Interactions at the PA-6/PA-66 Interface

F. Rybnikár and P. H. Geil

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For additional information:

Air Conditioning and Refrigeration Center
University of Illinois
Mechanical & Industrial Engineering Dept.
1206 West Green Street
Urbana, IL 61801

(217) 333-3115

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P. H. Geil, Principal Investigator

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INTERACTIONS AT THE PA-6/PA-66 INTERFACE

František Rybnikář and P. H. Geil
Polymer Group
Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign
1304 West Green Street
Urbana, IL 61801

ABSTRACT

Refrigerant tubing used in some mobile air conditioning systems has a nylon core, often consisting of nylon 6, nylon 66, or a copolymer thereof. A blend of the homopolymers would be more economical than the copolymer. This paper deals with the structural stability of such blends during processing. The crystallization and melting behavior of laminates and solution cast blends of nylon 6 and 66 were examined. Although they do not co-crystallize readily, their at least partial miscibility in the melt and possible co-incorporation as crystal defects causes reductions of the melting points and heats of crystallization and fusion of both polymers. The crystallization temperature of the nylon 6, however, increases with increasing nylon 66 content, up to ca. 60% nylon 66, a feature attributed to nucleation of the 6 by the 66.

INTRODUCTION

With growing interest in polymer blends knowledge of interactions at the phase boundaries is essential because the type and extent of interactions influence not only mechanical, physical and optical properties but also the process of nucleation and crystallization and the resulting morphology. Refrigerant tubing used in some mobile air conditioning systems has a nylon core, often consisting of nylon 6, nylon 66, or a copolymer thereof. A blend of the homopolymers would be more economical than the copolymer. This paper deals with the structural stability of such blends during processing and shows our results concerning the interface of poly-6-caproamide (PA-6) and poly (hexamethylene-adipamide) (PA-66). Even though PA-6 and PA-66 are widely used in practice, information on their behavior in blends is scarce (2-4).

EXPERIMENTAL

Materials. All measurements were performed with commercial samples of PA-6 Amilan (Toray Company) and PA-66 Nylon 66 (DuPont Company). Samples were in the form of pressed sheets of each polymer (type 1). Some measurements were also done with PA-6/PA-66 blends prepared by evaporating HCOOH from 0.5% blend solutions at 25°C (type 2).
Crystallization and melting. The course of crystallization and melting was investigated using a Perkin-Elmer DSC-4. Two discs (ϕ 6 mm), one of each polyamide, were placed in the DSC sample pan forming one contact area. The respective sample thickness was adjusted to get various PA-6 to PA-66 ratios, the total sample weight being 6-12 mg. The thermal history was always identical: heating (100°C/min) to 270°C, melting 3 min, cooling (20°C/min) to 100°C while recording the crystallization curve, heating from 100°C (20°C/min) to 270°C and recording the melting curve. Occasionally melting runs were done with as-prepared samples. The recorded data for the crystallization (T_c) or melting temperature (T_m) correspond to peak values and represent averages of at least two independent measurements. For wide angle x-ray diffraction a Scintag x-ray goniometer equipped with heating stage was used with Cu K_α radiation (Ni filtered) and a Ge solid state detector.

RESULTS

Crystallization and melting. Typical DSC crystallization and melting scans of individual PA-6 and PA-66 polymers are shown in Figs. 1 and 2. PA-66 crystallizes faster than PA-6 as follows from its narrower T_c range. As the samples were crystallized under nonisothermal conditions, the melting scans have, besides the main melting peak, one or two smaller peaks at lower T_m. The crystallinity of both polyamides is practically equal as follows from heats of fusion (see Table 2). DSC scans of laminated samples (type 1), at first glance, were such as expected for immiscible polymer blends. But a closer

examination revealed that the crystallization and melting of both individual polymers is influenced by the presence of the other polymer. This is apparent from the data in Tables 1 and 2 and Fig. 3. Especially at lower PA-6 content the crystallization range of the PA-6 component was broadened and shifted to higher T_c. Besides the main PA-6 T_c peak, there was also present a shoulder on the higher T_c side, marked by an arrow in Fig. 4. This crystallization shoulder has no counterpart in the melting run. It seems that the faster crystallizing material probably represents mixed crystallites with lower melting temperature.

