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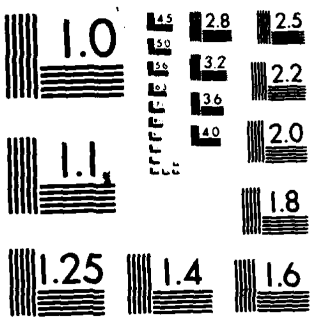
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Differential thermal analysis (DTA), high pressure differential thermal analysis (HP-DTA), and high temperature X-ray studies are combined to elucidate the origin of the two melting peaks in Nylon 11. The results of the studies suggest that two species of crystals are involved in the melting of Nylon 11 samples, crystallized at atmospheric pressure, when the environmental pressure is below 4 Kbars. At atmospheric pressure, the high melting species is predominant. However, under hydrostatic pressures, the high melting species

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undergoes phase transition to the low melting species before melting. The amount of the material involved in the transition depends on the pressure. At pressure of 4 Kbar or greater, the entire high melting species transforms to the low melting species. The melting behavior, at atmospheric pressure, of samples crystallized at high pressures also shows two melting peaks if the crystallization pressure is below 4 Kbars. The amount of the low melting species increases with increasing pressure and, at 4 Kbars or higher, only melting of the low melting species is observed. The X-ray photographs taken at room temperature suggest that samples crystallized between atmospheric pressure and 3 Kbars contain both the α-form and the δ'-form crystals but the samples crystallized at 4 Kbar and higher contain only the α-form crystal. However, it appears from X-ray scans taken at high temperatures near melting that the low melting species is of the δ-form and the high melting species of the δ'-form crystals for samples crystallized below 4 Kbars. The δ-form crystals result from the α-δ transition that occurs at 95°C. Moreover, the melting at high pressures (<4 Kbar) of samples crystallized at atmospheric pressure also appears to involve a δ'-δ transition. These results suggest that both the crystal forms, δ and δ', are stable at high temperatures, if the environmental pressure is below 4 Kbar, and that only the δ-form crystals are stable up to melting at pressures greater than 4 Kbar.

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HIGH PRESSURE MELTING AND CRYSTALLIZATION OF NYLON-11

by

P.K-K. Chen, B.A. Newman, J.I. Scheinbeim and K.D. Pae

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SYNOPSIS

Differential thermal analysis (DTA), high pressure differential thermal analysis (HP-DTA), and high temperature X-ray studies are combined to elucidate the origin of the two melting peaks in Nylon 11. The results of the studies suggest that two species of crystals are involved in the melting of Nylon 11 samples, crystallized at atmospheric pressure, when the environmental pressure is below 4 Kbars. At atmospheric pressure, the high melting species is predominant. However, under hydrostatic pressures, the high melting species undergoes phase transition to the low melting species before melting. The amount of the material involved in the transition depends on the pressure. At pressures of 4 Kbar or greater, the entire high melting species transforms to the low melting species. The melting behavior, at atmospheric pressure, of samples crystallized at high pressures also shows two melting peaks if the crystallization pressure is below 4 Kbars. The amount of the low melting species increases with increasing pressure and, at 4 Kbars or higher, only melting of the low melting species is observed. The X-ray photographs taken at room temperature suggest that samples crystallized between atmospheric pressure and 3 Kbars contain both the α-form and the δ'-form crystals but the samples crystallized at 4 Kbar and higher contain only the α-form crystal. However, it appears from X-ray scans taken at high temperatures near melting that the low melting species is of the δ-form and the high melting species of the δ'-form crystals for samples crystallized below 4 Kbars. The δ-form crystals result from the α-δ transition that occurs at 95°C. Moreover, the melting at high pressures (<4 Kbar) of samples crystallized at atmospheric pressure also appears to involve a δ'-δ transition. These results suggest that both the crystal

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HIGH PRESSURE MELTING AND CRYSTALLIZATION OF NYLON-11

P.K-K Chen, B.A. Newman, J.I. Scheinbeim and K.D. Pae

1. INTRODUCTION

Previous investigations [1-3] of the melting behavior of nylons at atmospheric pressure show the presence of two distinct endothermic melting peaks. Several explanations of the origins of these two peaks have been offered by different workers. However, these diverse explanations are somewhat confusing and suggest that the true origins of the two endothermic peaks are not known. Since similar crystal morphologies and structures are found in different nylons it is possible that a common origin for the phenomena exists.

Nylon-11 has been found to have at least four polymorphic crystal forms; the triclinic α-form and three pseudohexagonal forms (which we will term α, δ and δ' forms) with different d_{001} spacings [4-8]. Isothermal crystallization of nylon-11 from the melt [4] or casting from a phenol/formic acid solution [8,9] gives the α modification with two strong reflections (100) and (010) (with d-spacings at 4.44 Å and 3.73 Å). There is also an (001) reflection at d = 11.3 Å. Nylon-11 quenched from the melt gives the so-called "smectic" modification or δ'-phase with a single strong broad reflection at d = 4.11 Å and an (001) reflection at d = 11.3 Å. If the α-phase nylon-11 is heated above 95°C, the two higher angle reflections coalesce to give a single reflection at 4.16 Å as was observed previously [10]. The (001) reflection remains at 11.3 Å.

