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Effect of the crystallization on the phase transitions IV ↔ III and IV ↔ II of ammonium nitrate

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Abstract

The solid state phase transition path of ammonium nitrate is influenced by the manner of crystallization. Slow crystallization from water gives ideal crystals, which behaved differently from crystals prepared by rapid crystallization from the melt.

INTRODUCTION

The solid state phase transitions of ammonium nitrate (AN) in the temperature range 20–100°C and the effect of moisture on those transitions have been widely examined. The reported transition paths are [1]

$$\mathrm{IV} \xleftrightarrow{32.2^\circ\mathrm{C}} \mathrm{III} \xleftrightarrow{84.2^\circ\mathrm{C}} \mathrm{II} \quad \text{or} \quad \mathrm{IV} \xleftrightarrow{51^\circ\mathrm{C}} \mathrm{II}$$

The transition from phase IV to phase III is said to occur only if water is present [2, 3]; direct transition from IV to II occurs in dry samples [4]. According to Sjölin [2], water has an effect on the temperature of the IV ↔ III transition: with wet samples the temperature of the transition is near 32°C, whereas with dry samples it is near 50°C, which allows a direct transformation from phase IV to phase II to take place. Sjölin did his experiments with prilled AN prepared from the melt. Davey et al. [5, 6] recently worked with samples that had been crystallized from water or other polar solvents, and their results, like those of Sjölin, support the claim [3, 6–9] that water has a catalytic effect to the IV ↔ III transition.

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EXPERIMENTAL

The samples were prepared from "Baker Analyzed" reagent p.a. ammonium nitrate (NH_4NO_3). Crystallization was accomplished by two different methods, in both cases without seeding.

1. In the first method crystals were prepared by slow evaporation from aqueous solution at room temperature over a period of 2–3 days.
2. In the second method, dry AN was melted and then cooled to room temperature. Crystallization was rapid and took 1–2 h.

Transition temperatures and energies were determined by differential scanning calorimetry, with a Perkin-Elmer DSC-7 providing the instrumentation.

In single heating the scanning rate was 5.0°C $\min^{-1}$ and the measurement range was 25–100°C. In cycled heating the scanning rate was 2.0°C $\min^{-1}$ and the range was 25–60°C. In cycling, the sample was heated from 25 to 60°C and then cooled at the same scanning rate back to 25°C. The cycle was repeated three times. Cooling were carried out immediately after heating with no resting time in between.

The sample cups were aluminium, with perforations so that moisture could evaporate during the scanning.

Calibration was performed against indium (m.p. 156.6°C and ΔH 28.47 J g^{-1}) [10] and benzoic acid (m.p. 122.3°C) [8] and checked with n-octadecane (m.p. 28–30°C). Reported temperatures are onset temperatures of transitions.

Moisture contents of the samples were determined by Karl Fischer titration.

RESULTS AND DISCUSSION

Transition IV → II

When the crystallization was carried out from water at room temperature, crystals could grow slowly and appeared long and needlelike. The moisture content in these crystals was between 0.4 and 0.2 wt% (w-%). A part of the samples underwent a transition from phase IV to phase II, as shown in Fig. 1. The ΔH of the transition shown in the figure was 22.90 J g^{-1} (1.83 kJ mol^{-1}). According to the literature [7, 9] the ΔH range of the transition IV ↔ II is 20.25–24.00 kJ mol^{-1}. Since there is no peak between 80 and 100°C, the situation depicted in Fig. 1 is a total transition from phase IV to phase II. The ΔH and temperature of the transition in Fig. 1 are given in Table 1.

