Heat capacities of solid polyamides

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Heat capacities of 10 polyamides were analysed by using an approximate group vibration spectrum and fitting the skeletal heat capacity to a Tarasov function. New data were measured between 230 and 320 K for nylon 11, nylon 12, nylon 6.9, nylon 6.10 and nylon 6.12 by differential scanning calorimetry. A new method to account for the difference between C_p and C_v was tested. For all synthetic nylons good agreement could be obtained between experiment and calculation (nylon 6, nylon 11, nylon 12, nylon 6.6, nylon 6.9, nylon 6.10, nylon 6.12 and polymethacrylamide). Two poly(amino acids), (polyglycine and polyalanine) were also analysed and found to have larger discrepancies at higher temperatures, perhaps due to experimental error. The θ temperatures are similar for most polyamides and extrapolate to polyethylene for larger numbers of CH_2 groups.

(Keywords: crystalline; heat capacity; nylon; polyalanine; polyamide; polyglycine; polymethacrylamide; semicrystalline; vibrational spectra)

INTRODUCTION

This paper concludes the series of publications that led to the analysis of heat capacities of about 100 solid polymers[1-11]. The heat capacities were calculated based on approximate vibrational spectra and fitted at two points to experimental results collected in the ATHAS data bank[12]. The discrepancy between the experiments, measured often only over a limited temperature range, and the complete calculations, was less than $\pm 5\%$ in most cases. The calculated heat capacities for the solid state have been useful in analysing the experimental heat capacities of semicrystalline samples collected in the ATHAS data bank[12]. Between T_g and T_m this analysis allows us to establish definitive baselines in calorimetry curves and, therefore, to account for all effects additional to the vibrational contribution of the solid to the heat capacity. The discovery of a 'rigid amorphous' fraction in some polymers[13] as well as the classification of some mesophase transitions (condis phase transitions)[14,15] previously not understood thermodynamically were the most substantial advances based on these analyses.

Polymers containing the amide group are important for several reasons. Synthetic polyamides (nylons) are one of the largest families of thermoplastics used, and polyglycine (nylon 2) is the simplest polyamino acid and a building block of most of the biologically important proteins. On substitution, all other acids can be derived from glycine. In addition to the direct interest of these polymers, there is considerable general interest in their physical structure. The hydrogen bonding dominates the secondary structure by introduction of higher force constants and a large degree of coupling between chains compared to the previously analysed polymers, which showed only London dispersion and dipole forces. This effect of hydrogen bonding is expected to be most pronounced for polyglycine.

An effort was also made to check the validity of two assumptions that were previously used extensively in our calculations. First was the transferability of group vibration frequencies. This was done by obtaining results with approximate constructed dispersion curves and comparing them to published full dispersion curves. Second was the use of A_0 in the Nernst–Lindemann expression for the conversion of heat capacity at constant pressure (C_p) to heat capacity at constant volume (C_v) and vice versa as a third adjustable parameter was evaluated (see equations (1) and (2), below). An adjusted A_0 was obtained and compared with the thermodynamically derived A_0 based on experimental compressibility and expansivity.

COMPUTATION METHOD

The method used in our calculations has been described previously in detail[16,17]. The heat capacity is calculated from 0 to 1000 K based on vibrational data and limited experimental heat capacity data (two-point fit). This large temperature range goes beyond the stability range of crystal and glass and even beyond chemical stability. It is chosen to provide information for addition scheme applications where groups are included in high temperature polymers. Also, the knowledge of instantaneous properties at high degrees of superheating is needed for the analysis of laser damage and analogous effects.

