Thermal properties of amino acid type polyamides*

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We studied the thermal properties of nylons 4 to 12 using the DSC method. For the determination of melting points, a new technique of thermal treatment was used. It consists of giving a finite number of repeated cooling—heating cycles to polymers just below their melting points before the determination. This treatment allowed to eliminate the diversity of thermal history of various samples and led to "perfect" crystalline structure polymers. The obtained melting points were called "intrinsic" melting points. When this technique was not used, nylons 4 and 5 showed a melting behaviour different from the others because of their thermally degradable nature.

While some authors state that odd nylons have no glass transition, we found that every nylon gives two transitions between −10 and +80°C. The glass transition T_g lies between +35 and +85°C. In the case of even nylons, T_g is always followed by a crystallization which is known as cold crystallization for nylon 6. This phenomenon seems to be due to characteristic crystalline structure of even nylons.

The study of transitions and of melting points of nylons allowed us to consider a theoretic explanation of the crystalline structure of these polymers.

С помощью метода DSC изучались термические свойства полиамидов от 4 до 12. Для определения температур плавления применился новый метод термической переработки основанный на применении окончательного количества циклов охлаждение—нагревание полимера вплотную под и над его температурой плавления перед измерением. Указанный способ позволил исключение разниц в термической истории разных проб и предоставил полимеры с «превосходно» кристаллической структурой. Этим способом полученные температуры плавления назвали «внутренние» температуры плавления. Когда не применился этот метод, полиамиды 4 и 5 показывали поведение разное в сравнении с остальными полиамидами в последствии их термической деградабилиты.

Несмотря на утверждения некоторых авторов, что непарные полиамиды не имеют температуру стеклования T_c, мы нашли в каждом полиамиде два перехода между −10 и +80°C. T_c находится между +35 и +85°C. В случае парных полиамидов, после T_c наступает кристаллизация, которая у полиамида 6 называется холодной кристаллизацией. Это явление вероятно вызвано характеристической кристаллической структурой парных полиамидов.

Изучение T_c и температур плавления полиамидов позволило теоретическое объяснение их кристаллической структуры.

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The thermal properties of poly-ω-amino acids were studied by several authors [1—10]. The study of melting points and of glass transitions provided some information on the crystalline properties of the polymers. Perceptible structural differences were thereby pointed out between odd and even polyamides. Nylons 4 and 5 were less studied because they are rather difficult to prepare in high polymers, especially nylon 5, and very easily degraded by heating. Recently, high molecular weight samples of these polymers have been prepared in our laboratory [11—13]. We studied their thermal properties and compared them with those of nylons 6 to 12. The diversity of the results (melting points and glass transitions) according to the authors [1—10] results apparently from incomplete thermal treatment. We found a method giving a well defined thermal history which allows to obtain reproducible data.

Experimental

Preparation of the samples

Nylons 4 and 5 were prepared by anionic polymerization of the corresponding lactams using the tetraalkylammonium salts of lactams as catalysts and *N*-acetyllactams as initiators [11—13]. Nylons 9 and 11 were obtained by polycondensation of the corresponding amino acids and the others by hydrolytic polymerization of lactams. The resulting polymers were dissolved in formic acid, precipitated in ethyl ether, washed with cold water until the acid was completely removed, then dried under vacuum for 16 hrs at 80°C. The reduced viscosity measured in *m*-cresol (1 g of sample in 100 ml of solvent at 25°C) is about 8 for nylon 4, 4.7 for nylon 5, and varies between 1 and 2.5 for the others.

Measurements by DSC

All measurements were performed by a DSC Dupont 990 apparatus.

Meltings

The polymers (3 to 5 mg) were carefully introduced into the pan. All thermograms were registered under nitrogen flow of 50 cm^3/min. The heating rate for all experiments was 20°C/min. Various techniques were used:

— The samples were rapidly heated to 80—90°C below their melting points, then heated to melting (Fig. 2, curves *2*). This is called the 1st melting in the present article.

— After melting, the polymer was rapidly crystallized and remelted. This is denoted as the 2nd melting (Fig. 2, curves *3*).