This high temperature δ-phase appears to be somewhat similar to the "smectic" δ'-phase obtained by quenching the melt but the reflection at 4.16 Å appears much sharper than that obtained from the quenched nylon-11.

In contrast to the δ'-form obtained by quenching the melt, the γ-form grown from trifluoroacetic acid solution solution is stable against heat treatment, and can only be converted to the α-form by stretching, or melting and subsequent crystallization [8]. Furthermore, the cast film from a trifluoroacetic acid solution shows a different infrared spectrum from that of the α-form films. The spectrum of the films quenched from the melt show features common to both α and γ forms and appears to be an intermediate state. These results strongly suggest the existence of three different hexagonal crystal forms of nylon-11, which might be due to the different arrangements of CO-NH groups between adjacent chains.

In this study, a series of differential thermal analysis (DTA), high pressure differential thermal analysis (HP-DTA) and high temperature X-ray studies were conducted to investigate the effects of pressure on the melting behavior of nylon-11.

2. EXPERIMENTAL

Additive free samples of nylon-11 were supplied by the Rilsan Corp. The weight average and number average molecular weights of the samples were 20,000 and 8,000, respectively. The samples were dried in a vacuum oven at 80°C for one week before being used.

The melting behavior of nylon-11 at atmospheric pressure was studied using a DuPont 990 DTA and at high pressures using the high pressure DTA system (HP-DTA) as was described in a previous publication [11].

The X-ray diffraction data (CuK_{α} radiation) were obtained using a high temperature X-ray camera and a position sensitive detector (PSD). The PSD data were stored in a multi-channel analyzer and displayed on an oscilloscope screen. The X-ray data presented are photographs of the oscilloscope screen.

The samples used in the HP-DTA were first weighed and then melted on a hot plate. All the samples were of the same weight, 4.5 mg. One thermocouple tip of the HP-DTA plug was embedded into the molten sample and the sample was picked up from the hot plate. The sample was then air cooled on the thermocouple tip. This procedure provided the same amount of sample each time, and there was excellent thermal contact between the sample and the thermocouple. The sample was covered with a thin layer of epoxy to prevent diffusion of the pressure transmitting fluid into the sample when using high pressures and high temperatures. The sample, with the thin layer of epoxy, was dried for one day before testing. Some tests of the melting behavior of nylon-11 samples with and without the epoxy layer were conducted; this determined that the thin layer of epoxy did not affect the thermal behavior of the samples. In order to ensure that all samples had the same initial thermal history, they were first heated to a temperature of 205°C and cooled to room temperature using a cooling rate of 10°C/min in the HP-DTA. The entire experiment was repeated three times with different samples in order to check for reproducibility.

3. RESULTS

3.1 Melting Studies of Samples Crystallized at Atmospheric Pressure and Melted at Various High Pressures

Figure 1 shows the endothermic curves obtained at a series of pressure up to 6.5 kilobars, using the HP-DTA at a heating rate of 6°C/min. The sample melted at atmospheric pressure shows two melting peaks; the first melting peak is at 180°C, and the second melting peak is at 188°C. The area under the first melting curve is only about 7% of that under the second melting curve. At 1, 2 and 3 kilobars, the size of the low temperature melting peak has increased while the size of the high temperature melting peak decreased. At 4 kilobars, only the low temperature melting peak is observed. These changes of melting peaks indicate that the crystal structures or morphologies causing the two melting peaks are very sensitive to hydrostatic pressure.

Figure 2 illustrates the pressure dependence of the melting points. As pressure increased, the melting temperature increased. When the pressure was at or below 1 kilobar, the melting temperature of these two peaks had almost the same rate of increase; dT_m/dt = 31°C/Kbar. When pressure was above 1 kilobar, the melting temperature of the second peak increased at a slower rate than that of the first and finally the two peaks merged at about 4 kilobars. From 4 kilobars up to the maximum pressure tested, the melting peak had a linear rate of increase of 17°C/Kbar.

3.2 Melting Studies of Samples Crystallized at High Pressures

An extra sample was put into the high pressure cell to be used for X-ray diffraction studies. The cell was then pressurized and heated as described earlier. After the sample reached a temperature of 15°C above its melting temperature at that pressure, it was cooled to room temperature with a cooling rate of 7°C/min. The melting behavior of four such samples crystallized at 1, 2, 3 and 4 kilobars was then determined by using the DuPont DTA. Figure 3 shows the melting behavior at atmospheric pressure of the samples crystallized at high pressures. The melting behavior of samples crystallized at atmospheric pressure showed two melting peaks; the first melting peak was at 180°C, and the second melting peak was at 188°C. The samples crystallized at different pressures up to 3 kilobars exhibited the high temperature endothermic peak at approximately 188°C when melted at atmospheric pressure. However, the melting temperature and the size of the low temperature melting peak relative to the high melting peak increased with increasing crystallization pressure. When the sample was crystallized at 4 kilobars, only the low temperature melting peak was observed.

