Thermochimica Acta, 118 (1987) 287–294
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CRYSTALLINE SOLID TO PLASTIC CRYSTAL TRANSITIONS IN PENTAGLYCERINE–NEOPENTYLGLYCOL MIXTURES

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(Received 18 February 1987)

ABSTRACT

In this paper we analyse the crystalline solid to plastic crystal transition in two pentaglycerine–neopentylglycol (PG–NPG) mixtures, with 33% and 45% of PG respectively which have been submitted to different thermal treatments. We show the occurrence of a two-step process when the samples are cooled from the plastic crystal phase. This fact can be explained by assuming the presence of a metastable phase between the plastic crystal and the crystalline solid.

INTRODUCTION

Some molecular crystals of highly symmetrical molecules show rotational transitions in the solid state. These transitions give rise to a new phase, the plastic crystal phase, between the anisotropic crystal and the isotropic liquid, phases [1]. The crystalline solid to plastic crystal transition involves the formation of a large symmetrical structure (generally b.c.c. or f.c.c.) and a loss of orientational order with respect to the low temperature stable phase [2–4]. In the plastic crystals, the isotropy occurs at a lower temperature than the liquefaction [5].

We have studied the crystalline solid to plastic crystal transition that takes place in solid solutions of the polyols pentaglycerine (PG) and neopentylglycol (NPG) [6,7]. We observed that this process is isothermal for the NPG while it is not when PG is added. Also, a diminution in the initial temperature and in the enthalpy variation of the transition is obtained in PG–NPG mixtures.

In the present work we propose to point out the occurrence of a two-step process, each step with different kinetics, that takes place in the PG–NPG mixtures when we cool them from the plastic crystal phase.

EXPERIMENTAL

We prepared the mixtures A (33wt.% PG) and B (45wt.% PG) by

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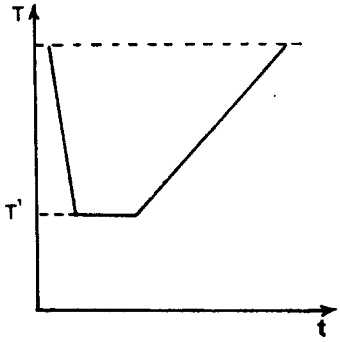

Fig. 1. Thermal treatment for the two mixtures studied.

dissolution of PG and NPG in water and subsequent evaporation of the solvent [6].

In Fig. 1 we show the thermal treatment to which we submitted the samples. The samples were cooled from the plastic crystal phase until a temperature T' higher than that of the transition from plastic crystal to crystalline solid, which takes place in the direct cooling from the high temperature stable phase. The initial temperature of the direct process is about 3° C and 23° C for the mixtures A and B respectively. After maintaining the samples at the temperature T' for different periods of time, they were subsequently heated up to the plastic crystal phase. The values of T' are 5 and 10° C for the mixture A and 26 and 35° C for the mixture B.

The measurements were made with a heat flux calorimeter working in differential. The ΔT signal was obtained by means of two thermoelectric modules of great sensitivity (Melcor FC06-32-06L) connected in opposition. We have acquired numerically differential and temperature signals with a sampling period of about 7 s. We used typical scanning rates of 0.5 K min^{-1}. The samples (mass in the order of 15 mg) were sealed in an aluminium crucible.

RESULTS

Figure 2 shows characteristic thermograms obtained for the mixture A. In these thermograms two peaks corresponding to two endothermic processes are clearly evident when the time of maintenance at the temperature T' is not too long. Also, in Figs. 3–5 we see the relative evolution of the areas corresponding to the two peaks with the time of maintenance of the mixture at the temperature T'.

This evolution is not visible for the mixture B in the treatment at $T' = 35$° C (see Fig. 6).