— The melted polymer was quenched by immersing it into liquid nitrogen, then remelted (Fig. 1, curve *2*).

— The polymers were heated to 8°C below their melting points for 30 min. Then they were melted (Table 1).

— A new technique was applied in order to eliminate earlier thermal history of the samples: The polymers were heated up to 8°C below their melting points, then cooled for 40°C and reheated. This procedure was repeated for 10 and 20 times. The rate of heating and cooling was 20°C/min (Fig. 2, curves *1a* and *1b*).

When the polymer is heated to melting, the curves show that the melting begins before the endothermal peak. This peak corresponds to the complete melting and we denote it as T_M. The extrapolated onset is the point of intersection of the tangent drawn at the point of greatest slope on the

Table 1
Melting and crystallization of nylons

Nylons	Melting* °C	Crystallization**		
		5°C/min	20°C/min	50°C/min
4	276	240	239	218
5	290	255	254	242
6	229	198	190	177
7	236	209	199	187
8	205	172	165	154
9	207	189	182	170
10	193	166	162	147
11	194	167	161	152
12	182	143—151	136	128

* Melting after heating 30 min at 8°C below melting point.
** Crystallization of melted nylons for various rates of cooling.
Atmosphere N_2 = 50 cm^3/min, heating rate 20°C/min.

leading edge of the peak with the extrapolated base line. We denote it as T_m (Fig. 1). This point was determined graphically.

Temperature calibration of the instrument was achieved for 10 and 20°C/min by the melting of an indium standard and was found to be independent of the rate for these two heating rates.

All temperatures indicated on the curves are corrected by means of the table supplied by the producer for chromel-alumel thermocouples.

Crystallization

The polymers, melted under nitrogen at a rate of 20°C/min, were cooled until the onset of crystallization. Three cooling rates were used: 5, 20, and 50°C/min (Table 1).

Transitions

The transitions can occur only in the amorphous zone. To make the nylons amorphous, they were melted several minutes at 50°C above their melting points and then quenched in liquid nitrogen. Nylons 4 and 5 which are more or less degraded on heating and mainly after melting [14] were quenched in liquid nitrogen as soon as they were melted. The quenched material was kept under cold nitrogen flow meanwhile the apparatus was cooled to −20°C, at this temperature the sample was inserted into the apparatus filled with nitrogen to avoid water condensation. Then the apparatus was cooled to −90°C and the heating began at −90°C. The heating rate was 50°C/min (except for nylon 6: 20°C/min). We found that when some water was condensed on the sample, the base line shift around the freezing point was so sharp that it was not possible to see any transition. However, no such a great shift of the base line was observed in our measurements. The relative magnitudes of the two phenomena reached easily the ratio 10 to 1, which allowed us to avoid any confusion.

Results

Meltings

Melting and crystallization results are summarized in Table 1. The temperatures correspond to the melting peak (T_M) and to the peak crystallization.

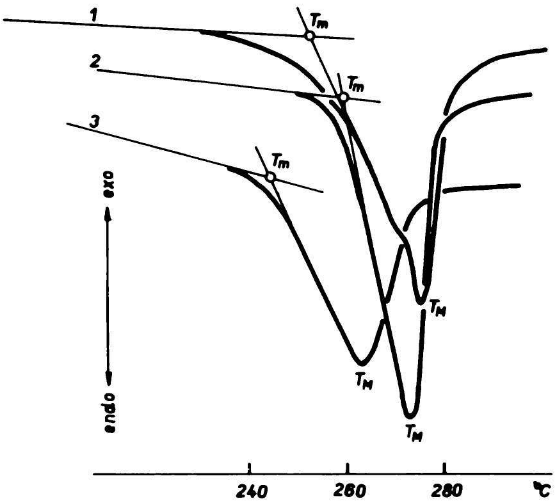

Fig. 1. Melting of nylon 4.
1. 1st melting; *2.* 2nd melting, the melted polymer was quenched in liquid nitrogen; *3.* 3rd melting, the melted polymer was cooled slowly.
Heating rate 20°C/min, atmosphere $N_2 = 50\ cm^3/min$, ΔT sensitivity 1°C/in.