First we will consider the melting and crystallization behavior of the PA-66 component. With increasing PA-6 content in the laminate the T_m, T_c, ΔH_m and ΔH_c-values of PA-66 slightly decrease. This is consistent with the assumption that during first melting a certain amount of PA-6 dissolves in PA-66 and acts as a diluent during crystallization and second melting. The situation concerning crystallization and melting of the PA-6 component is more complex. The decrease of T_m-values with increasing PA-66 content indicates that also in PA-6 some amount of PA-66 is dissolved and/or that the PA-6 crystals are smaller or more imperfect with increasing PA-66 content. On the other hand, the T_c-values of PA-6 component increase with increasing PA-66 in the laminate up to about 60% and then slightly decrease. To understand this trend one has to realize that the crystallization of PA-6 and PA-66 takes place under different circumstances. When PA-66 crystallizes, the PA-6 component is in the liquid state, whereas PA-6 crystallizes in the presence of solid PA-66. Because of similar chemical and crystal structure, it seems probable that PA-6 can easily nucleate on solid PA-66 surface. So, increasing PA-66 content may increase the overall crystallization rate of PA-6. However, it is noted the initial surface area of the laminates in contact was the same for all ratios; thus the amount of PA-66 surface area in contact with the PA-6 could increase only if there was diffusion of the PA-66 into the PA-6 and subsequent PA-66 domain formation. It is also possible that an increased concentration of PA-66 stays dissolved in the PA-6, explaining the decreasing crystallinity of PA-6, as is seen from the drop of ΔH_m or ΔH_c-values for large PA-66 content. We would expect higher T_m-values for the PA-6 component in the case of higher T_c, but apparently the lower T_m-values are due to dissolved PA-66 and possibly to some degree of co-crystallization. In the composition range < 40% PA-6, the ratio volume/surface area of PA-6 in the laminate diminishes and the effect of dissolved PA-66 on decreasing crystallization rate and crystallinity of PA-6 dominates. The results show that there is an important interaction of the solid PA-66 and liquid PA-6 interface. Although the original contact area is relatively small the surface nucleation influences the crystallization of a substantial portion of the PA-6 phase. As indicated this suggests substantial and large scale interdiffusion of both polyamides in the melt.

To investigate the mutual solubility of PA-6 and PA-66 more closely, we prepared films from PA-6/PA-66 blends (4:1, 1:1 and 1:4) by evaporating HCOOH from solutions at room temperature (type 2 samples). The films were white opaque and x-ray diffraction confirmed that they were crystalline in the α-modifications. It is noted x-ray diffraction cannot be used to distinguish a mixture of homopolymer crystals and co-crystallization. All reflections have similar spacings except for the PA-66 002 reflection (13.8°2), which is absent from the PA-6 pattern. This reflection was present in all of the samples with an intensity proportional to the PA-66 content. Also DSC scans showed that they were crystalline; the degree of crystallinity was about the same as that of films from the individual blend constituents, prepared from solution in the same way. The DSC melting scans of melt crystallized samples (second scans) showed again two separate melting peaks. If the concentration of one component was lower than 20% only single crystallization and melting peaks are seen, approaching that of the prevailing component. As was expected, by increasing the contact area between the two polyamides, the mutual interactions became more pronounced than in the type 1 samples. As it follows from Table 3 and Fig. 5 the T_m-values decrease markedly with increasing content of the second blend component which is consistent with mutual, at least partial solubility in the amorphous regions. From the shape of the T_m-composition curves if follows that the solubility of PA-66 in PA-6 is greater than vice versa.

In their crystallization behavior the two polyamides in the type 2 samples differ in the same way as was seen with type 1 samples. PA-66 T_c-values decrease monotonically with increasing PA-6 content to some limiting value, similarly as T_m-values. The T_c-values of PA-6, on the other hand, show again a maximum at the mid-composition. With increasing time or temperature in the melt the T_c and T_m-values of both polyamides shifted closer together and eventually merged into one broad peak for both laminates (Fig. 6a) and solution cast blends (the solution blends crystallized separately on initial crystallization, as shown by separate melting points and their morphology (to be published). This suggests that the two polyamides form a miscible solution in the melt after sufficient time which can be retained in the amorphous regions when cooled below T_m. Unfortunately, the T_gs of the homopolymers are sufficiently close that the effect of miscibility on them can not be determined. The broad melting range with "peaks" at temperatures below those of the corresponding pure components suggests co-crystallization, to some degree, and/or small imperfect crystals. However, annealing a sample such as 2' (Fig. 6) at a temperature such as 205°C, well below either T_m, the individual melting peaks reappeared similar to those in curve 1'. Although the thermal treatment in the melt could lead to transamidation and the formation of copolymers, their reappearance suggests the effects are due to small, imperfect crystals which are improved by the annealing.