In Figs. 7–10 we represent the area values corresponding to the two peaks obtained for each mixture in the different thermal treatments. We can see in

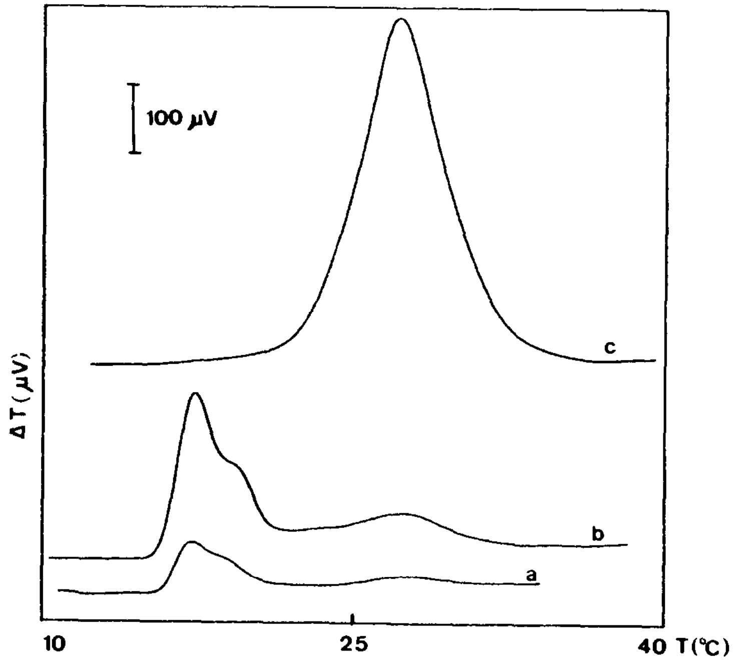

Fig. 2. Thermograms obtained for mixture A on heating from the temperature $T' = 5\,^\circ C$ for different times of maintenance: curve a, 30 min; curve b, 60 min; curve c, 300 min.

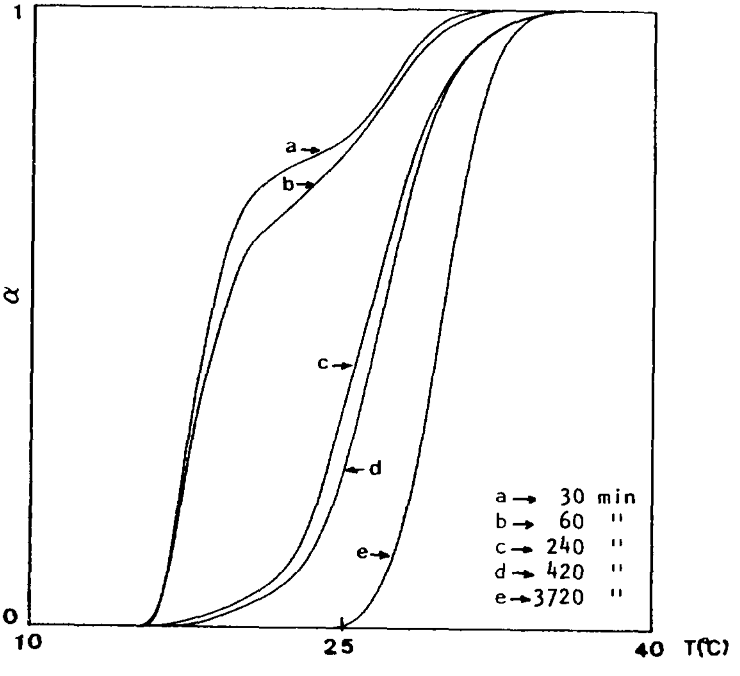

Fig. 3. Change in the degree of conversion α with temperature for mixture A at $T' = 5\,^\circ C$ for different times of maintenance.