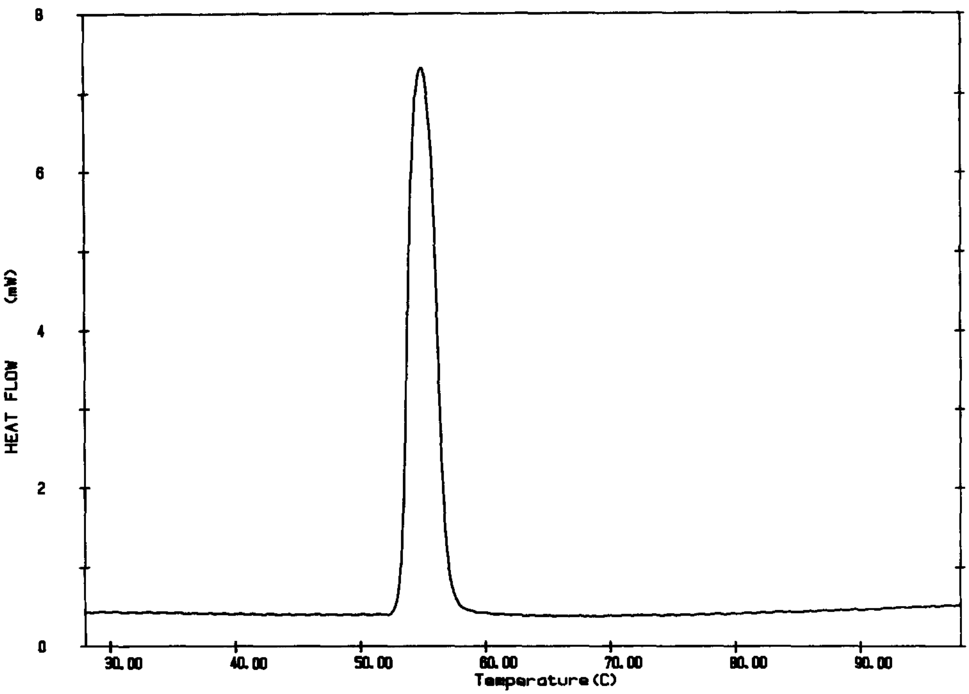

Fig. 1. DSC curve of a pure AN sample crystallized from water. The phase transition is IV→II. The temperature and the ΔH of the transition are given in Table 1.

TABLE 1

ΔH values and temperatures of the transitions depicted in Figs. 1 and 2.

Figure	Transition	ΔH ($J\,g^{-1}$)	Temperature (°C)
1	IV→II	22.90	53.35
2	IV→III	15.11	50.29
	III→II	15.13	85.99

Transition IV→III→II

When the crystallization was effected from the melt, no single crystals could be seen. These samples underwent transitions IV↔III↔II in spite of a moisture content varying between 0.01 and 5 wt%. Figure 2 shows the DSC curve of the transition path IV↔III↔II, and Table 1 gives the ΔH values and temperatures of the peaks seen in Fig. 2.

The energy of the transition IV↔III in Fig. 2 is $15.11\,J\,g^{-1}$ ($1.21\,kJ\,mol^{-1}$) and the temperature of the transition is near 50°C. According to Rasulić et al. [3] the ΔH of transition can vary between 16