When nylon 4 is melted, then quenched in liquid nitrogen, and remelted (Fig. 1, curve *2*), there is a very small difference between its T_M and temperature of the 1st melting (Fig. 1, curves *1* and *2*). When this nylon is melted, crystallized at a rate of 20°C/min, and remelted (Fig. 1. curve *3*), T_M is lower than temperature of the 1st melting (Fig. 1, curve *1*). The difference between T_M and T_m is greater in case of curves *1* and *3* than in the case of curve *2*. The T_m temperature of the quenched polymer (curve *2*) is higher than that of other polymer (curves *1* and *3*).

Fig. 2 gives the results of melting of some nylons after various thermal treatments: 10 and 20 cycles, 1st and 2nd meltings. It can be seen that after 10 and 20 cycles, T_M and T_m are always higher than those found for the 1st or the 2nd melting. Moreover, T_M and T_m increase with the number of thermal pulses for nylons 4, 5, and 12.

Fig. 3 shows the variations of the melting temperature of a thermally degradable nylon (*i.e.* nylon 4) after several melting-crystallization cycles. The temperature regularly decreases and two melting peaks appear.

When nylon is thermally stable (*i.e.* nylon 9), the variations of melting temperature after several melting-crystallization cycles are negligible. As it can be seen in Fig. 4, the melting temperature does not vary any more after the 3rd melting. It is the same for crystallization.

The results given in Table 1 indicate that the lower the rate of cooling, the higher is the temperature of crystallization. For nylon 12 (Fig. 5), two crystallization peaks appear. These two peaks might be due to the formation of different types of spherulites.

Fig. 6 shows the variations of the melting temperatures (T_M and T_m) *vs.* the inverse of the logarithm of the number of pulses. Two straight lines are obtained. These lines converge to the same point situated on the temperature axis for an infinite number of thermal pulses. The temperature thus obtained could be called the "intrinsic" melting temperature of the polymers, since it is free from the influence of the diversity of thermal history.

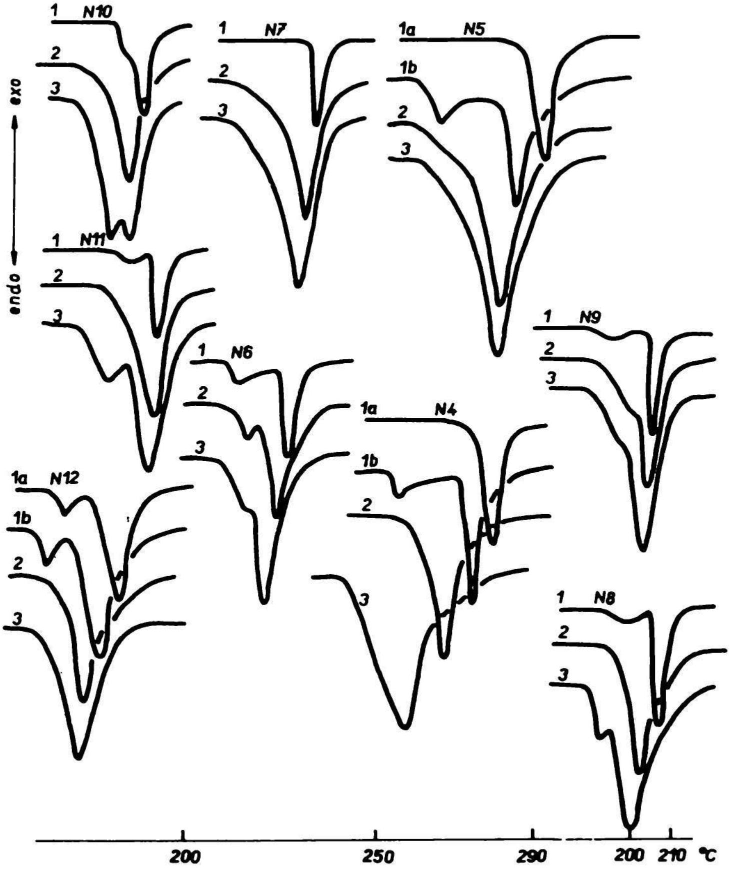

Fig. 2. Melting of nylons 4 to 12.
1a. 20 cycles; *1b.* 10 cycles; *2.* 1st melting; *3.* 2nd melting.
Heating rate 20°C/min, atmosphere $N_2 = 50\ cm^3/min$, ΔT sensitivity 1°C/in N4 means nylon 4, *etc.*

