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# THERMAL PROPERTIES OF NYLONS RELATED TO POLYGLYCINE

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**Abstract**—Aliphatic polyamides (homopolyamides 1.*n* and *n*.3 and copolyamides 2/*n*) were characterized in terms of their thermal properties. These series of isomeric polymers have single isolated methylene groups between the amide groups and crystallize in different forms intermediate between pseudohexagonal- and polyglycine II-like. Melting and glass transition temperatures are reported and compared with literature data. Thermogravimetry shows that an isolated methylene group imparts thermal instability to the nylons, depending on the detailed chemical structure. The copolyamides have sharp melting peaks and high crystallinity, when crystallized from solution, but crystallization from the melt is much slower. The heat-flow trends are discussed in relation to estimated heat capacities.

## 1. INTRODUCTION

Aliphatic polyamides (nylons) form one of the most important classes of polymers, both because of their industrial uses and their similarity to structures found in nature [1]. The first member of the series, nylon-2, is the simplest poly(amino acid), polyglycine. These similarities open a potential for biological applications, that could be coupled with the useful mechanical properties to give attractive final products. Indeed, nylon-2/6 has been shown to be biodegradable [2]. Unfortunately, the closer the structure gets to that of polyglycine, the more difficult it is to process the polymers.

In order to optimize nylon properties, the incorporation of isolated methylene groups between amide groups is of major interest. Given the two possible directionalities of the amide group in the repeating unit, a methylene can be introduced in three different ways between two amide groups, giving structures related to the helical form of polyglycine, PGII. The thus isolated methylenes are then combined with longer methylene sequences to impart greater flexibility to the final molecule.

Three families of nylons with isolated methylenes were synthesized for that purpose, via several different routines: homopolymers of the type 1.*n* ($n = 6$, 8, 10, 12) and *n*.3 ($n = 4$, 5, 6, 8), and alternating copolymers of the type 2/*n* ($n = 5$, 6, 12). For the series of nylons-1.*n*, the synthesis involves reaction of dinitrile with formaldehyde in a strongly acidic medium [3]. The structure of the repeating unit is:

$$[NH—CH_2—NH—CO—(CH_2)_{n-2}—CO—]$$

For the series of nylons-*n*.3, the synthesis involves a polycondensation of malonic acid with aliphatic diamines [4]. The structure of the repeating unit is:

$$[NH—(CH_2)_n—NH—CO—CH_2—CO—].$$

The copolyamides were synthesized using the method of activated esters, starting from the dimer [5]. The structure of the repeating unit of nylon-2/*n* is:

$$[NH—CH_2—CO—NH—(CH_2)_{n-1}—CO—].$$

The structural work has revealed that these nylons do not usually have crystal structures with planar zig-zag chains assembled in extended sheets, as is typical of commercial nylons. The reason is that the amide groups twist away from an all-*trans* conformation in order to optimize the formation of hydrogen-bonds. Note that nylons-*n*.2 (polyoxamides), not having an isolated methylene group, form extended sheets [6] as they can easily saturate all hydrogen-bonds in their planar zig-zag conformation. In principle, the nylons described in this work could adopt a conventional $\gamma$-type conformation, but the constraints imposed on the orientation of the amide groups by the presence of isolated methylene groups prevents the formation of such structure. It turns out that each of the observed structures is described by different torsional angles about the isolated methylene group, being in an amine (nylon-1.*n*), an amide (nylons-2/*n*), or a carbonyl (nylons-*n*.3) environment [7]. The copolymers 2/*n* possess hexagonal symmetry and can give, on crystallization from solution, hexagonal or trigonal morphologies, similar to PGII [5], depending on whether *n* is even or odd [8]. The nylons-1.*n* have an antiparallel orientation of neighbouring amide groups resulting in a single orientation of hydrogen-bonds, similar to that found in the $\gamma$ form but with shortened chain repeat distances [9]. Compared to these two families, nylons-*n*.3 have intermediate structures, with hydrogen-bonds pointing in two or three directions, 60° apart [10]. In some cases it appears that different crystalline forms are possible for nylons-*n*.3 [11].

Comparisons can be made between nylons that are isomers, in the sense that they have the same

Table 1. Fusion properties of measured polyamides*

| | Peak $T_m$(K) | | | |
|---|---|---|---|---|
| Nylon | Run 1 | Run 2 | Run 3 | Run 4 |
| 1.6 | 558 | — | — | — |
| 1.8 | 549 (43) | 455 (−4) | 417 (2) | — |
| 1.10 | 539 (31.1) | 487 (−10) | 510 (11) | 496 (10) |
| 1.12 | 532 (30.6) | 488 (−18.8) | 508 (13.7) | 506 (12.7) |
| 4.3 | 548 (15.7) | — | 538 (10.2) | 502 (−1.3), 537 (12.1) |
| 5.3 | 521 (16.8) | 439 (−9.6) | 514 (9.6) | 381 (−3.2), 512 (10.8) |
| 6.3 | 514 (19.7) | 468 (−13.7) | 510 (12.9) | 475 (−1.6), 510 (12.8) |
| 8.3 | 506 (23.6) | 449 (−11.7) | 500 (11.5) | 476 (−1.8), 499 (11.3) |
| 2/5 | 548 (19.8) | — | — | — |
| 2/6 | 549 (23.0) | 430 (−7.2) | 491 (5.3) | 417 (−2.4), 484 (2.3) |
| 2/12 | 503 (24.6) | 463 (−15.8) | 496 (15.5) | 489 (14.4) |

*The data are given as peak temperatures in K (always the high-temperature endothermic peak) and, in parentheses, total heat of fusion, in kJ $mol^{-1}$, with a negative sign for the exotherms. Runs 1, 3 and 4 are heating experiments, while run 2 is a cooling experiment, all performed at 10 K/min. For nylon-1.6, the value of $T_m$ represents a lower limit.

number of amide and methylene groups, only disposed differently in the repeat unit. In this paper, the thermal properties of the polymers described are investigated and correlated with the structural features.