The vibrational spectrum is somewhat arbitrarily separated into group and skeletal vibrations. The group vibrations are usually coupled to a limited degree only and their normal-mode distribution can be approximated by single frequencies and box distributions covering narrow ranges of frequencies. They are largely independent of the physical and chemical environment. A catalogue of characteristic group vibration frequencies for specific groups of atoms has been established. The strongly coupled skeletal vibrations must, in contrast, be approximated by a vibration spectrum starting at zero

frequency, consisting of a quadratic low frequency and a constant higher frequency distribution (Tarasov equation). The two parameters θ_3 and θ_1 ($\theta = h\nu/k$, where ν is the frequency in Hz and h and k are Planck's and Boltzmann's constants) describe the upper limits of the quadratic, largely intermolecular, and the constant, largely intramolecular, frequencies[18]. The complete spectrum is then inverted to heat capacity at constant volume, C_v, with the help of the Einstein function[16,17].

The final step in the computation is the C_p to C_v conversion. In the absence of experimental data on compressibility and expansivity this was done in the past using the empirical Nernst–Lindemann equation:

$$C_p - C_v = A_0 C_p^2 T / T_m^\circ \qquad (1)$$

where A_0 was found[19] to be approximately universal per mole of heavy atoms in the repeating unit ($5.11 \pm 2.41) \times 10^{-3}$ K mol J^{-1}. Although this equation was proved to be satisfactory, it gave unrealistically high heat capacities at high temperatures (above the equilibrium melting point). Improvements of the method were recently made possible using a temperature-dependent A_0[20]. The equation currently being used,

$$C_p - C_v = 3RA_{0,\text{new}} C_p^2 T / (C_v T_m^\circ) \qquad (2)$$

takes advantage of the fact that information on the number of excited vibrators at each temperature is available through the knowledge of the heat capacity itself. The simplifying assumption in the old method that the excited vibrators are approximated by three times the number of heavy atoms is thus improved upon. The new method significantly improves the high temperature C_p calculated. The calculations of heat capacities and their deviations from the experimentally measured heat capacities were done in all cases, both with the old[19] and

the new[20] methods. For all the recommended data in *Table 3*, below, only the new computation method was used. Note, for the comparison, that old A_0 values are computed per mole of heavy atom and must be multiplied by the number of heavy atoms for comparison with the new A_0 values, which are calculated per mole of repeating unit.

Detailed vibrational spectra are not available for most nylons, but exist for polyglycine. The approximate group vibrational spectra were thus constructed from the well known vibration frequencies of polyethylene[21] and polyglycine[22]. The crystal form I of polyglycine was chosen because it has a planar zigzag conformation like the nylons. *Table 1* gives the list of the group vibrations needed for the construction of all group vibration spectra of aliphatic nylons of the type nylon a with $a-1$ methylene units in its repeating unit. For a nylon of the type nylon $a.b$ (IUPAC) the spectrum is constructed in an analogous manner (considering $a+b-2$ methylene units and two amide groups), since it is known that the polarity of the chain causes no significant change in the group vibrations. For nylon 6 and nylon 6.6, full vibrational distribution curves are available for the isolated chain[23]. The group frequencies for nylon 6 are listed in *Table 2*. A comparison with the approximate spectra derived from *Table 1* shows that the agreement, even on the frequency level, is surprisingly good. Due to the different environment of each group in the crystal, the CH_2– modes of *Table 2* are split into five slightly differing frequencies. The approximate frequencies of *Table 1* always fall into the middle of the five modes. In the case of approximation by box distributions, each box of *Table 1* practically covers the same frequency range as given in *Table 2*. Converted to heat capacity, both frequency sets give practically indistinguishable results. The overall r.m.s. discrepancy between the two sets, when

Table 1 Group vibration frequencies in kelvin ($h\nu/k$) of a nylon with repeating unit $-[(CH_2)_a-CO-NH-]$