3.3 X-ray Studies of Samples Crystallized at High Pressures

The X-ray diffraction scans taken at atmospheric pressure of samples crystallized at different pressures are shown in Figure 4. The (100) and (010) reflections shifted to lower 2θ with increasing crystallization pressure and the angle between the reflections increased also. The relative intensity of the higher angle peak (at 2θ = 23.4°) also increased with increasing crystallization pressure. It is clear that systematic changes in peak position (2θ) and intensity occur. A number of explanations are possible. A degree of preferred orientation which depended on pressure could be one possible explanation. Differing fractions of the various crystal forms α, γ, δ, δ') or amorphous content might also give the same effect. Figure 5 presents diffraction scan profiles constructed assuming various compositions of α and δ'-forms presented as indicated. It can be seen that the changes could be interpreted as arising from a decreasing proportion of δ'-phase at high crystallization pressures.

3.4 High Temperature X-ray Studies

In order to ascertain what crystal structure changes occurred at elevated temperatures prior to melting, an X-ray study of a sample at various temperatures prior to the melting point was carried out. A sample crystallized at 2 kilobars was chosen because it showed two equal size melting peaks at atmospheric pressure. In Figure 6, the photograph taken at room temperature showed that the -phase was dominant (a). As the temperature increased, the two strongest peaks, from the (010) and (100) planes, approached each other, and at

95°C only a single sharp reflection on top of a broad peak was observed (b). The single sharp reflection shows that the crystal transition from the triclinic α-structure to the pseudohexagonal δ-structure has occurred as experimentally observed [10]. The broad peak is a superposition of scattering from the δ' structure and amorphous material. The remaining photographs, taken at various temperatures up to the melting point, show that the δ-phase and δ'-phase are the primary structures present at melting (c), (d) and (e). The last photograph was taken at a temperature of 13°C above the melting point (f), and only a broad peak originating from amorphous material in the melt was observed.

3.5 Annealing Studies

An annealing study at high pressure was also carried out. A sample initially melted and crystallized at atmospheric pressure by cooling at 10°C/min was subsequently heated to a temperature 10°C below the melting temperature of the low endothermic peak at 2 kilobars in the HP-DTA. The temperature of the sample was maintained for 10 minutes and cooled slowly at a rate of 6°C/min under the same pressure to room temperature. Then the sample was heated through melting at atmospheric pressure in the HP-DTA. The results, in Figure 7, show that there is very little change in the melting behavior. However, a small endothermic peak at lower temperature shifted from 156°C to 168°C during the heat treatment. This small endothermic peak is not observed consistently in this study.

4. DISCUSSION

Pennings et al. [1] observed two endothermic peaks in nylon-11 samples. The two melting temperatures changed only slightly with heating rate. Thus, the authors suggest that the lower endothermic peak was related to impurities resulting from the production history of the samples or to the presence of amorphous material which crystallized during heating. The results of our experiments show that the change of the two melting peaks is consistent with respect to pressure and cooling rate. This indicates that the explanation of an impurity inside the sample was not satisfactory.

Extended-chain morphology of nylon-11 has also been observed [1]. The extended-chain crystal content significantly increased when the annealing pressure was greater than 3 kilobars. The two endothermic peaks observed in this experiment were obtained only when the pressure was less than 4 kilobars. At higher pressures, only the low temperature melting peak was obtained. Therefore, it is believed that neither of the two endothermic peaks observed could be attributed to extended-chain crystals.

The results of the combined studies suggest that two species of crystals are involved in the melting of Nylon 11 (Figures 1 and 2) for samples crystallized at atmospheric pressure or when the environmental pressure is below 4 Kbars. At atmospheric pressure, the high melting species is predominant. However, under hydrostatic pressures, the high melting species undergoes a phase transition to the low melting species before melting. The amount of material involved in the transition depends on the intensity of the applied pressure. At pressures of 4 Kbar or greater, the entire high melting species transforms to the low melting species, and therefore only a single melting peak appears.

The melting behavior at atmospheric pressure of samples crystallized at high pressures also shows two melting peaks if the crystallization pressure is below 4 Kbars. The amount of the low melting species increases with increasing crystallization pressure and, at 4 Kbars or higher, only melting of the low melting species is observed (Figure 3).

The X-ray photographs taken at room temperature (Figure 4) suggest that samples crystallized at atmospheric pressure, 1 Kbar, 2Kbar, and 3Kbar contain both the α and the δ' crystal form but that samples crystallized at 4 Kbar and higher contain only the α crystal form (see Figure 5). However, it appears from X-ray scans taken at high temperatures near melting (Figure 6) that the low melting species is of the δ-form and the high melting species is of the δ'-form for samples crystallized below 4 Kbars. The melting of the δ-form crystals is the result of the α-δ transition that occurs at 95°C (Figure 6), as also observed previously [10]. Moreover, the melting at high pressures (<4 Kbar) of samples crystallized at atmospheric pressure also involves the δ'-δ transition (or the transition from the high melting species to the low melting species). These results suggest that the both crystal forms δ and δ' are stable at high temperatures if the environmental pressure is below 4 Kbar and that only the crystal δ-form is stable up to melting at pressures greater than 4 Kbar.