Transitions

We observed two transitions for nylons 4 to 12:

1. The first one is situated at about 0°C. It was observed by certain authors and explained as a direct result of an in-chain motion of subgroups [16]. This transition can be seen for all nylons in Fig. 7 even at two heating rates (20°C/min or less). At these heating rates, the transition is followed by a pronounced crystallization, and the polymer was not amorphous enough to have any T_g (except for nylon 6).

2. When a heating rate of 50°C/min is used, all polymers present a second transition between 37 and 85°C. According to [9, 16], this transition is identical with the glass transition for polyamides.

In the case of even nylons, T_g is always followed by a crystallization which is known as a cold crystallization for nylon 6 [10].

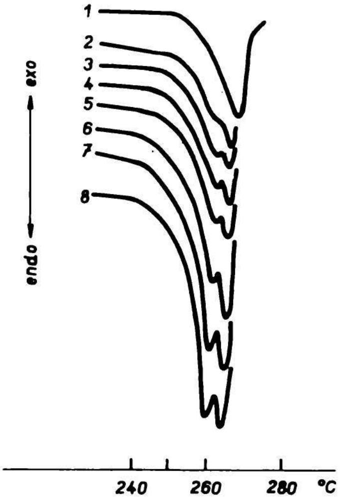

Fig. 3. Multiple meltings of nylon 4.
1. 1st melting; *2.* 2nd melting; *3.* 4th melting; *4.* 6th melting; *5.* 8th melting; *6.* 10th melting; *7.* 12th melting; *8.* 14th melting.
Heating rate 20°C/min, atmosphere $N_2 = 50$ cm^3/min, ΔT sensitivity 1°C/in.

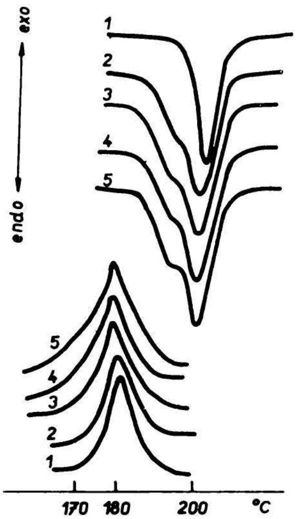

Fig. 4. Multiple meltings and crystallizations of nylon 9.
Heating and cooling rates 20°C/min, atmosphere $N_2 = 50$ cm^3/min, ΔT sensitivity 1°C/in.

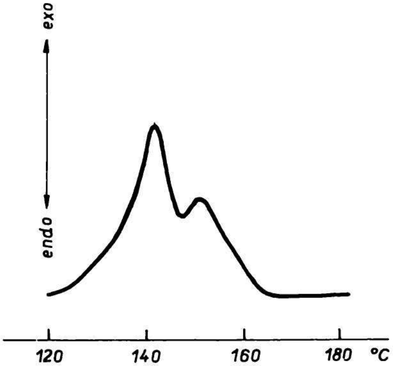

Fig. 5. Crystallization of nylon 12.
Cooling rate 5°C/min, atmosphere $N_2 = 50$ cm^3/min, ΔT sensitivity 1°C/in.

