by different thermal treatments. These Tg values were 81 K (crystal-I) and 83 K (crystal-II), respectively. The glassy liquid was also prepared by vapor condensation method, its Tg being 78 K (DTA-value).

Since the existence of the glassy state of crystalline material (glassy crystal) has been discovered in our laboratory[1)], it seems very plausible that one and the same compound would have more than one kind of glassy state, that is, the glassy state from the supercooled liquid (glassy liquid) and that from supercooled crystal (glassy crystal) at least. We report here the first successful finding of three kinds of Tg with cyclohexene.

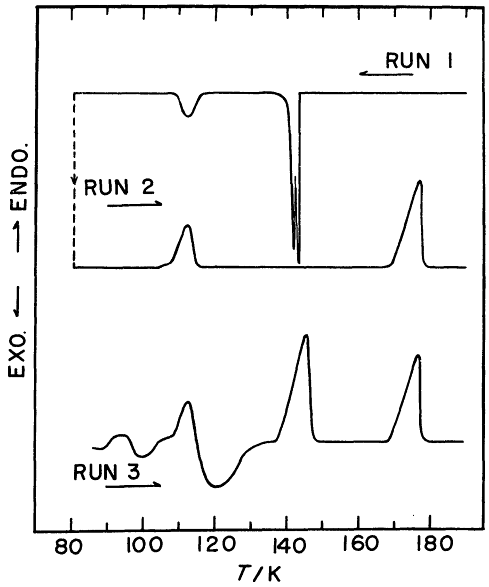

Fig. 1 DTA curves for the samples obtained from liquid.

Cyclohexene, obtained from Tokyo Kagaku Seiki Co., was degassed by freeze-pump-thaw cycles and distilled twice under vacuum. The purity of the material was determined to be 99.96 % by use of calorimetric method. Differential thermal analysis (DTA)[2)] was carried out, and the results are displayed in Fig. 1. Run 1 shows the cooling curve with the rate of ~-2 K min$^{-1}$, and Run 2 is the subsequent heating curve. Run 3 shows the heating curve of the rapidly cooled sample from high temperature crystalline phase (crystal-I). The thermogram Run 3 coincides with the result already reported by Adachi et al.[3)] except the different dimensions of the anomalies at 120 and 140 K. These results can be interpreted as follows. When a moderate cooling rate is adopted (Run 1), liquid crystallizes into crystal-I at ca. 130 K, and then crystal-I transforms into a newly found crystalline phase (crystal-III) reversibly. When the glassy crystal-I prepared by rapid quenching is heated up (Run 3), it recrystallizes into crystal-III at ca. 100 K after the glass transition at 92 K is over, and then the scccessive transformations of crystal-III→crystal-I→crystal-II→crystal-I→liquid take place at 115, 120, 140, and 170 K, respectively. Among them the rate of the irreversible transition from crystal-I to crystal-II at 120 K is sensitive to the purity and the thermal history of the specimen. This is the reason why the thermal behaviors in the temperature range 120∼140 K were different from each other in the six results of Run-2 and 3 in Fig. 1, Run 2, 3, and 4 in Fig. 4 (see below) and by Adachi et al.$^{3)}$ The phase relations are schematically illustrated in Fig. 2.

To investigate further the thermodynamic properties of crystal-III and glassy crystal-I, heat capacity measurement by adiabatic calorimeter$^{4)}$ was performed from 14 to 300 K. In this experiment glassy crystal-I was prepared by extremely rapid chilling of the specimen by introducing the liquid nitrogen into the calorimeter-can. The average cooling rate was about -40 K min$^{-1}$ between 220 and 80 K. For crystal-III, three series of measurements were performed with different samples. Thermal treatments adopted to obtain these different samples were as follows; for series-1, crystal-III was prepared by cooling the crystal-I (see Run 1 in Fig. 1) at the cooling rate of about -1 K min$^{-1}$, for series-2, crystal-III (obtained by the same procedure as series-1) was annealed at 77 K for ca. 36 hrs., for series-3, it was made through the phase transformation from crystal-I on which the heat capacity measurement (see Fig. 3) was accomplished and annealed at 80∼100 K for ca. 2 days. The results between 65∼115 K are shown in Fig. 3. Besides the big heat capacity jump due to the glass transition of crystal-I, there can be seen also a small heat capacity jump for crystal-III. The latter is also attributed to glass transition phenomenon

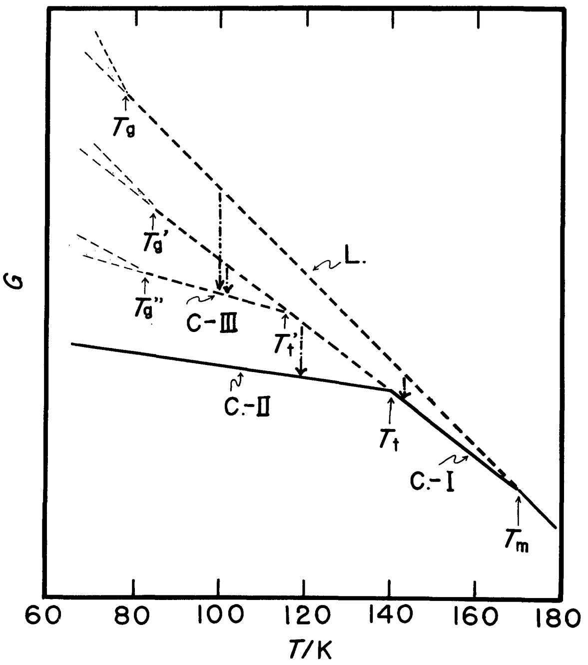

Fig. 2 Schematic Gibbs energy relationship between different states of aggregation. Tg:glass transition temperature, Tm:melting point, L:liquid, C:crystal. Arrows downward show the crystallization and irreversible transitions. (Except Tg for glassy liquid as well as temperatures indicated by downward arrows all the other transition temperatures are referred to the calorimetric data.)