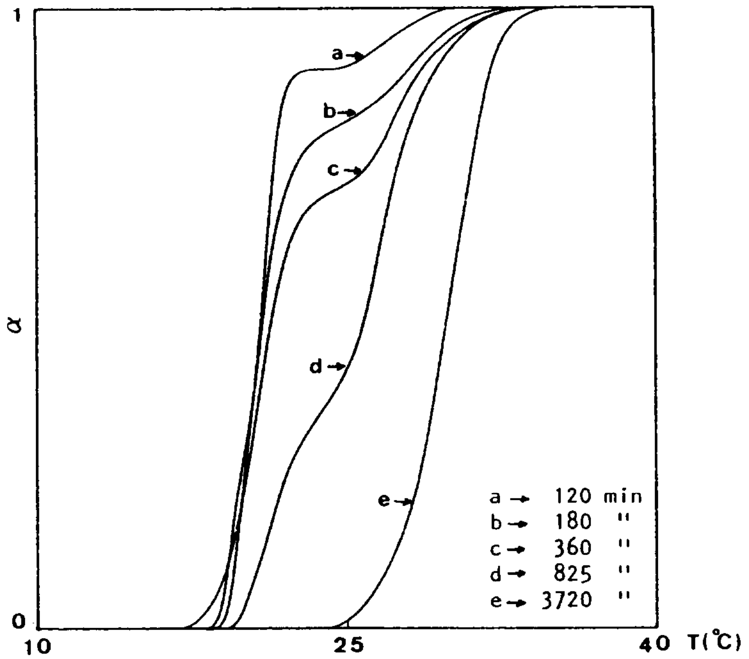

Fig. 4. Change in the degree of conversion α with temperature for the mixture A at $T' = 10\,°\mathrm{C}$.

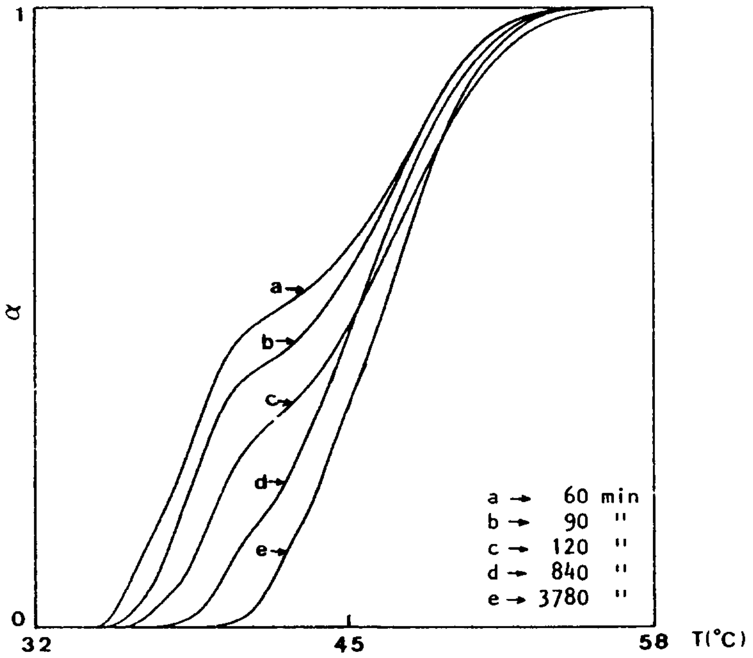

Fig. 5. Change in the degree of conversion α with temperature for the mixture B at $T' = 26\,°\mathrm{C}$.