## 2. EXPERIMENTAL PROCEDURES

### *Samples*

The optimum conditions for crystallization were found after synthesis, by observation with an optical microscope and were substantiated by subsequent X-ray diffraction. The solvents used were 1,4-butanediol and 2-methyl-2,4-pentanediol. Whenever possible, crystal mats were made for the diffraction studies. The molecular masses of the samples were obtained through intrinsic viscosity measurements (room temperature, dichloroacetic acid, concentrations of the order of 0.5 mg/ml), using the Mark–Houwink–Sakurada (MHS) equation. Due to the lack of MHS parameters for the polymers studied, the parameters used were taken from nylon-6.6 (for series *n*.3) and from poly($\beta$-alanine) for nylon-1.6. In all cases the molecular masses range from 5000 to 10,000. As all nylons, the samples absorb water when exposed to air. All samples were kept in a vacuum desiccator filled with $P_2O_5$ before measurement. Every time the desiccator was opened, the vacuum was renewed while the desiccator was heated to 340 K. This procedure was found to be adequate for drying the nylon samples and also rid them of remaining volatile solvents. Typical weight losses after this procedure ranged from 3 to 7%.

### *Calorimetry*

For all differential scanning calorimetry (DSC), a Perkin–Elmer DSC-4 with a TADS data station was used. In order to achieve lower than room temperatures, a cryostat containing a mixture of methanol and ethylene glycol was attached. The lowest achievable temperature in the DSC was thus 270 K. In order to avoid water condensation at these temperatures, a dry box was added with a constant, low flow of dry $N_2$. The instrument was calibrated for temperature ($T$) and heat of fusion ($\Delta H$) using an indium standard ($T_m = 429.75$ K, $\Delta H_f = 3.267$ $kJmol^{-1}$). The expected accuracy is 1–2 K for $T$ and $\pm 3\%$ for $\Delta H$. A baseline was always run and subtracted to avoid the effects of the changing environment. Unless otherwise noted, heating and cooling rates were 10 K/min. Optimum sample masses were 5–10 mg but sometimes less had to be used due to scarcity of sample. All experiments were done under a flow of dry $N_2$ through the calorimeter.

## 3. RESULTS

All fusion data (temperatures and heats of fusion) are included in Table 1 for the four runs performed for each polyamide. Peak temperatures are reported, as the onset temperature is more difficult to obtain and less reproducible. In case of multiple peaks, the highest peak temperature is given in Table 1. The sequence of four runs is illustrated in Fig. 1, for nylon-2/6. In the initial run (run 1), the sample was heated at 10 K/min through fusion and left in the melt, if stable, for 2–3 min. Occasional endothermic bumps in run 1 are caused by loss of remaining water

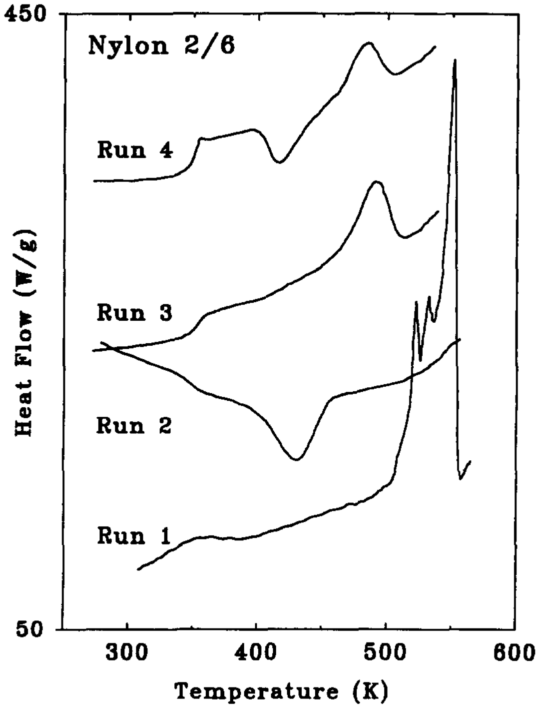

Fig. 1. Sequence of four DSC traces for initially solution-crystallized nylon-2/6. Run 1, heating of original sample; run 2, cooling; run 3, reheating after cooling; run 4, reheating after fast (320 K/min) cooling; rate in all cases was 10 K/min. Note that in Figs 1–4 the curves are displaced vertically by arbitrary amounts for clarity.