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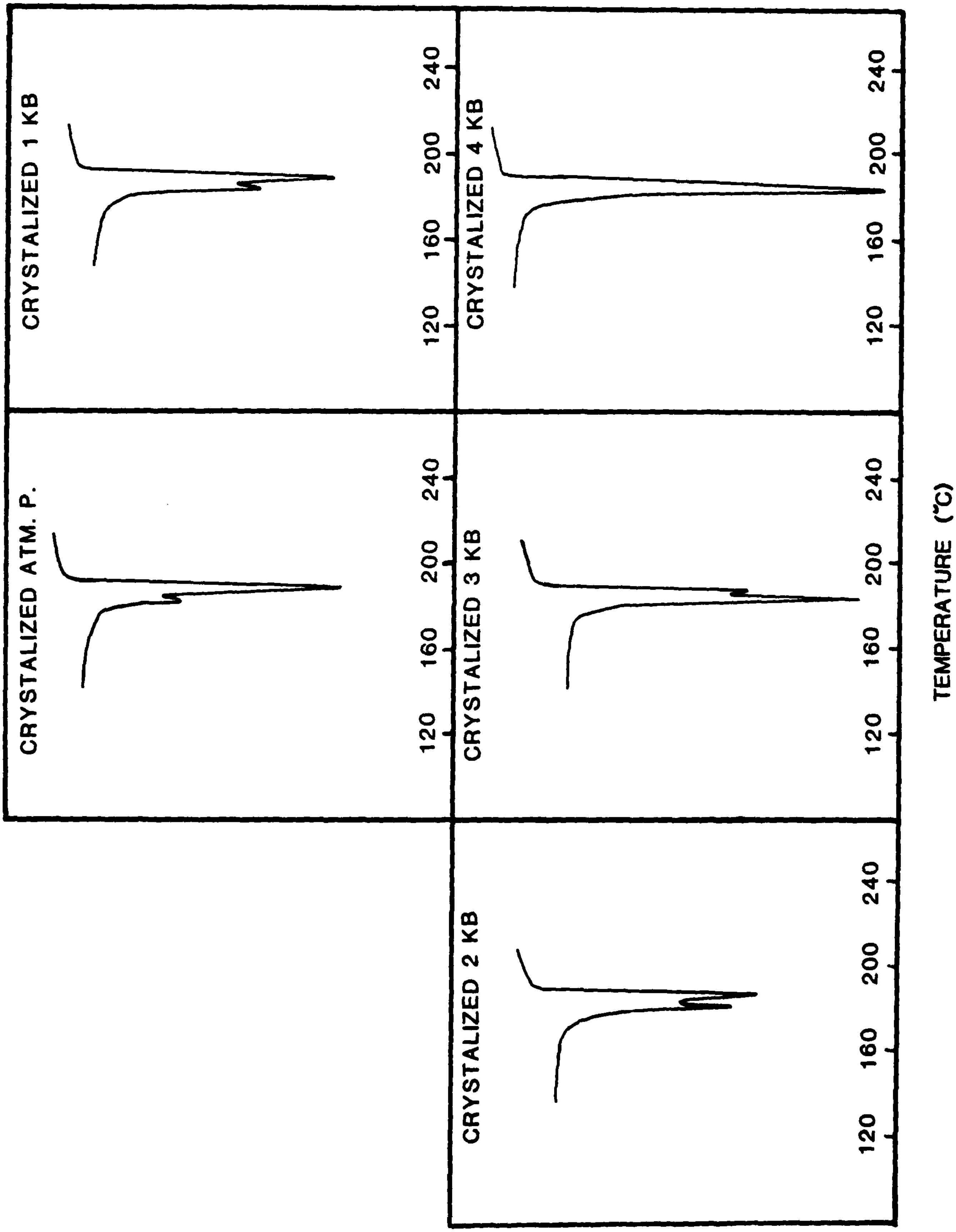
CAPTIONS FOR FIGURES