CONCLUSIONS

PA-6 and PA-66, in spite of a great similarity in chemical and crystal structure, cannot readily co-crystallize. This similarity, on the other hand, favors, at least partial mutual solubility in the melt which influences the crystallization and melting behavior of their laminates and blends. The crystallization rate of the PA-6 in the laminate and the blend is higher than in crystallizing PA-6 alone, due to the PA-6 nucleation on the solid PA-66 surface. The surface nucleation of the PA-6 component and mutual or at least partial solubility in the melt results in some degree of co-crystallization but as defective crystals. This is the reason the crystallization and melting behavior differs from that of pure blend constituents of other polymers. It is noted the results suggest a rapid mutual interdiffusion in the laminates as well as in the blends in the melt state. They also suggest considerable care would be needed in processing to produce reproducible properties, particularly if mixing is poor or melt residence times short.

REFERENCES

1. F. Rybnikář, J. Macromol. Sci-Phys., B27, 125 (1988).
2. H. Mitomo and H. Tonami, Chemistry of High Polymers, 27, 134 (1970).
3. E. S. Ong, Y. Kim and H. L. Williamson, J. Appl. Polym. Sci., 31, 376 (1986).
4. D. R. Paul and S. Newman, "Polymer Blends", Academic, New York, Vol. 1, 29 (1978).

Table 1. Crystallization and melting temperatures of PA-6/PA-66 polyamide contact laminates.

	PA-6			PA-66	
% PA-6	T_c, °C		T_m, °C	T_c, °C	T_m, °C
100	177.5		217.5		
90.8	176.7		217	228.5	260.5
89	178.8		217.1	228.2	255.6
83.2	179.3	192	216.6		256.8
81	177		217.6	228.2	257.3
72.5	177.2	193	217.2	229.2	258
65.7			215		257.1
62.6	180.2	192	215.6	229.9	256.7
53	180.4	192	215.8	230.6	257.3
48	181	190		229.8	
45.3	182.5	193	215.6	230.2	257.2
42	181.4	192	215	230.2	256.8
37.4	182.8		215.7	230.9	257.7
27.3	181.1	192	214.9	228.8	259.3
20	180.5	189		228.4	
17	179.8	189		228.4	
16.8	182	193	215	229	259.3
15.5	180.7	192	214.9	228.5	259.8
0				230	259

Table 2. Heat of melting and crystallization of PA-6/PA-66 polyamide contact laminates.

	PA-6		PA-66	
% PA-6	ΔH_c, cal/g [a]	ΔH_m, cal/g	ΔH_c, cal/g	ΔH_m, cal/g
100	15.7	16.7	-	-
90.8	14.6	15.8	12.2	15.3
89	15.4	16.7	11	15.6
83.2	15.3	15.9	12.2	15.6
81	15.2	16.5	12.5	15.4
72.5	15.1	16.4	12.8	15.5
67.5	-	14.5	-	16.4
62.6	15.5	16.4	13.4	14.9
53	15.1	15.1	12.7	15.2
48	13.4	-	13.1	-
45.3	15.8	15.6	12.9	16
42	14.1	14	12.6	15.5
37.4	15.3	14.5	12.9	16
27.3	13.4	10.1	13.5	16.2
20	8.9	-	15.1	-
17	9.9	-	14.7	-
16.8	9.1	9.2	14.1	17.2
15.5	8.8	8.6	14.3	17.1
0	-	-	15.5	17.6

[a] per gram of PA-6 or PA-66 in the laminate.

Table 3. Crystallization and melting temperatures of PA-6/PA-66 blends prepared by evaporation of 0.5% HCOOH solution at 25°C

	PA-6			PA-66	
% PA-6	T_c, °C		T_m, °C	T_c, °C	T_m, °C
100	177.5		216	-	-
80	187.6	200s	211.2	212	247
50	188		207	216	249.3
20	175b		200.1	220	250
0	-		-	230	259

s - shoulder

b - very broad peak

FIGURES

Fig. 1. DSC crystallization scans of PA-6 and PA-66 during cooling from 270°C to 100°C. The cooling rate is 20°C/min.