Table 2. Glass transition temperatures for the studied polyamides*

| Nylon | $T_g$(K) |
|---|---|
| 4.3 | 346 |
| 5.3 | 338 |
| 6.3 | 323 |
| 8.3 | 328 |
| 2/5 | 366 |
| 2/6 | 350 |
| 2/12 | 328 |

*The midpoint temperatures are taken from the run performed with the quenched sample, except if that was not possible because of a noisy or broad signal.

in the samples. Then cooling was performed at 10 K/min to the lowest achievable temperature to observe crystallization from the melt and check the reversibility of the transition (run 2). If decomposition appeared to have occurred, the sample was taken out of the instrument at room temperature and weighed. A second heating was done (run 3), in order to check the reproducibility of the transitions. In the case of solution-crystallized samples (run 1), the second heating (run 3) refers thus to the melt-crystallized sample. After fusion, the sample was cooled abruptly (at a nominal rate of 320 K/min) to 270 K, with a view to observe the existence of a glass transition and to see if crystallization could be suppressed. Then the final heating run (run 4) was performed. The glass transition temperatures, shown

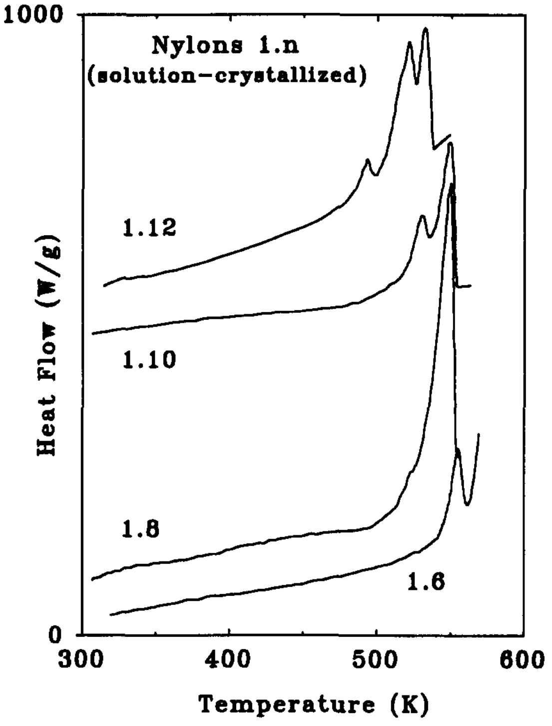

Fig. 2. DSC traces for solution-crystallized nylons-1.*n* (run 1, heating of original sample).

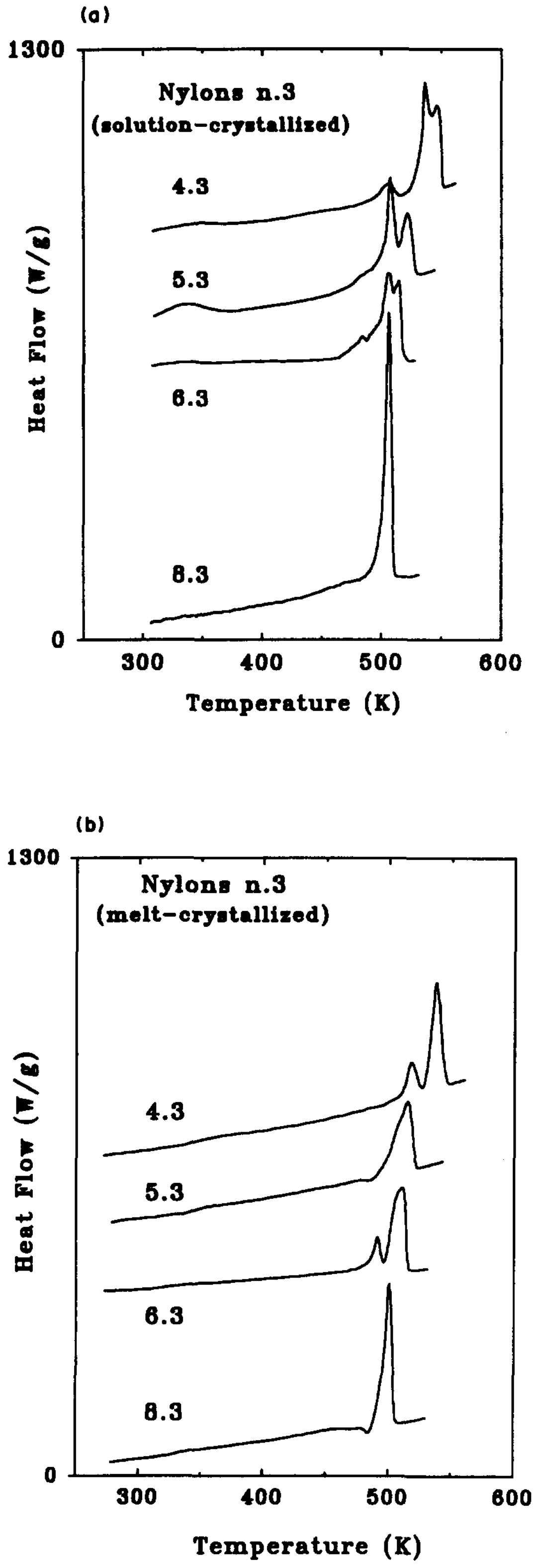

Fig. 3. DSC traces for nylons-*n*.3. (a) Solution-crystallized samples (run 1, heating of original sample). (b) Melt-crystallized samples (run 3, reheating after cooling from the melt). Note the step-like increase in the heat flow signal around 320–350 K, indicating a $T_g$.