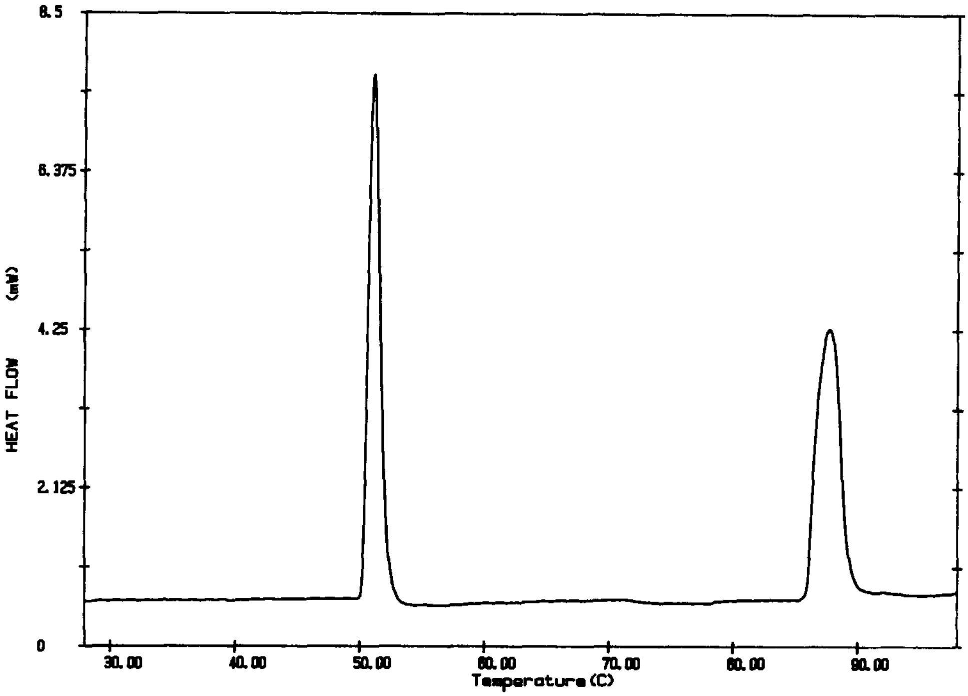

Fig. 2. DSC curve of a pure AN sample prepared from the melt. Transitions are IV → III and III → II. Energies and temperatures are given in Table 1.

and 20 J g^{-1} and the temperature range is 43–51°C. The ΔH is small because it depends on the temperature of the transition being smaller at higher temperature than at lower temperature [2]. The energy of transition III → II is 15.13 J g^{-1} and the temperature is 85.99°C.

All but one of the 60 samples prepared from the melt underwent the transition IV → III → II.

Mixed transitions

Results for the crystals prepared from water were not always the same. We carried out 25 crystallizations and found four different types of thermal behaviour. Conditions were the same in all crystallizations, and we can not explain why there should be different behaviour.

The first type was pure IV ↔ II, which occurred four times (see Fig. 1). In the second type (Fig. 3) the endothermic transition IV ↔ II was followed by the exothermic transition II → III and finally the endothermic transition III → II. This type occurred 12 times. In the third type (illustrated in Fig. 4) the transitions IV → II and IV → III occurred at the same time. Six samples exhibited this path. The fourth type was a combination of types two and three (Fig. 5) and there were three samples

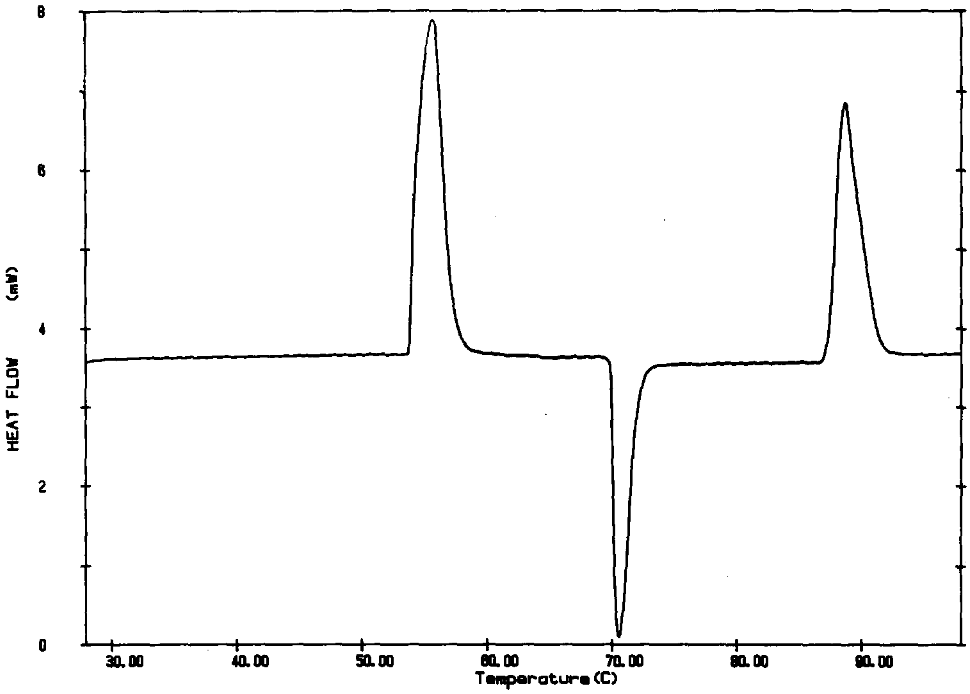

Fig. 3. DSC curve of an AN sample that undergoes first the transition IV→II and then exothermic transition from phase II to phase III.