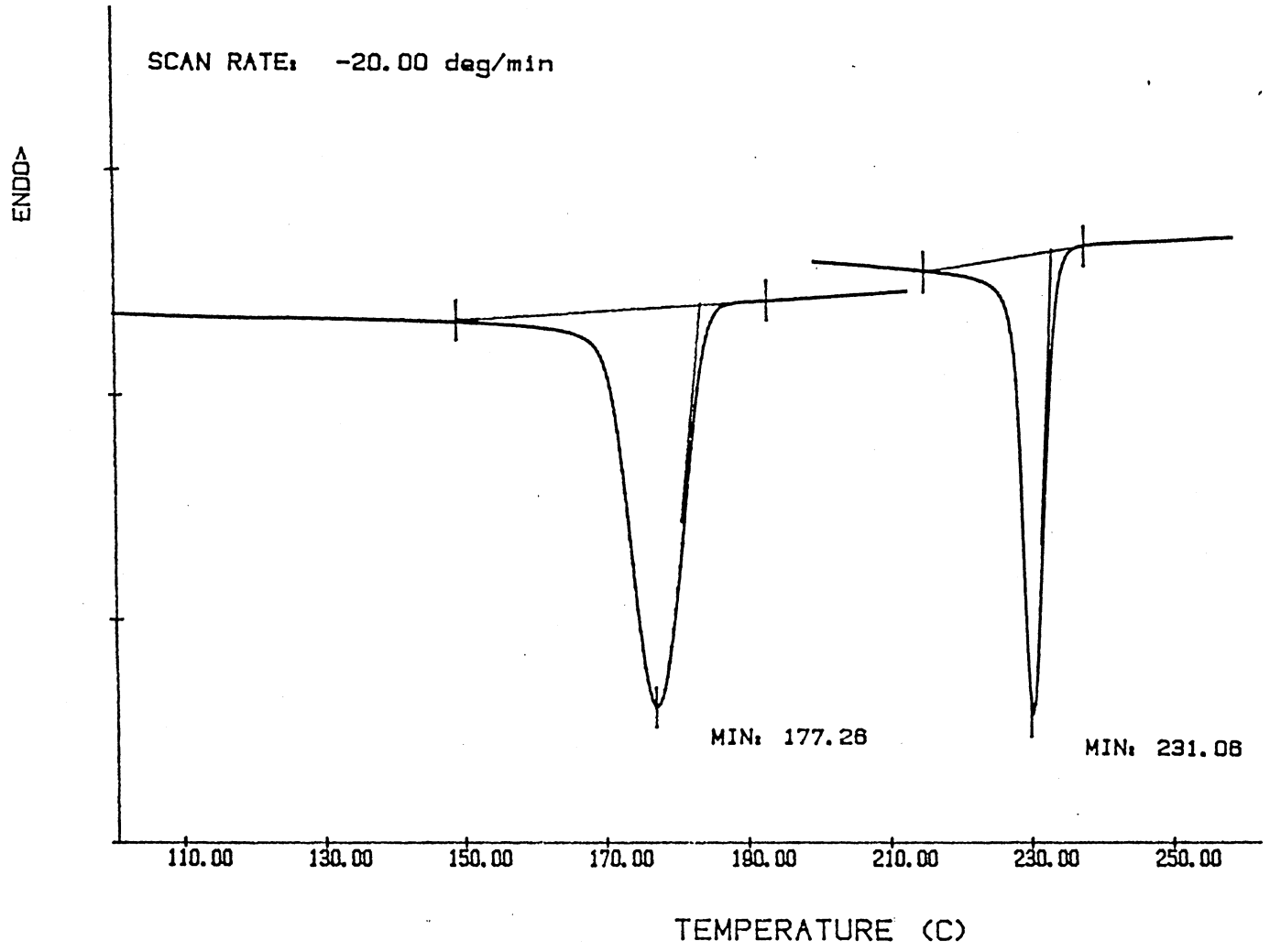
Fig. 2. DSC melting scans of PA-6 and PA-66 crystallized by a standard procedure shown in Fig. 1. Heating rate was 20°C/min.

Fig. 3. DSC measured melting (second scan) and crystallization temperatures, heats of crystallization and fusion of PA-6/PA-66 contact laminates as a function of blend composition.

Fig. 4. DSC crystallization scan of the PA-6/PA-66 (1:1) contact laminate. Arrow shows the additional shoulder of PA-6 crystallization peak at higher T_c.

Fig. 5. DSC measured melting and crystallization temperatures of PA-6/PA-66 solution prepared blends as a function of blend composition.