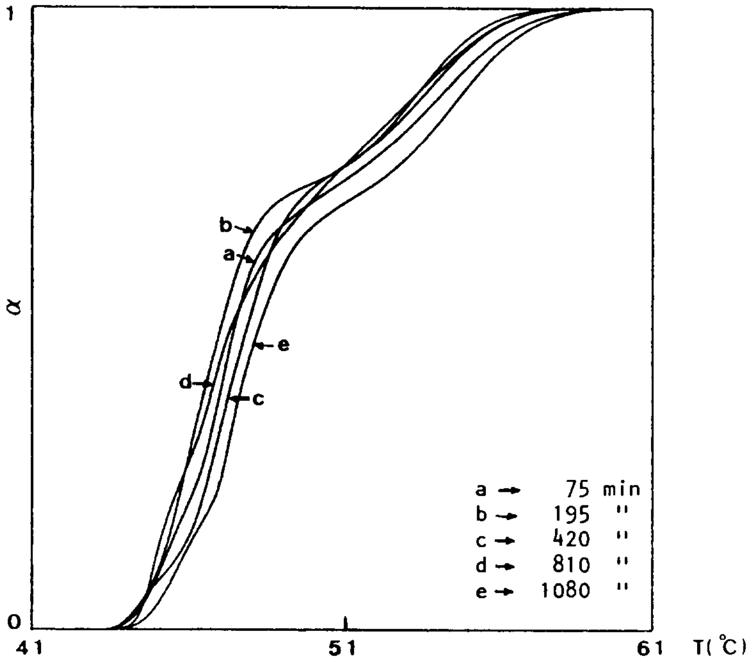

Fig. 6. Change in the degree of conversion α with temperature for the mixture B at $T' = 35\,°C$.

Figs. 7, 8 (mixture A for $T' = 5\,°C$ and $T' = 10\,°C$ respectively) and 9 (mixture B for $T' = 26\,°C$) that the first process disappears while the second one grows continuously until the total ΔH value obtained in the direct heating from the crystalline solid phase is reached.

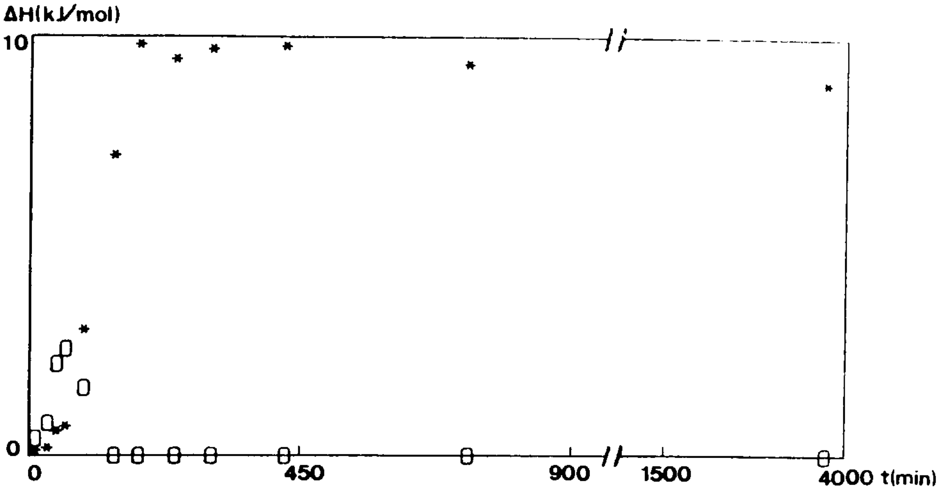

Fig. 7. Area values corresponding to each peak in the mixtures A vs. the time of maintenance at $T' = 5\,°C$: □, M → P; *, C → P.