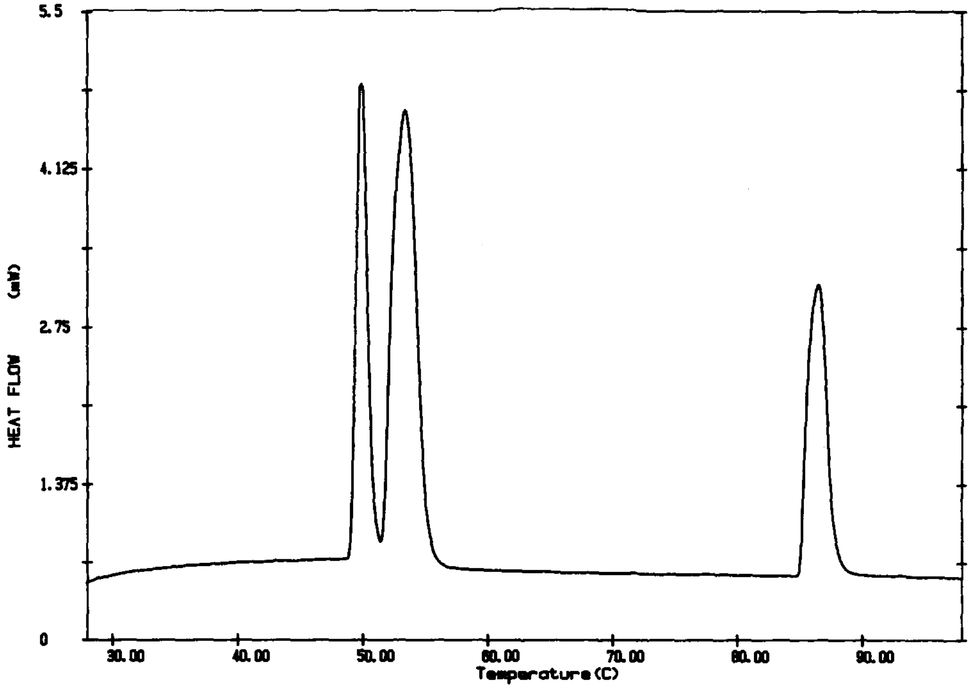

Fig. 4. DSC curve of an AN sample that exhibits transition paths IV↔III and IV↔II simultaneously.