Fig. 6. DSC crystallization and melting of PA-6/PA-66 (1:1) type 2 blend. Curves 2 and 2' belong to a sample melted 40 min at 270°C, whereas 1 and 1' were melted at 270°C for 3 min.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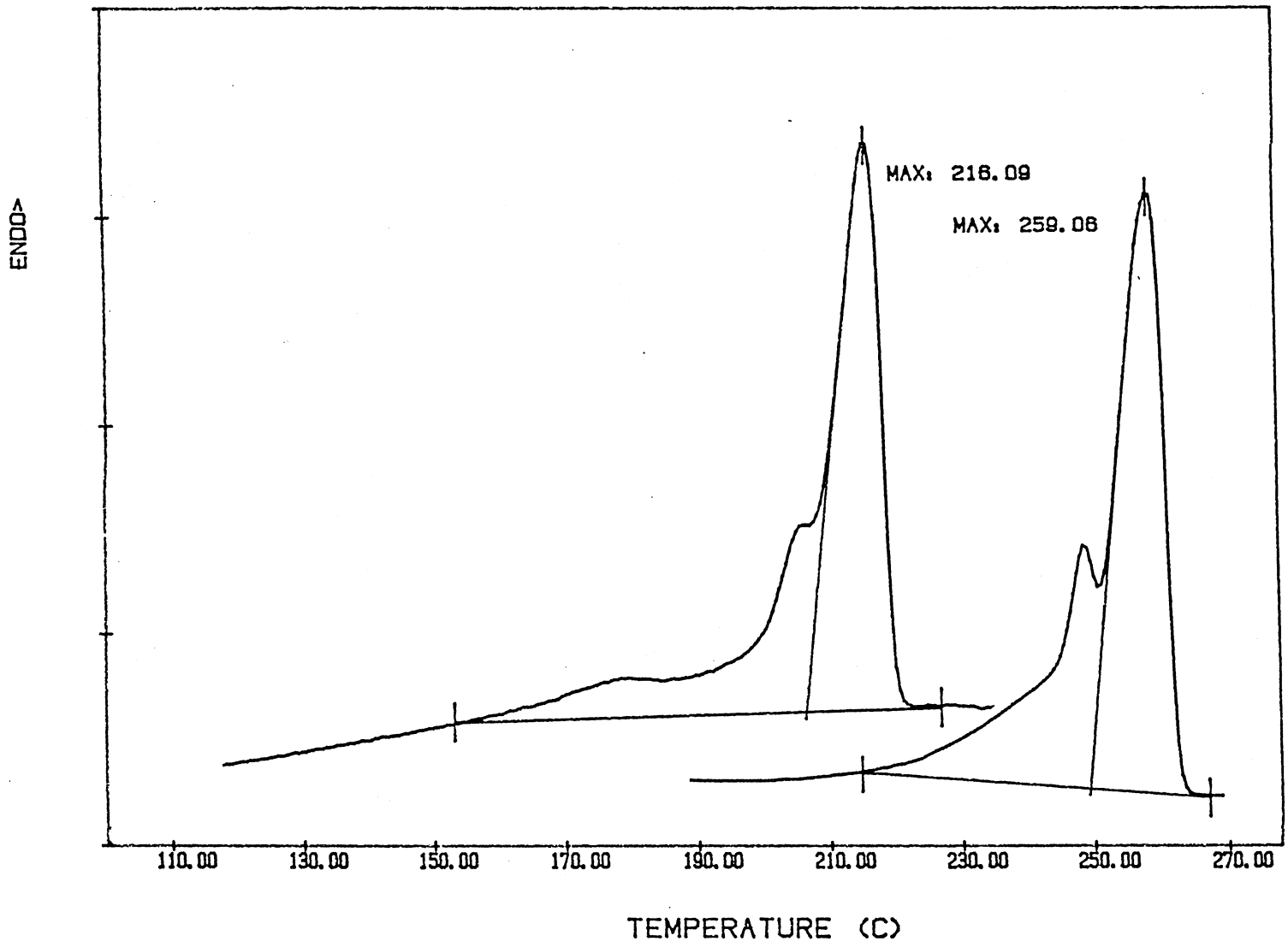