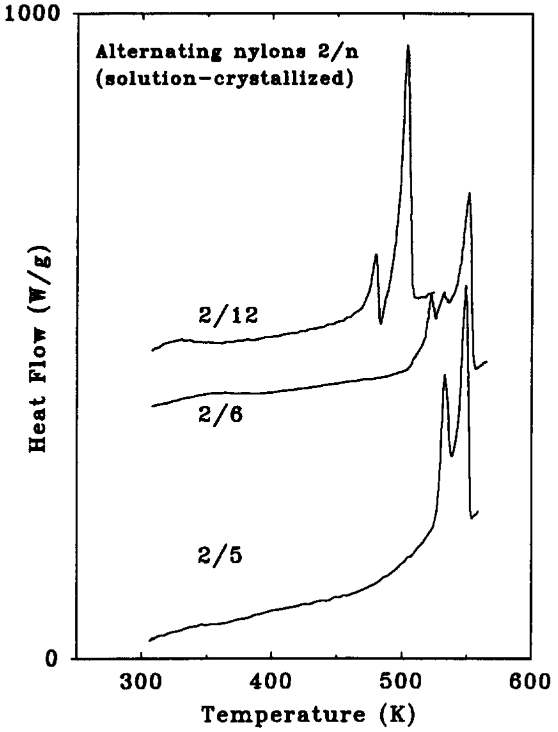

Fig. 4. DSC traces for solution-crystallized alternating copolyamides 2/*n* (run 1, heating of original sample).

in Table 2, usually come from this last run. If a $T_g$ could not be seen in run 4, the run where the $T_g$ was the most evident is included. Only qualitative values of $\Delta C_p$ could be obtained under the given experimental conditions. Selected DSC data out of a total of *ca* 150 DSC runs are summarized in Figs 1–4.

The crystallinity of a sample can be estimated from calorimetry only if a value of heat of fusion is known for 100% crystalline (equilibrium) samples ($\Delta H_f^{eq}$). These values can be found, however, in the literature only for well-characterized samples of commercial interest. For polyamides, well-established heats of fusion exist for nylon-6 [12] and nylon-6.6 [13]. For the newly synthesized samples, a procedure to estimate the heats of fusion based on the additivity of properties [14] has been used as a first approximation [15]. The group contributions to the heat of fusion of the amide and methylene groups are 2.9 and 3.8 kJ mol$^{-1}$, respectively (Table 5.5 of Ref. [14]). In the case of nylon-6.6, this procedure would give an equilibrium heat of fusion of 43.8 kJ mol$^{-1}$, lower than the accepted value of 57.8 kJ mol$^{-1}$. For our estimates, we normalized the given group contributions so that the accepted value was obtained for nylon-6.6. This gives values of 3.8 and 5.0 kJ mol$^{-1}$ for the amide and methylene groups, respectively. Using these contributions, approximate equilibrium heats of fusion for all polyamides can be calculated and are listed in Table 3. The heats of fusion of Table 1 can

Table 3. Estimated crystallinities*

|  |  | $\%w^c = \Delta H^{meas}/\Delta H_f^{eq}$ |  |  |
|---|---|---|---|---|
| Nylon | $\Delta H_f^{eq}$ (kJ mol$^{-1}$) | Solution crystallized | Melt crystallized | M/S |
| 1.6 | 33 | (>100) | — | — |
| 1.8 | 43 | (100) | (1) | — |
| 1.10 | 53 | (59) | (21) | — |
| 1.12 | 63 | 49 | 22 | 0.45 |
| 4.3 | 33 | 48 | 31 | 0.65 |
| 5.3 | 38 | 44 | 25 | 0.57 |
| 6.3 | 43 | 49 | 30 | 0.61 |
| 8.3 | 53 | 45 | 22 | 0.49 |
| 2/5 | 33 | 60 | — | — |
| 2/6 | 38 | 61 | 14 | 0.23 |
| 2/12 | 68 | 36 | 23 | 0.64 |

*The column denoted "M/S" refers to recovery of crystallinity on melt crystallization, compared to the original, solution-crystallized samples. Parentheses indicate that a decomposition contribution to the fusion endotherm makes the measured heat of fusion, and thus the calculated crystallinity, uncertain. As specified in the text, the values included in this table probably define lower limits for the crystallinity.

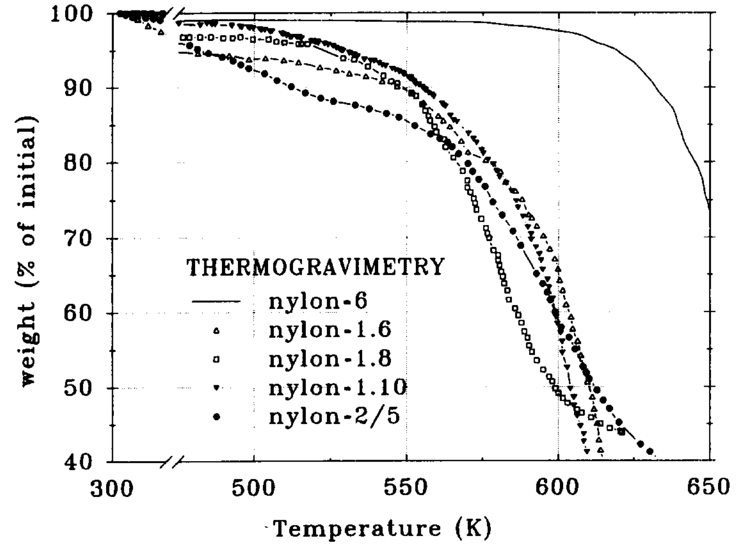

Fig. 5. Thermogravimetry for nylons-6, -1.6, -1.8, -1.10, and -2/5, given as mass loss in % as a function of temperature in K; heating rate was 10 K/min.

be converted to crystallinity values, as reported in Table 3. Given the normalization performed to obtain the $\Delta H_f^{eq}$ values, the crystallinities quoted in Table 3 probably represent lower estimates and the actual crystallinity could be up to 10% higher.