	Approximate vibrational modes	Number of vibrators	Frequency
CO–NH– (7)	C=O stretching (amide I)	1.00	2370–2428
	N–H in-plane bending + C–N stretching (amide II)	1.00	2181–2193
	N–H in-plane bending + C–M stretching + N–C stretching (amide III)	1.00	1862–1875
	O=C–N in-plane bending (amide IV)	0.32	863–885
		0.68	885–1061
	N–H out-of-plane bending (amide V)	1.00	1009
	C=O out-of-plane bending (amide VI)	1.00	886
	N–H stretch	1.00	4764
CH$_2$– ($6 \times a$)	Asymmetric stretching	1.00	4148
	Symmetric stretching	1.00	4098
	Bending	1.00	2075
	Wagging	0.35	1977
		0.65	1698–1977
	Twisting	0.52	1874
		0.48	1690–1874
	Rocking	0.04	1494
		0.59	1038–1494
		0.37	1079
CH$_2$–CH$_2$– ($a-1$)	C–C stretching	0.34	1378–1638
		0.31	1525
		0.35	1378–1525
CO–CH$_2$– (1)	C–C stretching	0.37	1392–1417
		0.63	1258–1392
NH–CH$_2$– (1)	N–C stretching	0.28	1583–1600
		0.46	1482–1583
		0.26	1459–1482

Table 2 List of group frequencies of nylon 6[a]

Einstein terms		Box terms		
N	v (K)	N	v_L (K)	v_U (K)
1.00	2365.0	1.00	2128.0	2132.0
1.00	2253.0	1.00	2119.0	2125.0
1.00	2043.0	1.00	2101.0	2104.0
0.50	1975.0	1.00	2076.0	2081.0
0.30	1055.0	0.50	1988.0	1991.0
1.00	1878.0	0.50	1991.0	1994.0
1.00	1876.0	0.15	1970.0	1973.0
1.00	1843.0	0.35	1973.0	1975.0
1.00	1001.0	0.15	1961.0	1965.0
1.00	836.0	0.70	1938.0	1961.0
5.00	4148.0	0.15	1934.0	1938.0
5.00	4098.0	0.15	1866.0	1870.0
0.10	4764.0	0.65	1870.0	1893.0
		0.20	1893.0	1896.0
		0.15	1822.0	1827.0
		0.70	1799.0	1822.0
		0.15	1794.0	1799.0
		0.20	1731.0	1734.0
		0.40	1734.0	1742.0
		0.40	1742.0	1750.0
		0.20	1620.0	1623.0
		0.80	1591.0	1620.0
		0.25	1555.0	1558.0
		0.65	1558.0	1575.0
		0.10	1575.0	1578.0
		1.00	1531.0	1534.0
		0.15	1505.0	1508.0
		0.70	1482.0	1505.0
		0.15	1476.0	1482.0
		0.45	1453.0	1458.0
		0.55	1458.0	1466.0
		0.15	1342.0	1347.0
		0.75	1347.0	1384.0
		0.10	1384.0	1387.0
		0.70	1055.0	1062.0
		1.00	1780.0	1783.0
		1.00	1683.0	1689.0
		1.00	1581.0	1584.0
		1.00	1368.0	1374.0
		1.00	1211.0	1214.0
		1.00	1102.0	1104.0
		1.00	1046.0	1048.0

[a] Deduced from Reference 23 by selecting isolated, narrow frequency distributions as Einstein terms and breaking broader frequency distributions into frequency ranges of constant numbers of vibrators (box distributions)

included in a full heat capacity computation, was $0.32 \pm 0.50\%$ (70–310 K). Similar results are obtained for nylon 6.6. For consistency with previous calculations and to stress the predictive ability, the approximate spectra were used for all polyamides, particularly since it is more difficult to transfer the split modes from nylon 6 and nylon 6.6 to other nylons.

Due to the relocation of ATHAS from Rensselaer Polytechnic Institute (RPI) to the University of Tennessee in Knoxville (UT), all our programs that were previously running on the mainframe IBM 3081 at RPI were transferred to the VAXcluster at UT. Except for minor programming differences, the main change was the use of a new algorithm for the numerical integration of the Debye functions. Instead of the subroutine D01AGF from the NAG library, the function D01AHF from the same library is now used*. The previous subroutine used the Clenshaw–Curtis self-adaptive integration method.