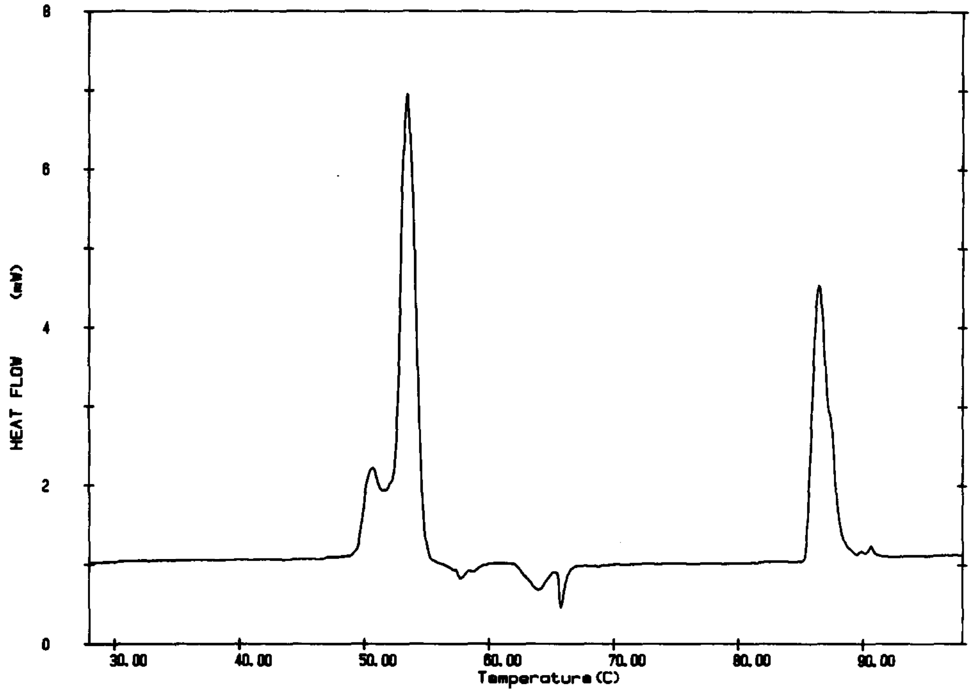

Fig. 5. DSC curve of an AN sample that undergoes endothermic transitions IV→II, IV→III and exothermic transition II→III.

TABLE 2

ΔH values and and temperatures of the transitions described in Figs. 3 and 4.

Figure	Transition	ΔH ($\mathrm{J\,g^{-1}}$)	Temperature (°C)
3	IV→II	23.17	53.80
	II→III	−11.93	69.94
	III→II	16.87	87.50
4	IV→III	5.86	49.12
	IV→II	10.61	51.74
	III→II	6.37	85.07
5	IV→III	[a]	≈49
	IV→II	[a]	52.55
	II→III	≈(−2.5)	57.12[b]
	III→II	10.23	85.49

[a] Transitions IV→III and IV→II appear in the same peak.

[b] Transition is a combination of small peaks.

of this type. The energies and temperatures of the transitions described in Figs. 3, 4 and 5 are given in Table 2.

From the energy of the transition III ↔ II one can calculate how large a part of sample with mixed phase transitions has undergone the phase transition IV → II and how large a part the phase transitions IV → III → II. The calculation is done by measuring the ΔH of the transition from phase III to phase II and comparing it with the ΔH of the pure transition III → II. The ΔH of the pure transition III ↔ II is about $16\,J\,g^{-1}$. (According to the literature, the ΔH of the pure transition III ↔ II varies between 15.5 [9] and 16.8 [7] $J\,g^{-1}$ (1.24–$1.34\,kJ\,mol^{-1}$). ΔH varies because it depends on the temperature and ΔH of the transition IV ↔ III. In spite of this, the value of the ΔH of transition III → II allows a good approximation of the proportion of the transition path IV → II in the range 25–100°C.

The sample of Fig. 3 must have completely changed to phase III in the exothermic part since, according to the ΔH of transition III → II, 100% of the sample underwent that transition. In the sample of Fig. 4, where transitions IV → III and IV → II occur at the same time, 37.8% of the sample underwent transition IV → III and the rest IV → II. Forty per cent of the sample in Fig. 5 was in phase II before the transition III → II.

Langfelderova and Ambrović [11] noticed an exothermic transition like that shown in Fig. 3, but they did not offer any interpretation. We assume here that, in the exothermic part, the sample goes from phase II to phase III. The exothermic part may appear immediately after the endothermic transition IV → II or, as in Fig. 3, near 70°C.

Cycling of the samples

When an AN sample crystallized from water was cycled three successive times in the range 25–60°C, the proportion of the transition IV → II became smaller each time, as shown in Fig. 6. The moisture content of the sample in Fig. 6 was 0.20 wt%. Table 3 shows the ΔH values and temperatures of the cycles. There are both heating and cooling cycles, and it can be seen that the ΔH of transition IV ↔ II becomes smaller in each heating cycle. The sample of Fig. 6 either changes transition path or is metastable.

The phenomena described above may be understood more clearly from the cycling, in the same temperature range, of an AN sample prepared from the melt (Fig. 7). The moisture content of the sample was 0.05 wt%. In the first heating stage the sample went to phase III. The ΔH of transition was $15.72\,J\,g^{-1}$ and the temperature 49.49°C. On further heating