The samples that appeared to be less stable were studied by thermogravimetry in a $N_2$ atmosphere. An additional thermogravimetry experiment was done with nylon-6, a stable, commercial sample, in order to have a reference sample. The results are shown in Fig. 5. In the case of nylon-6, no mass loss is seen until 580 K, almost 100 K above fusion. About 50% of the mass is then lost within 70 K. In contrast, for nylon-1.6, -1.8, -1.10, and -2/5, mass loss begins at 520, 500, 500 and 440 K, respectively. For all four polymers, 10–20% of their initial mass is already lost at the temperature where fusion was noted in the DSC experiments. In the case of nylon-2/5, the behaviour is more complex, as the mass loss occurs in two stages, the second starting at about the temperature of fusion determined by DSC.

For a quantitative discussion of the temperature region between $T_g$ and $T_m$, heat capacities are needed [15]. They were not measured because of software limitations of the instrument. Using previous measurements and calculations of heat capacities of commercial nylons [16] and homopolypeptides [17], we computed estimates of the limiting heat capacities, of the solid crystal below $T_g$, and of the isotropic melt above $T_m$, as points of reference [18]. For the solid, the Tarasov treatment was used with estimated $\Theta_1$ values, and a $\Theta_3$ value of 100 K. The estimate of $\Theta_1$ involved taking the average of the values for nylon-6.6 [16] and polyglycine [17] for nylon-4.3, and assuming an approximate decrease of 20 K for every additional methylene group. For details of the computations, the reader is referred to the cited literature. The specific parameters used for the current calculations are shown in Table 4. The heat capacities for the molten states were estimated from earlier developed addition schemes [15] giving the heat capacity as a function of the number of methylene and amide groups. The heat flow data were then linearly adjusted so that the heat capacities at the lowest and highest temperatures matched those of the solid and the melt, respectively. We used the described analysis for nylons-*n*.3 only, as it was the only series where enough homologues were available for the discussion of trends. The match of heat capacity and heat flow could, in addition, not be applied to nylons-1.*n* and -2/5, as they decompose in the melt. An example of the calculation and the deviations found from the experimental heat flow is shown in Fig. 6 for melt-crystallized nylon-8.3 (run 3).

Table 4. Parameters used for the calculation of the heat capacity of solid nylons-*n*.3

| Nylon | $\Theta_1$(K) | $T_m^\circ$(K) | No. skeletal vibrations |
|---|---|---|---|
| 4.3 | 690 | 580 | 18 |
| 5.3 | 670 | 560 | 20 |
| 6.3 | 650 | 550 | 22 |
| 8.3 | 610 | 540 | 26 |

## 4. DISCUSSION

The data are discussed separately for the three families of nylons. The thermal properties are compared within each series, with the other two series, and with commercial nylons. The melting temperatures are given special attention and are compared with literature data on other nylons.

### *Series 1.n*

The DSC traces shown in Fig. 2 indicate thermal instability for the samples of this series. There is no well-behaved melt baseline after the fusion peak, and the transition observed on heating is not reversible or

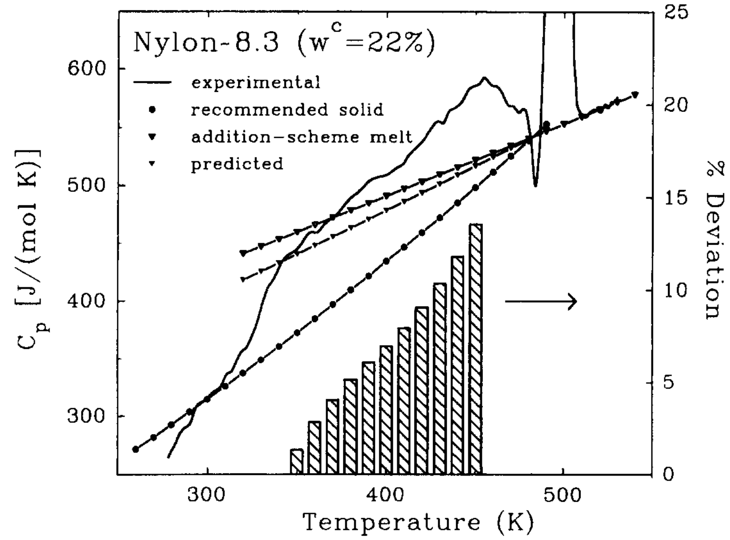

Fig. 6. Heat capacities of nylon-8.3. The solid line represents the experimental data. Filled circles give the computed vibration-only heat capacity of the rigid solid. The open triangles represent the addition-scheme heat capacities of the melt. The filled triangles refer to the expected heat capacity of a 22% crystalline sample. The bars show the deviation of experiment from prediction.

reproducible. The decomposition on fusion is also directly observed as the sample had flowed out of the Al cup of the calorimeter and has changed to a brownish colour. A substantial mass loss was measured, reaching 40% for nylon-1.6. No crystallization is seen on cooling. These decomposition effects are most evident for nylon-1.6 and become less so as the length of the paraffinic component increases. In the case of nylon-1.6, both the shape of the endothermic peak, as well as the data for two samples run (mat and powder) differ to an extent that cannot be due only to the size and quality of crystals.