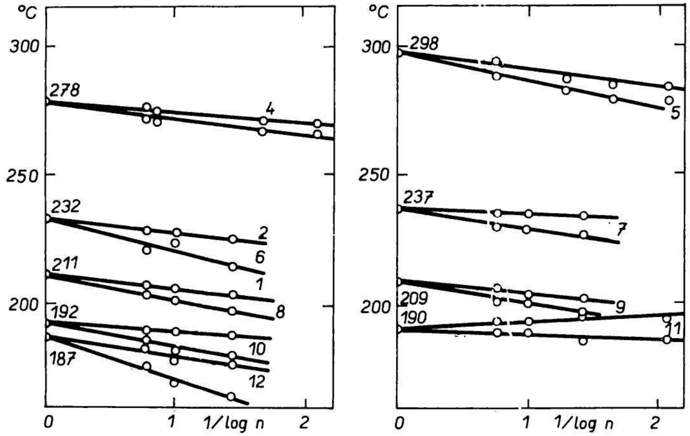

Fig. 6. Variations of the melting points of nylons 4 to 12 *vs.* the inverse of the logarithm of the number of cycles.
1. (lower curves): T_m points; *2.* (upper curves): T_M points.

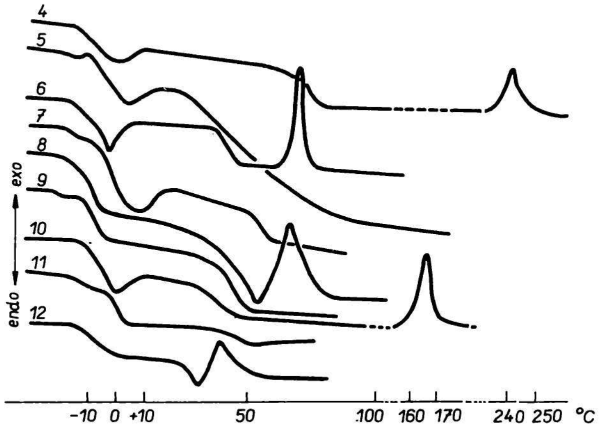

Fig. 7. Transitions and cold crystallization of nylons 4 to 12.
Nylons 4, 5, and 7 to 12: heating rate 50°C/min, nylon 6: 20°C/min, atmosphere $N_2 = 50$ cm^3/min, ΔT sensitivity 0.2°C/in.

Discussion

Melting

Nylons 4 and 5

The thermal data on these nylons reported in the literature are very dispersed. It is mainly due to their low molecular weight and to their thermal instability. With our samples of a high molecular weight we studied two representative cases: processing by melting and crystallization (drastic conditions) and processing by thermal pulses. The former was possible owing to the relatively high thermal stability of our samples. Contrary to other polyamides showing stabilization beyond the 3rd melting, nylons 4 and 5 when melted and crystallized repeatedly several times, give a decrease of the melting temperature. It is known that the degradation of these two nylons proceeds both by depolymerization and regeneration of the monomer and by random scission of the chain, which is further followed by new depolymerization [14]. The decrease of the melting temperature would therefore be mainly due to the dissolution of the polymer in the regenerated monomer and probably also to the decrease of the molecular weight of the sample.

When melting and crystallization are repeated several times, the appearance of two melting points is observed. This phenomenon is not peculiar to nylons 4 and 5, and would be due to different type of spherulites formed in a single phase when the polymer is crystallized [15].

With the second method (see detail below), we observed that the melting temperature regularly increases with the number of thermal pulses until about 28 pulses and then suddenly drops (case of nylon 4 for example; nylon 5 tolerates a rather high number of thermal pulses). This fact shows that until this limiting number of pulses, there is practically no degradation. We can therefore assume that the curves of Fig. 6 corresponding to nylons 4 and 5 are entirely free from disturbances due to the degradation.

Pulse treatment of polymers

The imperfections of the crystalline structure which have a baneful effect upon the thermal properties of the polymer, are usually eliminated by a suitable thermal treatment. However, all known kinds of treatments were either slow or rather incomplete. We therefore developed a new method suited especially to the study of the thermal properties of easily crystallizable polymers which consisted in applying several thermal pulses to the polymers. It is a dynamic and continuous method in contrast to the static and batchwise methods of thermal treatment used until now. When the polymers are treated by this method, T_M and T_m shift to higher temperatures as the number of thermal pulses increases, whereas the melting peak becomes stronger and sharper. This means that the local irregularities in the structure of the polymer disappear and the polymer tends to become more perfectly crystallized. Thus, the melting temperature obtained as the limit for a finite number of thermal pulses would be the "intrinsic" melting temperature of the polymer, corresponding to a "perfect" crystalline structure. This method makes it possible to suppress the influence of the former thermal history and treat the samples with a uniform "infinite" thermal history.