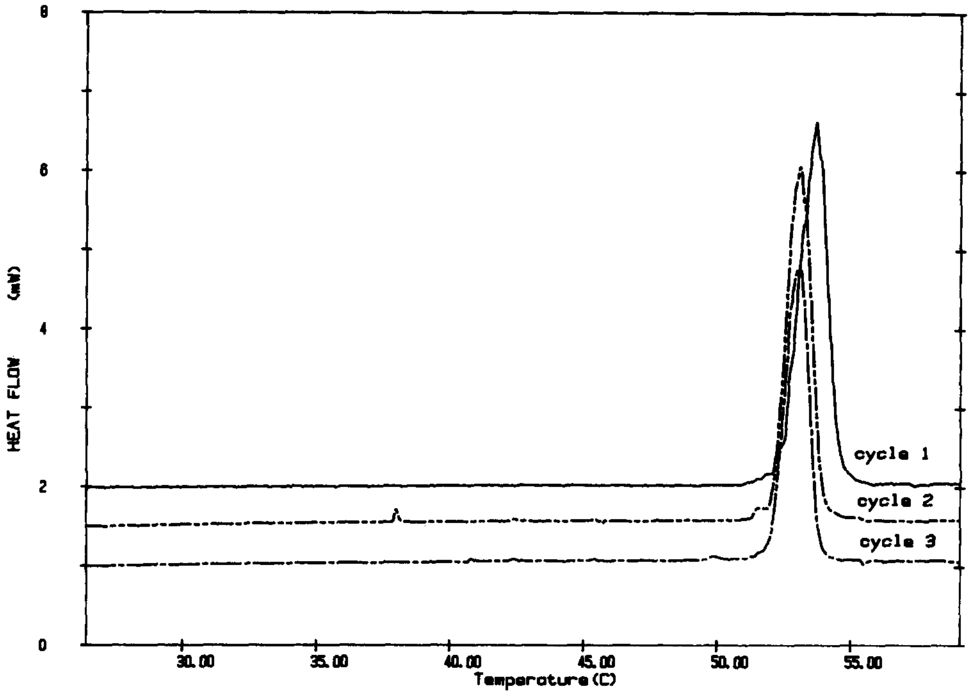

Fig. 6. DSC heating cycles of an AN sample that undergoes transition IV↔II. During cycling the ΔH is reduced from 22.56 to 16.03 J g^{-1}.

and cooling cycles no transition was seen at all, and it can be concluded that, after the first cycle, the sample remains in phase III. The evidence for this is seen in Fig. 8 where, between the second and third cycles, the sample was allowed to stand for 12 h. After the first cycle the sample was in phase III, but during the delay time after the second cycle a part of the sample changed back to phase IV.

TABLE 3

ΔH values and temperatures of the heating and cooling cycles of the sample described in Fig. 6.

Cycle	ΔH (J g^{-1})	Temperature (°C)
1 (heating)	22.56	52.47
(cooling)	−20.05	45.29
2	19.85	52.34
	−16.51	46.65
3	16.03	52.26
	−11.41	46.54