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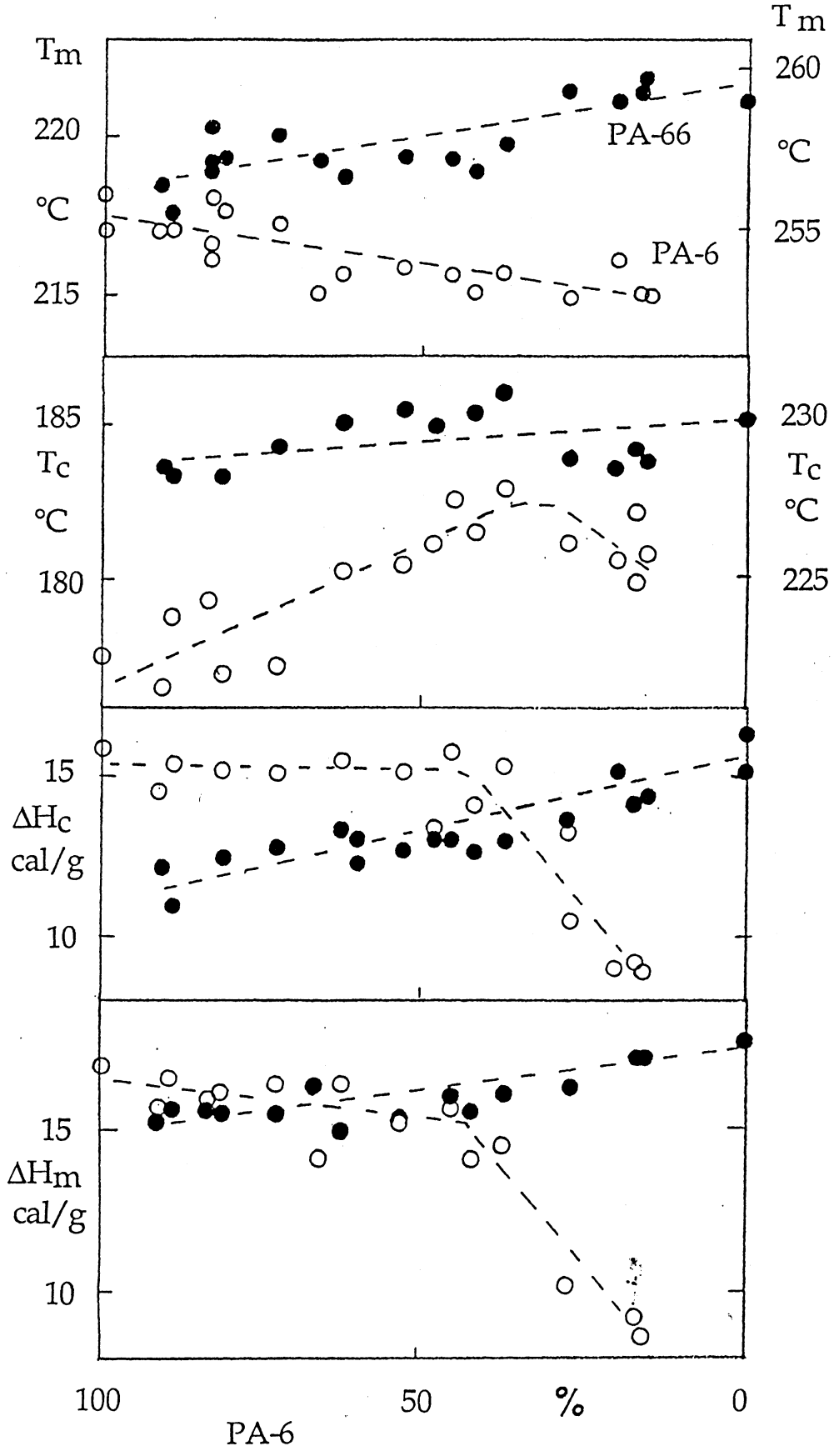
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°C
215
PA-66
PA-6
T m
260
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255
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Tc