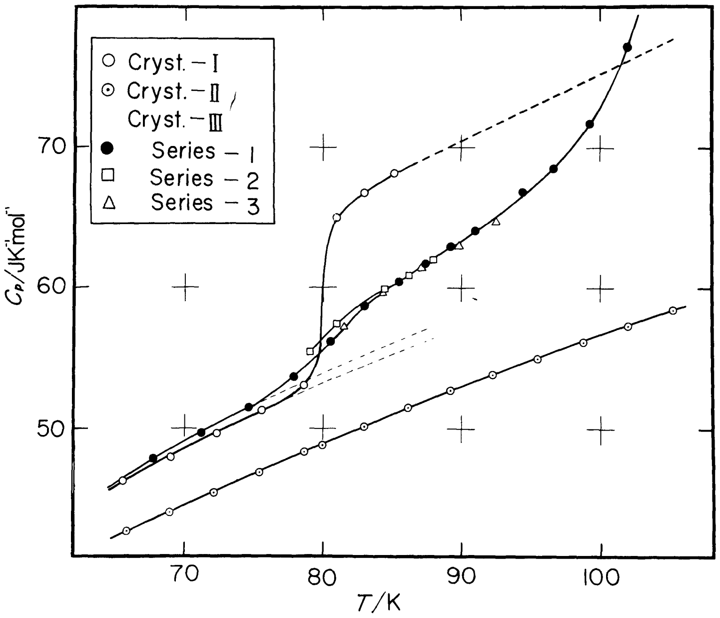

Fig. 3 Heat capacity curves for crystal-I, crystal-III, and crystal-III.

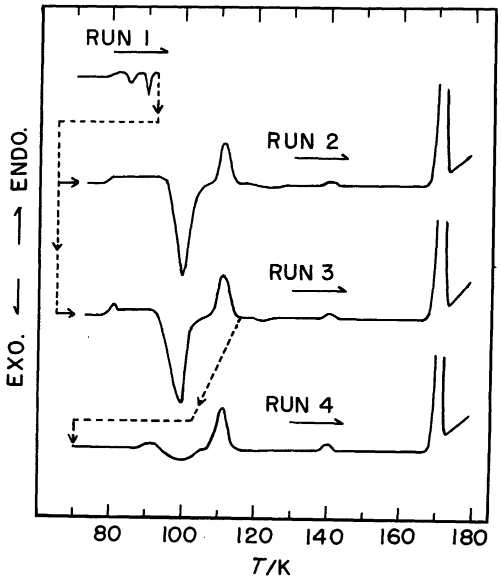

Fig. 4 DTA curves for the samples condensed from the vapor.

because the activation enthalpy of relaxation phenomenon (7 kJ mol$^{-1}$) determined was different from that of crystal -I (18 kJ mol$^{-1}$). These results for crystal-III were well agreed each other for series-1, 2, and 3 above Tg, being the additional annealing effect observed for series-3. Glass transition temperature (Tg), heat capacity jump at Tg, and residual entropy at 0 K were 81 K, 11.4 J K$^{-1}$mol$^{-1}$ and 11.7 J K$^{-1}$mol$^{-1}$for crystal-I and 83 K, 3.6 J K$^{-1}$mol$^{-1}$ and 2.6 J K$^{-1}$ mol$^{-1}$ for crystal-III, respectively. The glass transition temperature of crystal-I (81 K) is lower than that (92 K) determined by DTA method, owing to the long period of time for the measurement of heat capacity. On the other hand the glass transition temperature of crystal-III (83 K) was obtained only by calorimetric method. Differential thermal analysis by use of the special equipment of vapor condensation type5) was also performed, and the results are shown in Fig. 4. Run 1 is the heating curve of the sample condensed form vapor directly onto the sample holder maintained at 68 K. Runs 2 and 3 show the heating curves after the temperature cycling between 68 K and 92 K. For Run 3 sample was annealed for an hour at 77 K prior to the measurement. Run 4 shows the heating curve after the temperature cycling between 68 K and 118 K and corresponds to Run 3 in Fig. 1. Although some small *exothermic* anomalies in Run 1 cannot be assigned yet, there are several evidences to conclude that each base line shift to *endothermic* direction in these runs (Run 1,2 and 3) at 78 K is the manifestation of glass transition of liquid, e.g. the annealing effect characteristic of glass transition shown in Run 3. Therefore we can conclude that three kinds of glassy state of one and the same compound were realized for the first time. It is a remarkable fact that these glass transition temperatures are not so different from each other in spite of the difference in their states of aggregation.

## references

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