A comparison of the various available integration methods was made in Reference 16. The new subroutine, based on the Patterson method, is considered by NAG to be more universal and efficient. The new integration method contains many refinements compared to versions previously discussed[16,17]. A family of interlacing high precision rules using 1, 3, 7, 15, 31, 63, 127 and 255 nodes is applied in sequence to the integrand. If no two successive rules can be found that agree within the required relative accuracy, the range is subdivided and the process of applying the rules and subdividing is repeated until the chosen accuracy is achieved for all sub-intervals. The programs using the new method seem to be working faster on the VAX than the old method on the IBM 3081. Since the VAX is expected to be slower, it should be deduced that the new method is now preferable. Results obtained with both methods, using a program inverting heat capacity to θ temperatures, show a difference only in the fifth decimal place for C_v at higher temperatures and no differences for θ temperature values that are recorded to two decimal places.

EXPERIMENTAL

All measurements were made on a Perkin–Elmer DSC-2. Mechanical refrigeration was used to cool to 220 K, and both temperature and heat of fusion were calibrated using standard materials (tin, indium, p-nitrotoluene and n-dodecane). Heat capacity was calculated after subtraction of an empty-pans run and a comparison with measurements on sapphire were repeated for every set of measurements.

The samples used were purchased from Scientific Polymer Products Inc., NY, USA. Before measurement, they were heated 10–15 K above their melting point and kept there for 5 min to erase the thermal history. Then the samples were cooled to 220 K at 2.5 K min^{-1} for crystallization, and measurements were made by heating at 10 K min^{-1}. From the measured heats of fusion the crystallinity of the samples was estimated to range between 30 and 40%. The experimental results on heat capacities are listed in *Table 4* and are currently being quantitatively analysed to give information about the glass and melting transitions[24]. The data represent a single run that, when repeated, yielded results within 2% of the set used.

RESULTS

Nylon 6 (polycaprolactam)

From compressibility and expansivity data of nylon 6 at 293 K A_0 was calculated to be $0.001\,378 \text{ K mol J}^{-1}$ per mole of nylon 6, using the old method[19]. With experimental heat capacities from 70 to 240 K (data bank[12]) $\theta_1 = 544.2 \pm 3.5 \text{ K}$ can be determined. Taking into account the low temperature data, $\theta_3 = 67.4 \text{ K}$ is determined at 100 K. Using these values and the 14 skeletal modes, the calculated C_p agrees with the experimental data with an average and r.m.s. error of $-0.04 \pm 0.91\%$ (70–310 K)†. The error appears to be fluctuating randomly from 0 to 270 K and then increases gradually as T_g (313 K) is approached.

If one repeats the computation with the universal value

of A_0, 0.000 639 K mol J^{-1}, one can again get θ temperatures ($\theta_1 = 522$ K and $\theta_3 = 133$ K). The error of the computed C_p is in this case higher, still remaining below 5%. If one assumes that the C_p–C_v difference is due totally to a wrong value of A_0, one can adjust the universal A_0, using it as a third adjustable parameter. The values reached then are $A_0 = 0.001 233 \pm 0.000 083$ K mol J^{-1}, $\theta_1 = 535.7 \pm 8.5$ K and $\theta_3 = 94.2 \pm 21.8$ K. The final error in this case is naturally smaller, $-0.34 \pm 0.56\%$ (70–310 K). In all three calculations θ_3 is the most affected since the experimental data reach only barely to the low temperatures needed to assess θ_3. The best fit for θ_3 would be expected in the 10–30 K temperature range.