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180
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%
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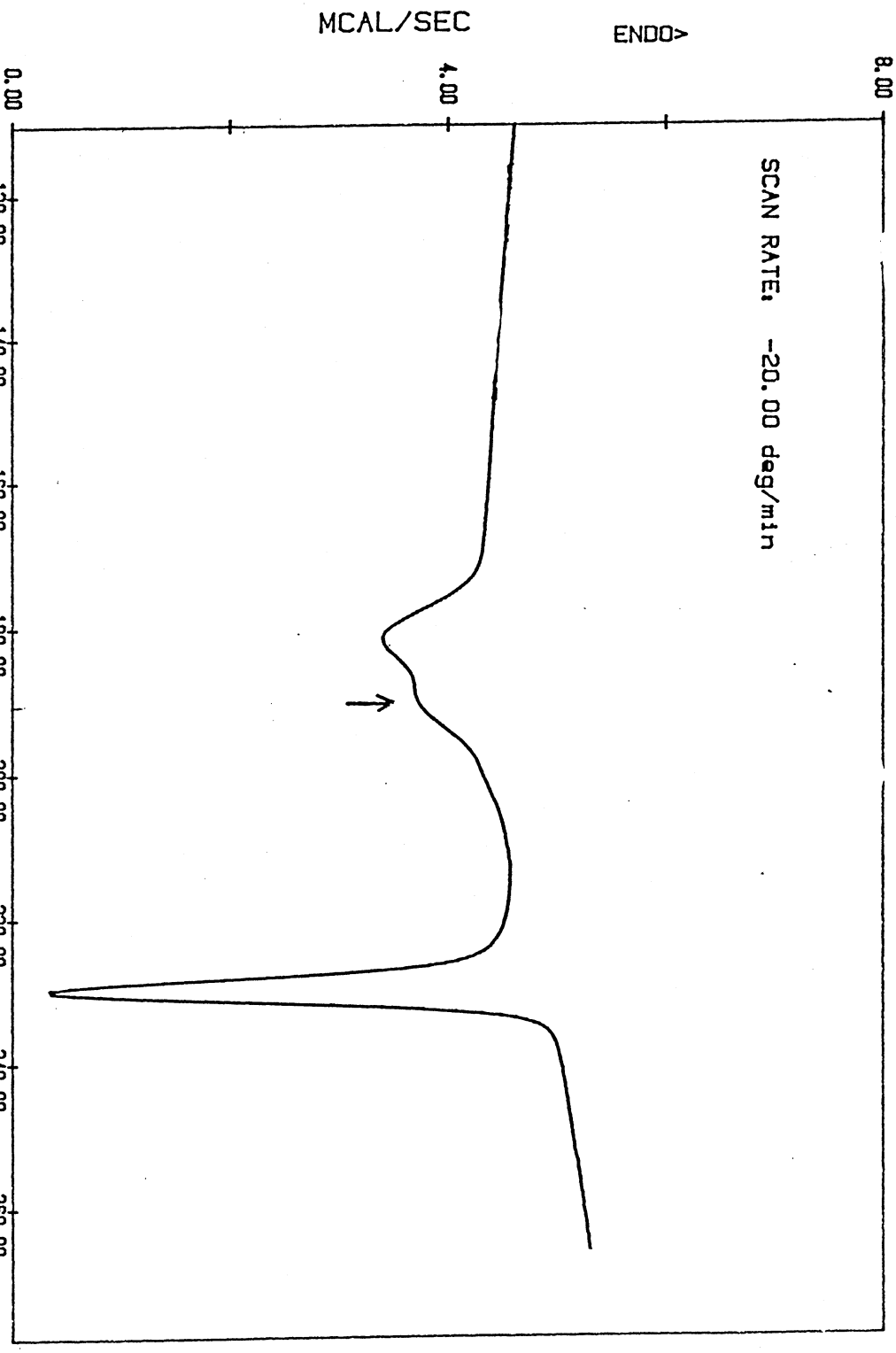
PA-6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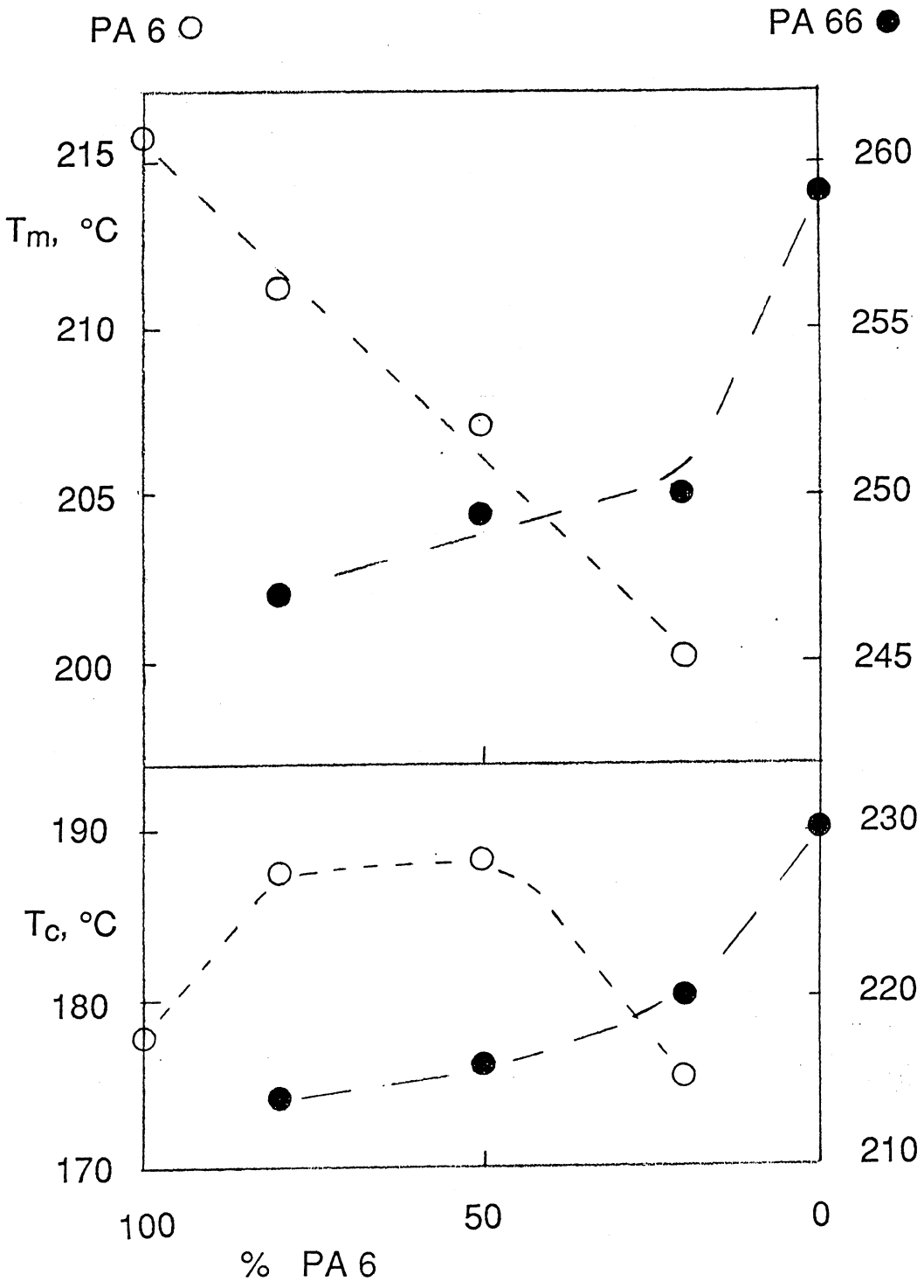