The peak for nylon-1.8 is smoother but ultimately does not reach the baseline of the stable melt. On immediate cooling, some broad crystallization exotherm is noted but at temperatures much lower than the melting temperature (perhaps 10% of the molten crystals recrystallize). The newly grown crystals are poor and probably of low molecular mass. The area under the endothermic peak for nylon-1.8 from Table 1 would correspond to a 100% crystalline sample, but most likely has a large endothermic component due to decomposition.

In the case of nylon-1.10, both the mat and the powder show well-defined fusion peaks and a somewhat stable signal is reached for a few degrees in the melt. The mass loss after run 1 was 5–6% for both samples. The mat has a higher fusion peak, as expected from better formed crystals, but two populations of crystals are noted, indicating recrystallization [12]. On cooling after fusion, both samples have exothermic peaks, indicating that crystallization does occur. On subsequent heating, even after fast cooling, about 30% of the original heat of fusion can be recovered, albeit in peaks that are broader and displaced to lower temperatures. The mat has larger and better defined peaks than the powder, indicating less decomposition. A crystallinity of 59% could be estimated for the original crystals. When compared to the discussion of nylon-1.12, below, this may be a reasonable crystallinity but the amount of decomposition is too large to have any confidence in the value.

The results for nylon-1.12 indicate better thermal stability than nylon-1.10, as no mass loss was seen after the standard series of four DSC runs. The parameters of fusion decrease on thermal cycling and small exotherms appear on the DSC traces at lower temperatures, indicating perhaps poor crystallization of partially decomposed molecules. The crystallinity for the solution-crystallized sample can be estimated at 49%, reduced to less than half after melt crystallization. The cooling trace from the melt has both a primary (sharp) and a secondary (broad) crystallization exotherms as often seen for nylons [19]. We were not able to identify the glass transition for this polymer.

The thermogravimetry of Fig. 5 indicates that nylons-1.6, -1.8 and -1.10 start decomposing at about 480 K, i.e. 75, 65 and 55 K below their respective fusion peaks. The mass losses at the fusion peak temperature are 12, 10 and 6% for the three nylons. If water loss is corrected for, the mass losses become 8, 6 and 4%. The thermogravimetry results confirm, therefore, directly that thermal stability increases in the order 1.6, 1.8, 1.10, as already inferred from the DSC experiments. The more stable commercial polymer, nylon-6, had, in comparison, a mass loss that begins only 80 K above the fusion peak. In other words, the three 1.*n* nylons studied by thermogravimetry are considerably less stable than nylon-6. The thermal stabilities of the nylons-1.*n* follow the trends well-known for polyureas (repeating unit [NH—$(CH_2)_n$—NH—CO—], sometimes referred to as nylons-*n*.1) [20]. The first two even-*n* members of the polyurea series melt with decomposition above 580 K. With increasing number of methylene groups, the concentration of potential rupture points decreases, making the polymer more stable. Note also that polyglycine (nylon-2) melts with decomposition above 600 K [21]. Adding, in a sense, a second component to polyglycine to produce the nylons-1.*n* decreases the melting temperature somewhat but does not improve thermal stability.

The preceding discussion shows that the fusion data contain an endothermic decomposition contribution, especially for the low homologues. The data become thus less quantitative for the shorter methylene sequences. Only the heat of fusion of run 1 for nylon-1.12 in Table 1 may be reliable. The melting temperatures are more representative of the samples, although for nylon-1.6 the higher peak(s) may be obliterated by decomposition.

### *Series n.3*

An initial characterization of a series of nylons-*n*.3 ($n = 2$, 3, 4, 5, 6, 10, 12) has been published [4]. Compared to the 1.*n* series, the nylons-*n*.3 are more stable through their temperatures of fusion, especially since they melt at lower temperatures. Their DSC traces are illustrated in Fig. 3(a), for solution-crystallized (run 1), and Fig. 3(b) for melt-crystallized (run 3) nylons-*n*.3. Multiple melting peaks are seen for solution-crystallized samples, a very common observation in thermal studies of nylons [12]. Irradiation studies of nylons have proven conclusively that the double melting peaks are the result of perfection of the original crystals, melting of the perfected crystals and recrystallization occurring successively during heating [22]. In the absence of specific evidence for a polymorphic transition (usually from diffraction studies), reorganization on heating adequately explains the observations.

The $T_g$ values are listed in Table 2. They decrease with increasing number of methylene groups in the repeating unit, as expected [24]. Indeed, nylons-6.3 and -8.3 have $T_g$ values identical to commercial nylons, such as nylon-6.6.