Melting of nylons

Several authors [17, 18] had reported the zigzag form of the melting point curve for polyamides. *Champetier* [18] explains this phenomenon by the lack of 50 per cent of hydrogen bonds in the crystal structure of even polyamides, and this also accounts for the low melting points of these nylons. According to *Bunn* [17], the number of hydrogen bonds would not vary according to whether polyamide is even or odd, because the chains can be disposed in antiparallel way. He ascribes therefore the low melting points of the even nylons to other causes, for example the propagation of vibrations along odd-numbered chain segments.

Since all polyamides are the assembly of a high number of crystallites, some edges of crystal sheets inevitably would occur in the crystallized polymers. At these edges, two chains which are in contact and which belong to two different crystallites would be packed parallel or antiparallel with the same probability. When the polymer is an odd nylon, all amide groups of these chains could afford hydrogen bonds, whichever the packing is parallel or antiparallel. On the contrary, in case of an even nylon, the probability of formation of hydrogen bonds would diminish by fifty per cent when these two chains are packed in parallel, which might introduce a rather disorganized interval between the marginal chains of crystallites and create a local disturbance in the polymer. The thermal movement of these marginal chains would start at lower temperature in even nylons and propagate to the neighbouring chains to demolish the crystallites. This may be the reason why even nylons have lower melting points than the neighbouring odd nylons.

When the "intrinsic" melting point is plotted *vs.* the number of amide groups per 100 atoms of the main chain (Fig. 8), the zigzag disappears for higher nylons and

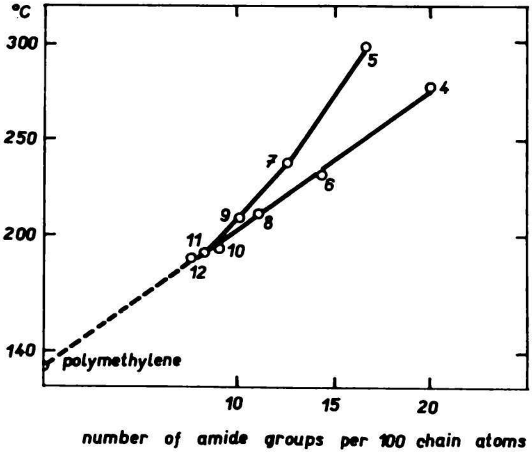

Fig. 8. "Intrinsic" melting temperature *vs.* the number of amide groups per 100 chain atoms.

the melting points are situated in the order of the carbon number, except for nylons 4 and 6. It is significant to state that these two nylons are the only ones in the series of even nylons to contain predominantly α form, whereas the other even nylons are generally in γ form for the major part [19, 20].

Transitions

Polyamides can be considered as "block" copolymers composed of the following units [16]

$$—(CH_2)_n— \quad \text{and} \quad —(CONH)— .$$

This assumption allows an explanation of the two transitions observed. The lower one is not the glass transition but might correspond to in-chain motion of subgroups, probably methylene links [16]. The glass transition is due to the rearrangements of the tridimensional network formed by the hydrogen bonds. According to some authors [10], odd nylons have no glass transition because the hydrogen bonding is complete for these nylons in both parallel or antiparallel configurations. Actually these nylons presented more difficulties, but we succeeded in obtaining the glass transition by using a high heating rate (50°C/min). Indeed, under these conditions the phenomena of crystallization did not screen the transition.

The existence of cold crystallization for even nylons only seems to be characteristic. It may be closely related to the microfine structure of odd and even nylons.

Conclusion

We established a method for thermal treatment of nylons. This method allows to obtain both "perfect" crystalline and spherulite structure. The melting points thus obtained can be considered as the "ideal" melting points of the poly-ω-amino acids. The study of transitions allowed us to point out some differences in crystalline structure of odd and even nylons.

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