Fig. 1	Melting Behavior of Nylon 11 at Various Pressures as Indicated
Fig. 2	The Pressure Dependence of Melting Peaks of Nylon 11
Fig. 3	Melting Behavior of Nylon 11 at Atmospheric Pressure for Samples Crystallized at Various Pressures as Indicated
Fig. 4	Photographs of X-Ray Diffraction Profile of Nylon 11 at Atmospheric Pressure for Samples Crystallized at Various Pressures as Indicated
Fig. 5	Constructed X-Ray Diffraction Profiles for Nylon 11 with Assumed Compositions of the α - and the δ'-Forms
Fig. 6	Photographs of X-Ray Diffraction Profile of Nylon 11 at Different Temperatures as Indicated
Fig. 7	Melting Behavior of Nylon 11 at Atmospheric Pressure for Samples Annealed at 2 KB and 227°C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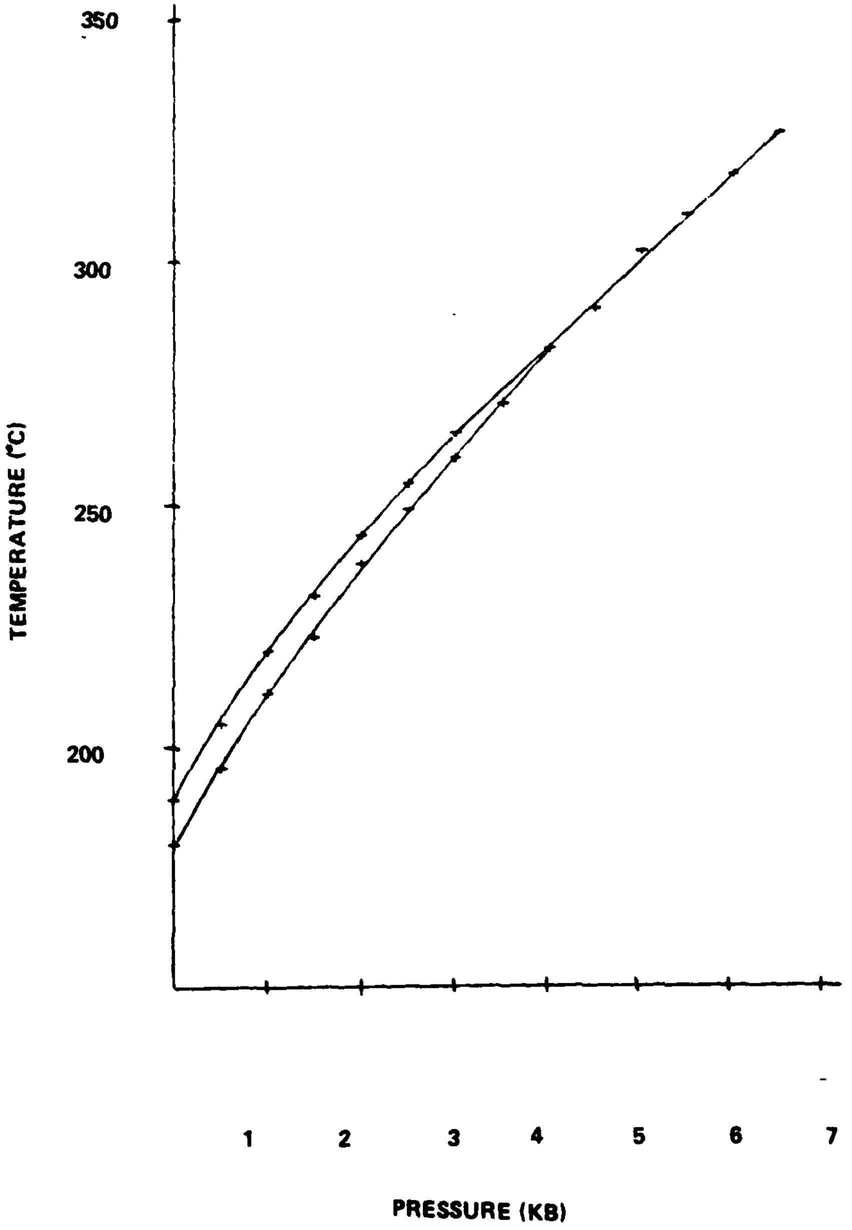
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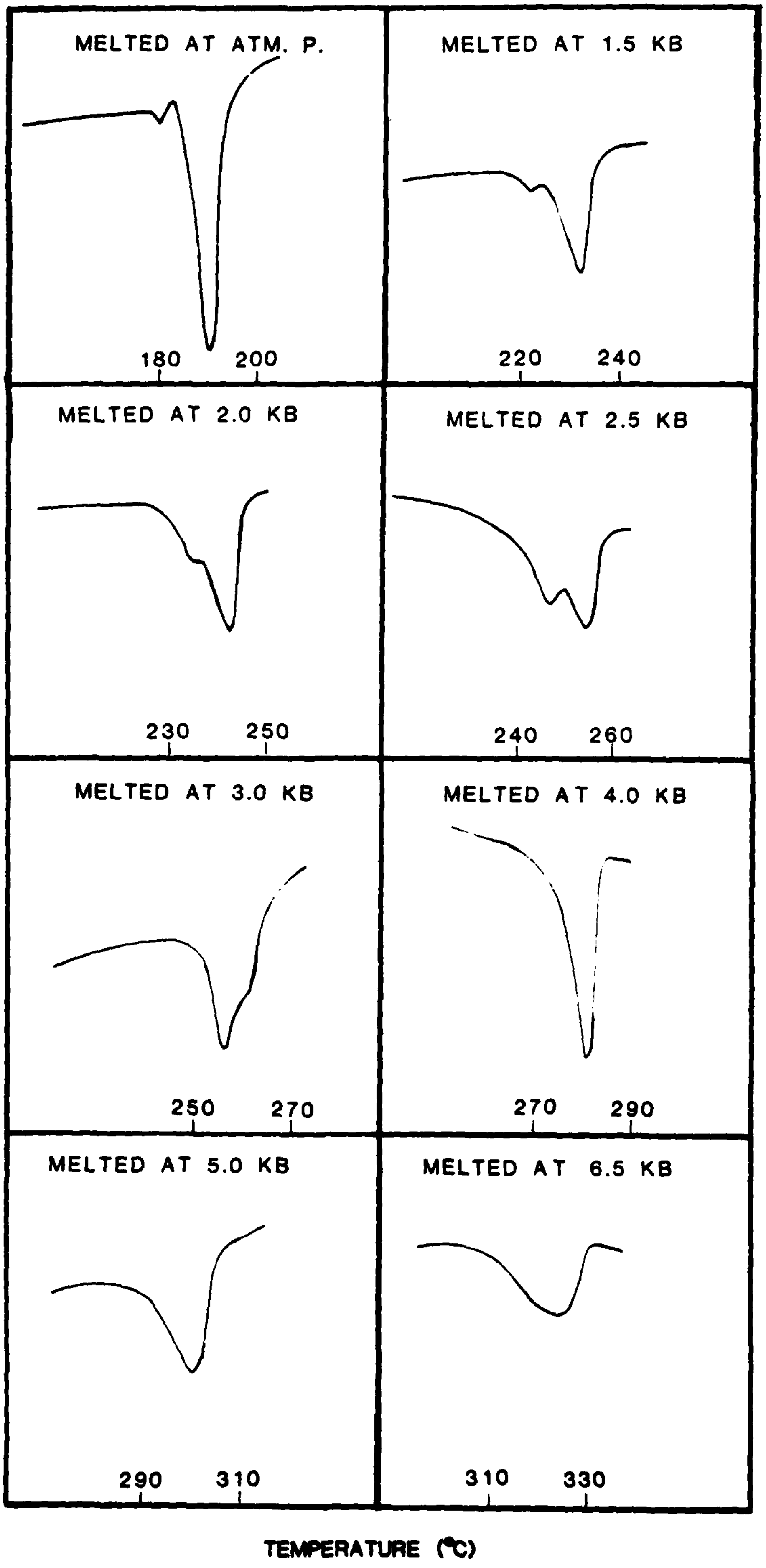
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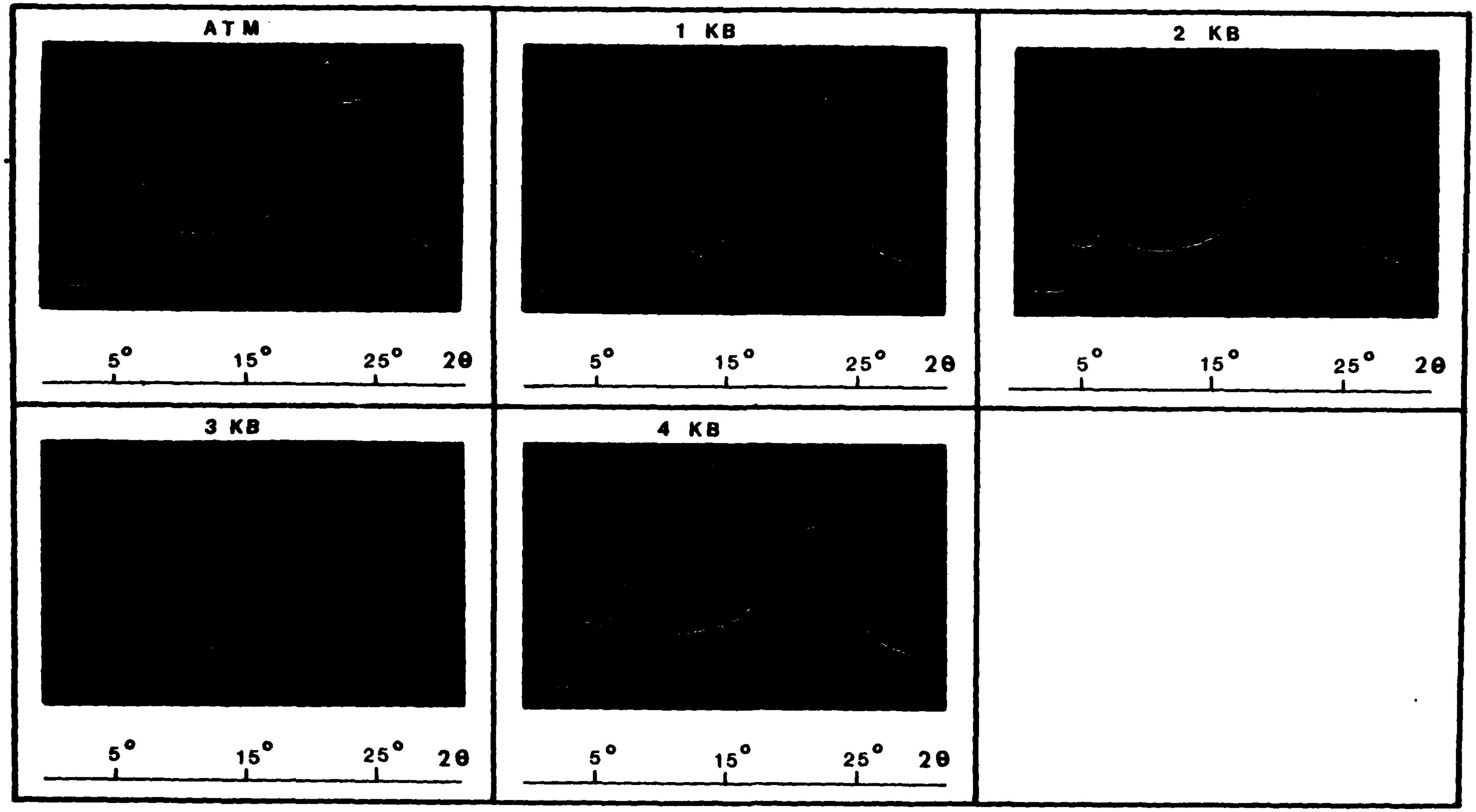
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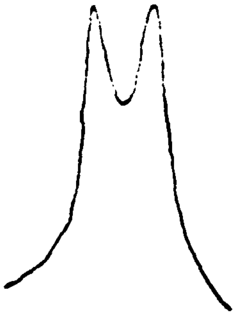