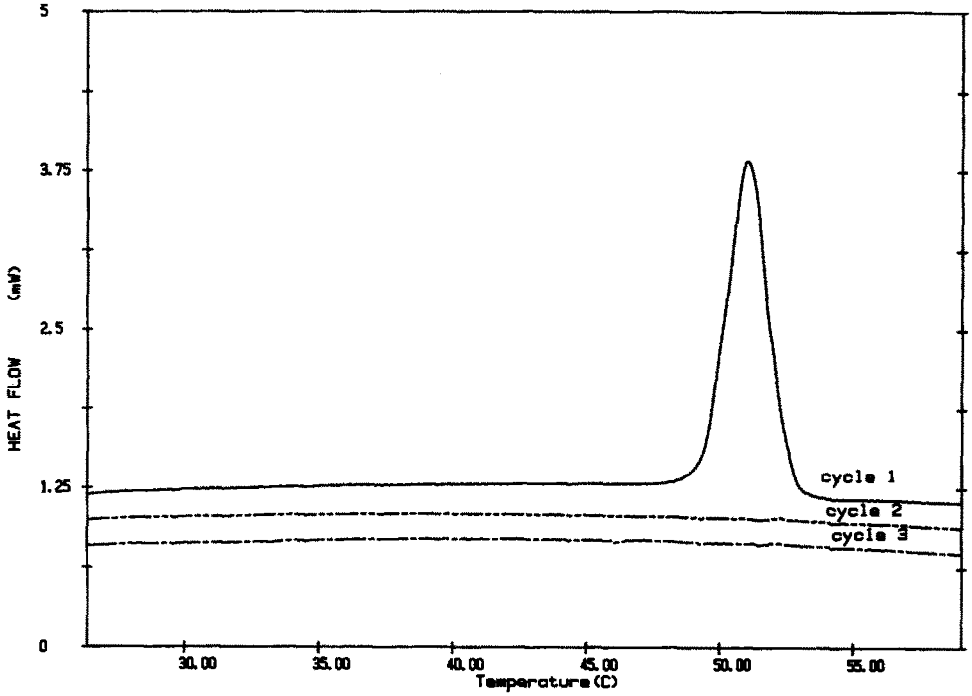

Fig. 7. DSC heating cycles of an AN sample that undergoes transition IV↔III. During cycling the sample stayed in phase III.

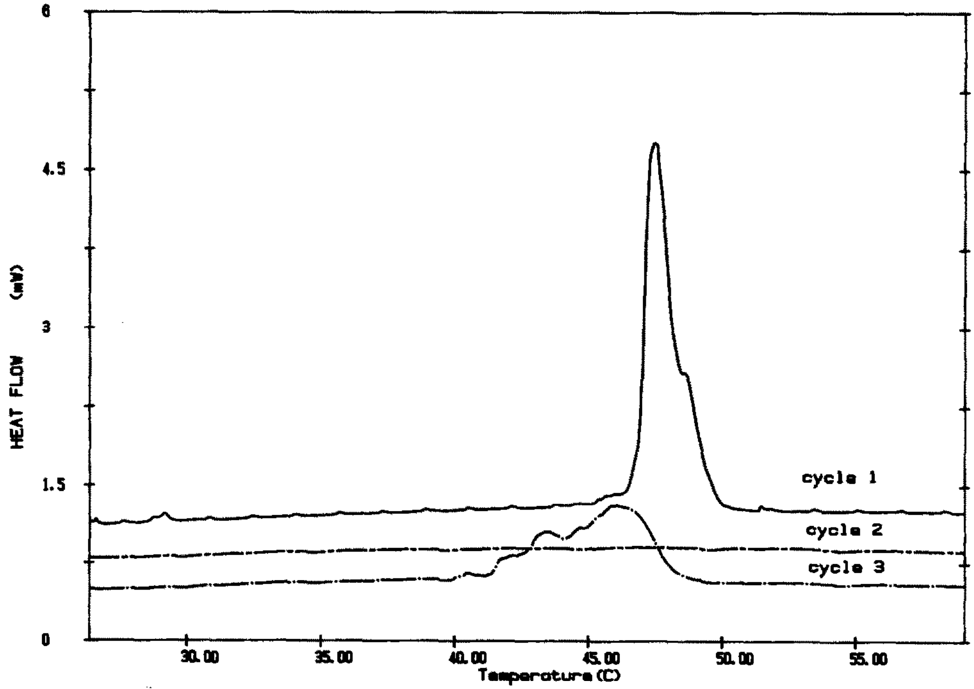

Fig. 8. DSC heating cycles of an AN sample that undergoes transition IV↔III. Between the second and third cycles there is a 12 h standing time.

CONCLUSIONS

When AN samples were crystallized from saturated aqueous solution and evaporation of the water was slow, ideal crystals were formed. The first transition in these crystals was from phase IV to phase II. The temperature of the transition varied on heating between 53 and 56°C, whereas on cooling it was near 46°C. Transition IV ↔ II easily changed to transition IV ↔ III.

When the crystallization was carried out from the melt, virtually all of the samples went through the transition path IV ↔ III ↔ II. The kinetics of the transition IV ↔ III depended on the moisture content of the sample. On heating, the transition temperature varied between 35 and 51°C and on cooling, between 30 and 25°C. (In this work the temperature range used in the cooling and heating cycles was 25–60°C, so nothing can be said about temperatures lower than 25°C.) The temperature of the transition III ↔ II was near 85°C.

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