Crystallization from solution and from the melt can be compared by inspection of Fig. 3(a) and (b). The high-temperature peaks of the solution-crystallized samples disappear after melt crystallization, possibly because of more reorganization during heating for the former samples. Even faster cooling quenches about 10% of the sample, as deduced from the area of the premelting exotherm for run 4 of nylons-4.3, -6.3 and -8.3, included in Table 1. The behaviour of nylon-5.3 is different in two ways: a supercooling of 82 K is noted in run 2, larger than for the other nylons-*n*.3. In addition, a large crystallization exotherm is seen above the glass transition, after fast cooling. Slower crystallization from the melt is thus observed for nylons-$n$.3 with an odd number of methylene groups in the amine segment. The conformational analysis of nylons-$n$.3 revealed that the pair of torsional angles about the isolated methylene group can either have always a positive sign, giving a right-handed threefold helix, or can alternate in sign for consecutive repeat units, giving two hydrogen-bond directions 60° apart [7]. Given the symmetry of the repeat unit, it can be suggested that the two cases correspond to $n$ odd and even, respectively. The formation of a helix would, accordingly, display slower crystallization kinetics, as seen in this work.

Figure 6 shows the heat capacity comparison for nylon-8.3. In addition to the heat capacity of the solid and the melt, the prediction for a semicrystalline sample of 22% crystallinity is also shown. Noting the approximations employed, our results indicate fair agreement of experimental and predicted heat capacities for nylons-4.3 and -6.3, and higher experimental values for nylons-5.3 and -8.3, the latter shown in Fig. 6. The higher measured heat capacity could come from reorganization on heating, i.e. melting and recrystallization of poor crystals. This interpretation would be in agreement with the fact that nylon-8.3 melts with a single sharp peak, and could be expected given the larger number of methylene groups. The large reduction of the crystallinity after melt crystallization for nylon-8.3 (see ratio M/S in Table 3) is also explained by the fact that the premelting area is not included in the integration of the fusion peak. In order to calculate the correct crystallinity, the low-temperature fusion should be included in the heat of fusion of Table 1. It can be obtained by integrating the difference of experimental minus predicted heat capacity. For nylon-8.3 it reaches 5 kJ mol$^{-1}$, equivalent to almost 40% of the measured heat of fusion. The disregard of the premelting phenomena thus explains the lower crystallinities, and lower M/S ratios seen in Table 3 for melt-crystallized nylons-5.3 and -8.3.

### *Alternating copolyamides 2/n*

The DSC data for the solution-crystallized copolymers are shown in Fig. 4. The first two samples in the series have similar $T_m$ and crystallinity, while nylon-2/12 melts lower and has a lower crystallinity. Compared to the homopolymer isomers, nylons-2/$n$ are more stable thermally than nylons-1.$n$, but less so than the nylons-$n$.3. Nylon-2/5 decomposes on fusion, as noted by the absence of exotherms on subsequent cooling, and more directly by thermogravimetry. The thermogravimetry results (Fig. 5) indicate a mass loss of 15% at the peak temperature of fusion, even higher than for nylon-1.6. This is in contrast to the DSC trace, that shows a well-behaved fusion peak, reaching a stable melt, in spite of the fact that no exotherms are obtained afterwards. The two-step shape of the thermogravimetry curve points towards the explanation: the first step, accounting for about two thirds of the mass loss, represents loss of remaining pentachlorophenol solvent. This is shown by heating the sample at 500 K for 1 hr, after which a 13% mass loss is observed, leaving the shape of the fusion peak unchanged. The rise of the signal in the DSC run of unheated sample (missing in the case of the heated sample) is the manifestation of the loss of solvent during the DSC experiment. The real mass losses, representing polymer decomposition, are thus comparable to the case of nylon-1.10. This is why a reasonable fusion peak is seen for nylon-2/5. During the second heating run, a $T_g$ can be detected at 366 K, perhaps representing lower molecular mass polymer. Provided the $T_g$ observed unambiguously for nylon-2/6, however, the value given in Table 3 for nylon-2/5 is probably a lower limit for the $T_g$ of nylon-2/5 of higher molecular mass.

Nylon-2/6 is more stable than nylon-2/5, and the sequence of four DSC traces is shown in Fig. 1. The weight loss through the four runs is 8%, including some water lost during run 1 (see endothermic bump in Fig. 1). The initial fusion peak (run 1) indicates high crystallinity while the cooling trace (run 2) reveals slow crystallization, established by the large supercooling of 119 K (see Table 1), and a $T_g$ on cooling at 349 K. The resulting melt-crystallized sample melts 58 K lower with a reduced $\Delta H_f$ (run 3). On heating, the glass transition occurs around 350 K with a sharp jump in heat capacity. Cooling in the calorimeter at 320 K/min (nominally) renders the sample 100% amorphous, as evidenced by the equality of the areas of the exotherm and endotherm above $T_g$ and by the large increase of $\Delta C_p$ at $T_g$ (see Fig. 1).

The thermal observation is thus that crystallization of nylon-2/6 from the melt is very difficult, much more so than for nylon-5.3. The difference of solution- and melt-crystallized nylon-2/6 is so vast that different crystalline forms might be involved. Indeed for the copolyamides-2/$n$, it makes a difference whether the chains are parallel or antiparallel, in contrast to nylons-1.$n$ and -$n$.3. Antiparallel chains can saturate all hydrogen-bonds with no need for twisting, giving planar chain-folded lamellae. A planar crystalline form has in fact been observed on crystallization from dichloroacetic acid, a weaker hydrogen-bonding solvent, and on epitaxial crystallization, a process that induces disposition of the chains on planar extended sheets [5]. It can be suggested that cooling from the melt gives such planar crystals with antiparallel chains, and that this form is kinetically favoured but thermodynamically disfavoured. The chains that cannot even crystallize into the poor crystals give a glass, consistent with the observation of a $T_g$ on cooling. A lower melting temperature and heat of fusion, as seen on crystallization from the melt (run 3) and from the glass (run 4) are in agreement with this picture. Crystallization from good hydrogen-bonding solvents, however, gives chains that need to twist for saturation of hydrogen-bonds. This causes the hexagonal symmetry observed experimentally [5] and higher $T_m$ and $\Delta H_f$, as noted in this work.