Using the full vibrational spectrum (*Table 2*)[23] and the θ temperatures just determined, the error is $-0.36 \pm 0.66\%$ over the same temperature range. Basing the complete analysis on the group vibrations of *Table 2* one gets $\theta_1 = 543.2 \pm 9.5$ K from 70 to 290 K and $\theta_3 = 78.4 \pm 24.7$ K from 90 to 100 K. The final error of this set is $-0.34 \pm 0.68\%$. Having proved that the change in θ temperatures and the improvement of the error when using the full vibrational spectrum are not significant, we can safely ignore the full spectrum and continue using the constructed approximate spectrum for all nylons. The final recommended data are obtained with the new C_p–C_v conversion method and the θ temperatures listed in *Table 3* ($A_0 = 0.008 01$ K mol J^{-1}). The final error is $1.68 \pm 0.60\%$ (70–310 K). The heat capacities (calculated and experimental) are shown in *Figure 1* and the error in *Figure 2*. The error, although larger than that obtained with the old method, is still below the experimental uncertainty. In addition, C_p is predicted to reasonable values up to 660 K, compared to 450 K with the old method.

Nylon 11 (polyundecanoamide)

The heat capacity for nylon 11 was measured in this laboratory as described in the experimental section and
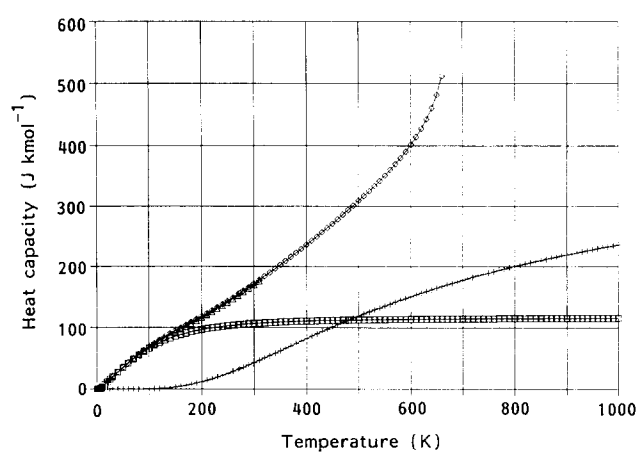
Figure 1 Heat capacity of nylon 6: □, skeletal vibration contribution; +, group vibration contribution; ◇, calculated C_p; △, experimental C_p
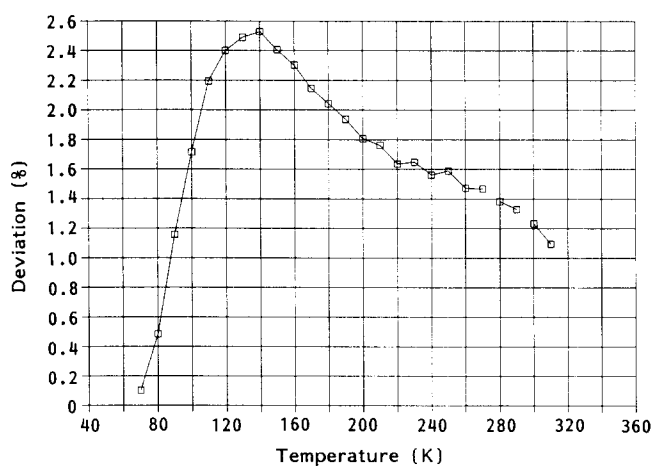
Figure 2 Heat capacity difference $C_{p,calc} - C_{p,exp}$ for nylon 6 as a function of temperature