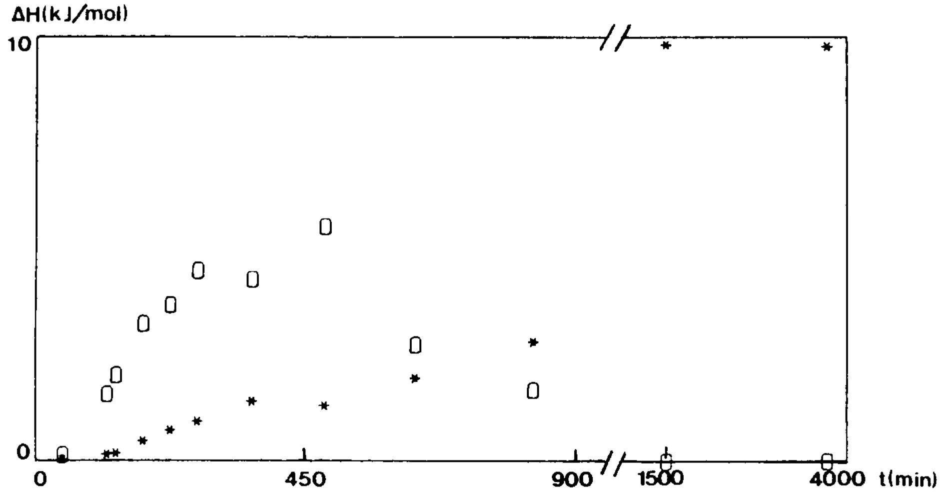

Fig. 8. Area values corresponding to each peak in the mixture A vs. the time of maintenance at $T' = 10°C$: □, M → P; *, C → P.

In Fig. 10, which corresponds to the mixture B for $T' = 35°C$, we observe an evolution different from that in Figs. 7–9. The area of the first process tends asymptotically towards approximately 3 kJ mol^{-1}. In this case, the asymptotic value of the total area (sum of the areas of the two peaks) is

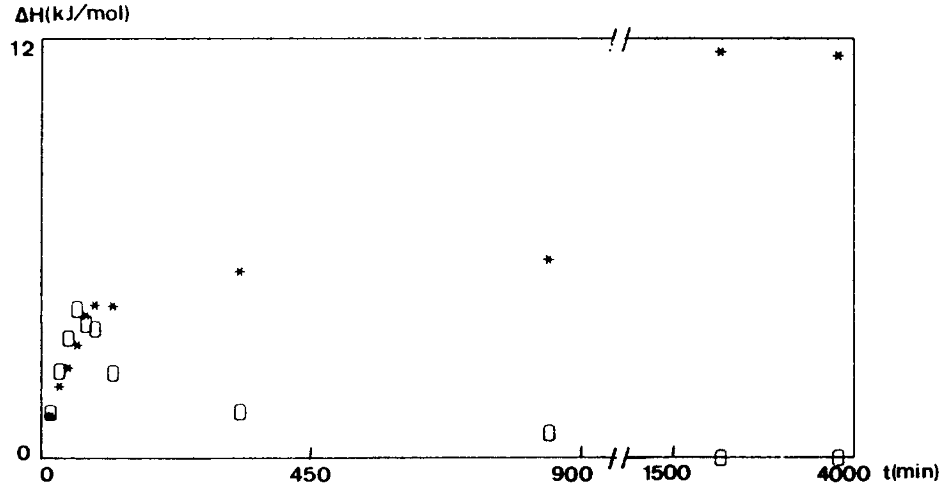

Fig. 9. Area values corresponding to each peak in the mixture B vs. the time of maintenance at $T' = 26°C$: □, M → P; *, C → P.