PA 6 ○
PA 66 ●
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210
205
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T_m, °C
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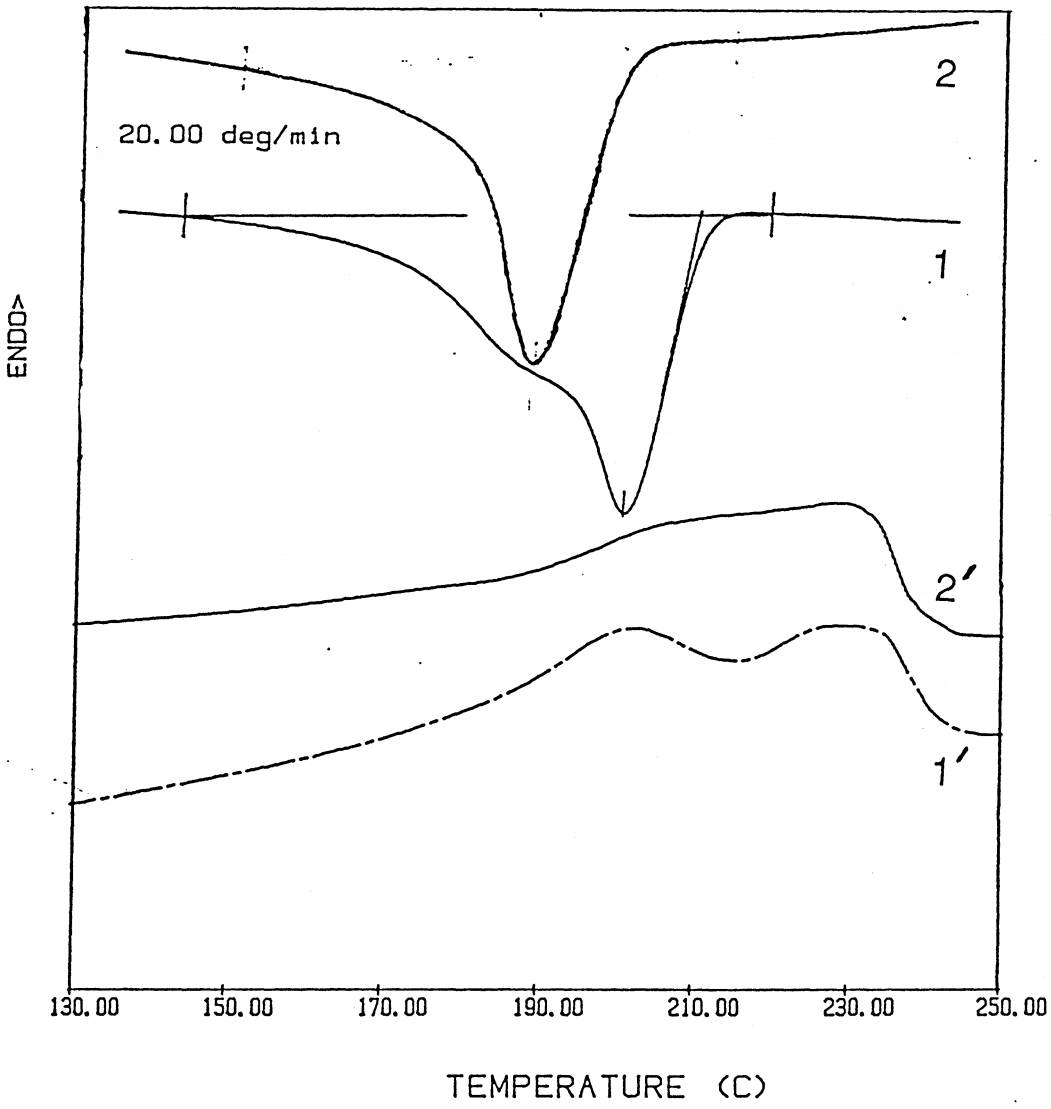
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