The solution-crystallized sample of nylon-2/12 has a lower crystallinity than all other samples in Table 3. A deep exotherm separates the two peaks on initial heating, possibly indicating recrystallization to a more stable crystal form. This is the only sample where such a statement can be made, based solely on the thermal analysis data. A single peak on cooling could correspond to crystallization of one crystal form. Indeed only a low-temperature shoulder is seen on second heating. In contrast, the trace after fast cooling is similar to the original trace, with an exotherm separating the two peaks. The melting temperature is 7 K lower than in run 3, a larger difference than for all the other samples.

### *Trends in melting temperatures*

Studies of the melting of many nylons have established two trends [23]: first, $T_m$ decreases with increasing number of methylene groups, naturally approaching ultimately the $T_m$ of polyethylene. Second, nylons-a with an odd number of carbon atoms (e.g. nylon 7) melt at higher temperatures than their even analogues. For nylons-*a.b*, the trend is a decrease of $T_m$ in the order even–even > odd–even > even–odd > odd–odd. In most plots of $T_m$ of nylon vs number of methylene groups, a low-$T_m$ and a high-$T_m$ line can thus be drawn.

The melting temperatures quoted [24] for nylons-1.6 and -1.10 are 579 and 541 K, respectively. The comparison with the new data in Table 1 is favourable for nylon-1.10, but the value for nylon-1.6 is 21 K lower, perhaps due to earlier decomposition for our sample. The data included in Table 1 for nylons-1.*n* show the expected trends within the series and when comparing nylons-1.10 and -1.12 to nylons with the same adipoyl moiety (e.g. with nylons-*n*.10 and -*n*.12, respectively). For nylon -1.8, a comparison is more difficult as nylon-4.8 is the first known member of the series. Overall the nylons-1.*n* melt at higher temperatures than their isomers (i.e. 1.6 compared to 4.3 and 2/5, 1.8 to 6.3, and 1.10 to 8.3), as has been discussed in the past [3] and explained by the presence of "secondary hydrogen-bonds". It is now known that all the hydrogen-bonds are formed and are equivalent. The high $T_m$ should be correlated with the special conformation about the isolated methylene group but more work with model compounds is needed to elucidate this point. In that respect, note that $\gamma$-nylon-6 melts higher than $\alpha$-nylon-6 [24], and that the hydrogen-bonds in nylon-6 are stronger for the $\gamma$ form than for the $\alpha$ form [25].

The melting temperatures of nylons-*n*.3 from Table 1 are in good agreement with the work of Paiaro *et al.* [4]. Another earlier value for the melting of nylon-5.3 is 57 K lower than given in Table 1 [24], and is most likely in error. Comparing nylons-4.3, -6.3 and -8.3 with other nylons having the same amine segment (e.g. with nylons -4.*n*, -6.*n* and -8.*n*, respectively) shows they are in line with the literature data [23, 24], being on the low-$T_m$ line of the odd–even alternation.

Nylon-2/6 melts 16 K higher than its homopolyamide isomer, nylon-4, most likely because of the three-dimensional nature of its hydrogen-bond network compared to the sheet structure found in $\alpha$-nylon-4. The lower $T_m$ of nylon-2/12 is a result of the larger number of methylene groups. Note that nylon-2/12 melts at almost the same temperature as its isomer nylon-7. As expected, the contribution of the special amide conformation to the melting temperatures becomes less apparent for longer methylene sequences. Nylon-2/6 melts higher than the corresponding nylon-5.3, while 2/5 melts at the same temperature as 4.3. This difference is again most likely related to the different crystal structures, as nylon-4.3 appears more hexagonal than 5.3, and 2/5 is trigonal whereas 2/6 is hexagonal [10].

The high melting temperature noted for solution-crystallized nylons-2/5 and -2/6 are characteristic of *isodimorphism* phenomena, studied extensively for random and alternating copolymers [26]. The incorporation of a glycine repeat unit in a nylon lattice (or vice versa) is not felt as the introduction of a defect, instead a new structure is formed, intermediate (and with an intermediate $T_m$) between polyglycine and nylon-5 or -6. In fact, regular nylon copolymers should rather be viewed as homopolymers with a larger repeat unit.

## 5. CONCLUSIONS

(a) New data on $T_m$ and $T_g$ are reported for nylons-1.*n*, -*n*.3 and -2/*n*. The data fit existing literature data on other homologous nylons: both $T_g$ and $T_m$ decrease with increasing number of methylene groups, while for $T_m$ an odd–even effect is seen.

(b) Nylons-1.*n* melt higher than corresponding nylons-2/*n* and -*n*.3 with equal number of methylene and amide groups, because of different organization of the hydrogen-bonds.

(c) For equal number of methylene and amide groups, thermal stability depends on chemical structure, decreasing in the order $COCH_2CO >$ $COCH_2NH > NHCH_2NH$. Stability increases for longer methylene sequences.

(d) Nylon-2/6 crystallizes to high perfection from solution but much less so from the melt, perhaps due to the precise chain disposition required for crystallization in this highly ordered polymer.

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