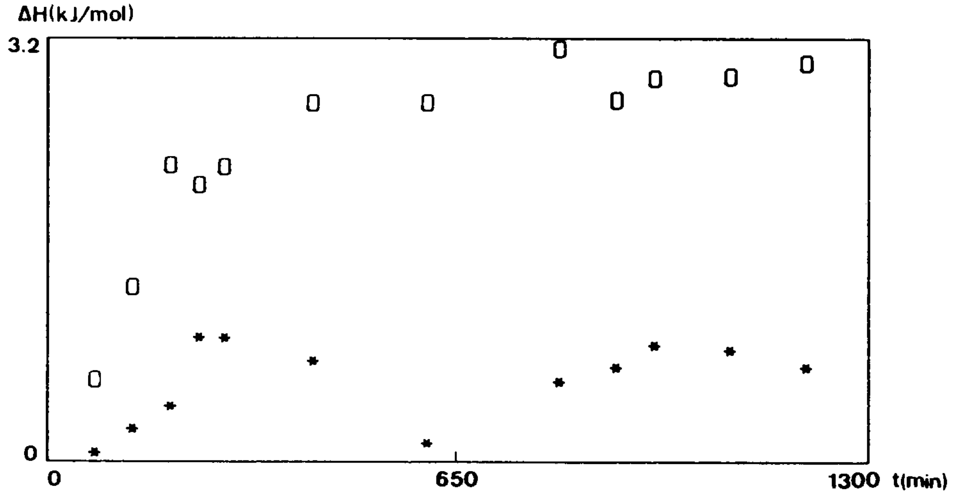

Fig. 10. Area values corresponding to each peak in the mixture B vs. the time of maintenance at $T' = 35\,°C$: □, M → P; *, C → P.

about a half of that we obtain for the mixture B when we maintain it at 26 °C.

DISCUSSION

We clearly see (Figs. 3–6) the existence of two peaks and their evolution with the time of maintenance at the temperature T'. The appearance of two processes and their evolution with time can be explained if we assume the existence of a metastable phase M. The crystalline solid phase appears on cooling from this metastable phase. The different processes are sketched in Fig. 11. When we cool the plastic crystal phase P, stable at a high temperature, the P → M process takes place, i.e. the M phase appears. This phase transforms slowly into C (crystalline solid phase). Our results indicate that the P → M process is faster than the M → C process (see Figs. 7–9).

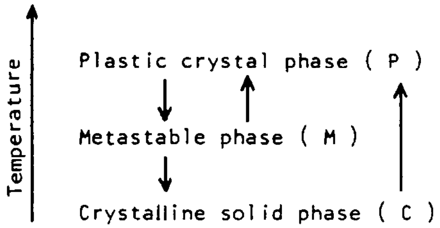

Fig. 11. Scheme of the different processes between the plastic crystal and the crystalline solid phases.

For both samples, on heating from the temperature T', the M → P and the C → P processes occur. When the time of maintenance is very short no conversion from M to C takes place and, therefore, only the process M → P occurs. If we maintain the samples at the temperature T' for a long period of time (more than 15 h) only the process C → P appears on heating (Figs. 3–5 and 7–9) except for the mixture B at $T' = 35\,^{\circ}\mathrm{C}$. For this mixture B (at $T' = 35\,^{\circ}\mathrm{C}$) the process M → C is not completely finished even if t is about 62 h. This is clearly shown in Figs. 6 and 10 in which two peaks are always present. We think that 35 °C is far from the initial temperature of the exothermic process in the direct cooling (23 °C) and, for that reason, the M → C transition is not completed.

CONCLUSIONS

The results obtained in the thermal treatments to which we have submitted the mixtures PG–NPG (33% and 45% in PG) indicate the possible existence of a metastable phase M in the plastic crystal to crystalline solid transition.

The formation of the crystalline solid phase on cooling from the plastic crystal phase, proceeds through an intermediate phase M. The plastic crystal to M phase process is faster than the M to the crystalline solid phase process.

We propose in the near future to carry out X-ray diffraction at different temperatures in order to obtain information about these transitions between plastic crystal and crystalline solid phases. Also, we will extend this study by analysing the behaviour of mixtures with higher concentrations of PG.

REFERENCES

1 J. Timmermans, J. Phys. Chem. Solids, 18 (1961) 1.
2 W.J. Dunning, J. Phys. Chem. Solids, 18 (1961) 21.
3 L.A.K. Staveley, Ann. Rev. Phys. Chem., 13 (1962) 351.
4 L.A.K. Staveley, J. Phys. Chem. Solids, 18 (1961) 46.
5 G.W. Gray and P.A. Winsor, Liquid Crystals and Plastic Crystals, Wiley, New York, 1974.
6 J. Font, J. Muntasell, J. Navarro, J.Ll. Tamarit and J. Lloveras, Sol. Energy Mater., 15 (1987), in press.
7 J. Font, J. Muntasell, J. Navarro and J.Ll. Tamarit, Sol. Energy Mater., in press.