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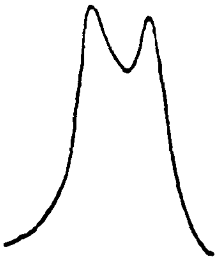

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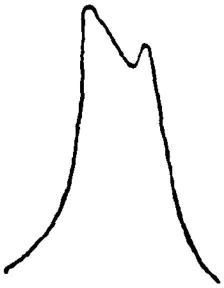

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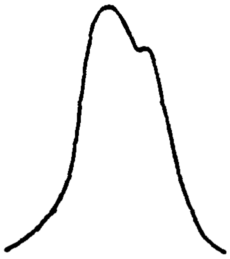

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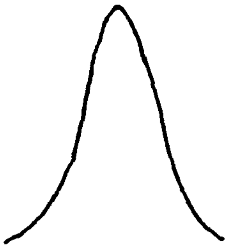

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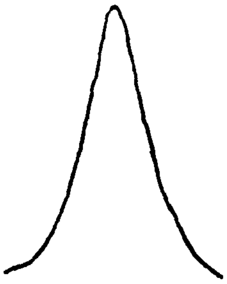

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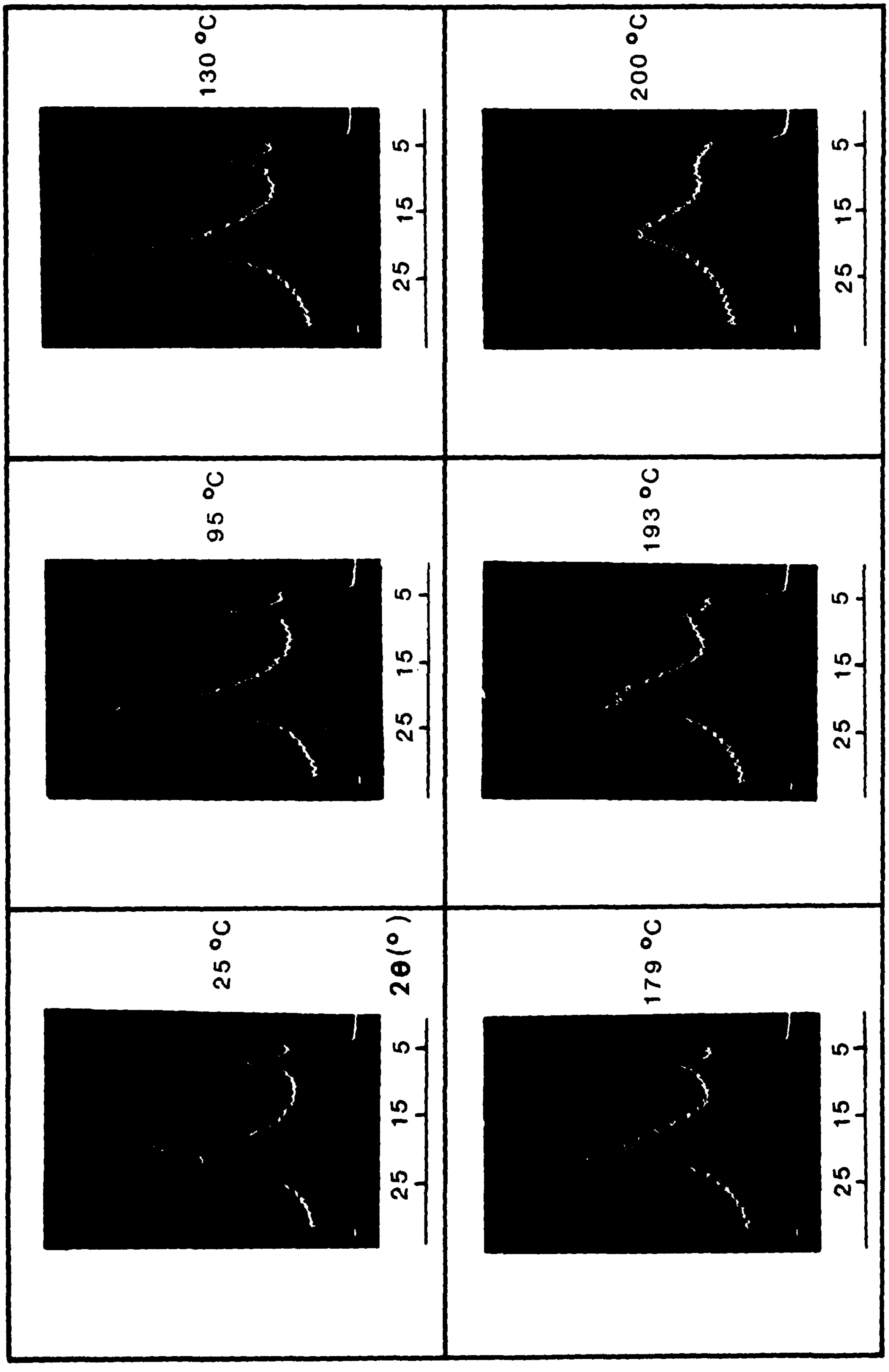
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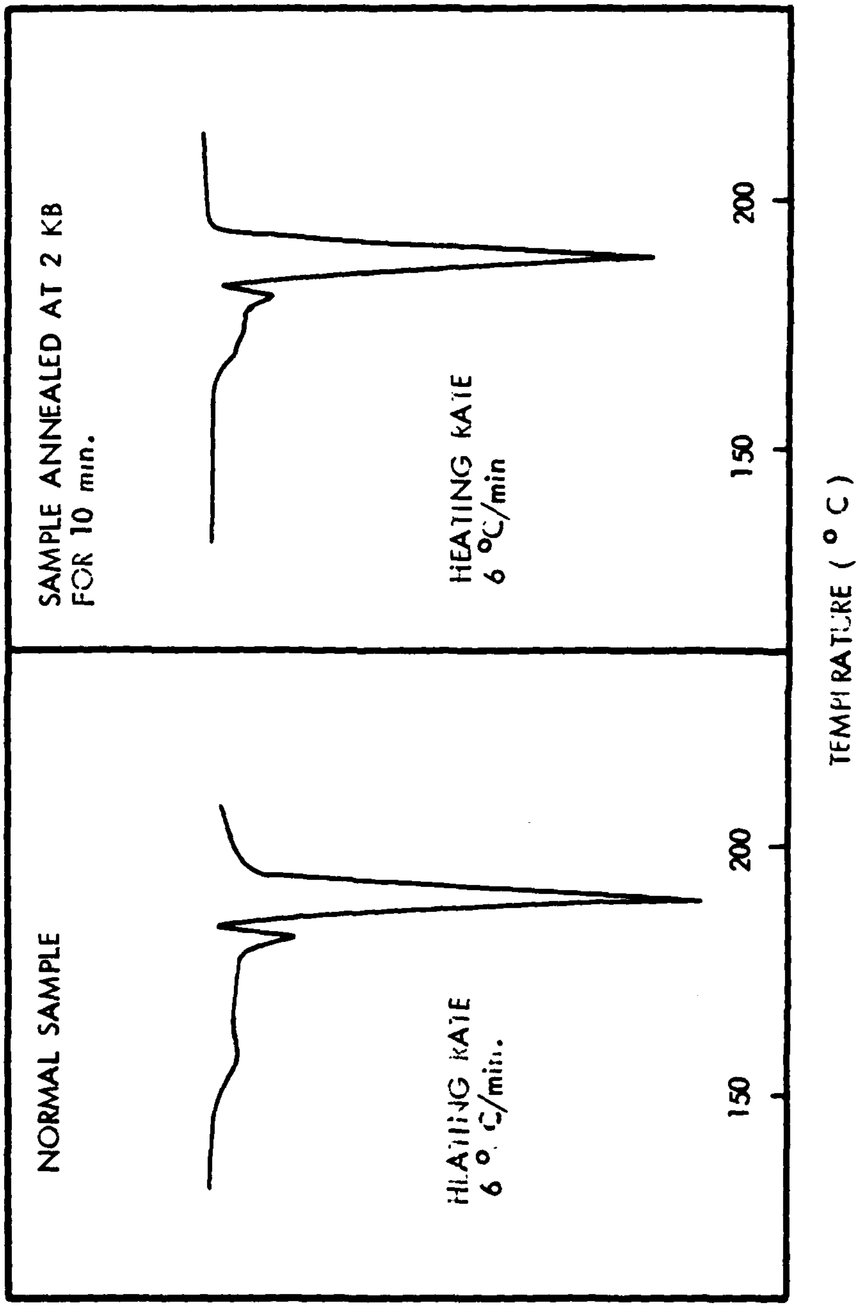
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