Table 3 Recommended parameters for polyamide heat capacities

Polymer	Number of skeletal modes	T_m°	θ_1 (K)[a]	θ_3 (K)[a]	Error average ± r.m.s. (%)[b]	Experimental C_p data range (K)
Nylon 6	14	533	544.2 ± 3.5 (70–240 K)	(67.4) (at 100 K)	1.68 ± 0.60 (70–310 K)	70–313 (T_g)
Nylon 11	24	493	(419.8 ± 10.1) (230–300 K)	(67.4) (from nylon 6)	−2.64 ± 1.75 (203–300 K)	230–321 (T_g)
Nylon 12	26	500	455.3 ± 18.5 (230–300K)	(67.4) (from nylon 6)	−0.68 ± 0.81 (230–300 K)	230–310 (T_g)
Nylon 6.6	28	574	613.7 ± 8.1 (230–280 K)	84.2 ± 0.6 (230–280 K)	1.12 ± 0.27 (230–320 K)	0.3–4.0 and 230–323 (T_g)
Nylon 6.9	34	500	578.5 ± 40.0 (230–280 K)	(84.2) (from nylon 6.6)	1.20 ± 1.00 (230–310 K)	230–332 (T_g)
Nyloh 6.10	36	506	542.8 ± 24.6 (230–280 K)	(84.2) (from nylon 6.6)	0.60 ± 0.18 (230–300 K)	230–321 (T_g)
Nylon 6.12	40	520	(533.2 ± 30.3) (230–310 K)	(84.2) (from nylon 6.6)	−0.42 ± 0.65 (230–310 K)	230–319 (T_g)
Polymethacrylamide	11	590	580.8 ± 20.8 (70–260 K)	142.6 ± 19.3 (60–90 K)	0.20 ± 1.62 (60–300 K)	60–300
Polyglycine I	6	555	(528.1)	(96.4)	–	150–370
Polyglycine II	6	555	528.1 ± 34.9 (12–20 K)	96.4 ± 3.3 (12–20 K)	−1.78 ± 4.01 (1.6–20 K)	1.4–20 and 150–370
α-Polyalanine	9	573	626.6 ± 45.6 (60–160 K)	61.9 ± 2.4 (60–160 K)	2.00 ± 5.31 (60–160 K)	1.6–300
β-Polyalanine	9	573	632.7 ± 60.3 (40–110 K)	72.0 ± 3.5 (40–110 K)	1.43 ± 8.84 (40–110 K)	1.6–300

[a] Values in parentheses give the temperature range used for fitting the θ temperature

[b] Values in parentheses give the temperature range of comparison with the experiment in 10 K steps (more frequent for temperatures below 30 K)

Table 4 Experimental heat capacity $(J K^{-1} mol^{-1})$

T (K)	Nylon 11	Nylon 12	Nylon 6.9	Nylon 6.10	Nylon 6.12
230	238.21	254.02	321.53	340.87	381.78
240	249.26	264.10	332.44	354.28	395.57
250	259.99	273.91	343.66	368.18	410.52
260	271.30	283.95	355.33	381.97	425.77
270	282.66	294.77	368.40	395.52	439.95
280	294.13	305.98	381.85	409.72	458.63
290	306.97	318.56	395.27	426.59	475.42
300	320.91	334.49	408.08	441.82	494.48
310	342.10	358.69	425.33	463.60	520.21
320	371.22	383.52	454.51	497.00	553.29

the data are included in *Table 4*. Initially, for the C_p to C_v conversion, the old experimental A_0 for nylon 6 was used, corrected for the appropriate number of heavy atoms, $0.000\,848\ K\,mol\,J^{-1}$. Using this parameter one obtains $\theta_1 = 401.4 K$ at $230 K$. With $\theta_1 = 401.4 K$ and $\theta_3 = 67.4 K$ (guessed at, based on the value from nylon 6) the error is -1.91 ± 0.75 $(230-300 K)$. The fact that θ_1 decreased continuously above $230 K$ led to an effort to adjust A_0. After doing this we finally obtained $0.000\,946 \pm 0.000\,009\ K\,mol\,J^{-1}$, $\theta_1 = 419.8 \pm 10.1\ K$ and an error of -0.43 ± 0.34 $(230-300 K)$. To assess the merits of the A_0 adjustments mentioned before, a recalculation was done starting from the universal value of A_0. The first attempt to calculate θ_1 did not give any reasonable θ_1 values and gave skeletal C_v higher than the classical Dulong–Petit limit, an obviously impossible result. By adjusting the A_0 values twice we get $A_0 = 0.000\,918 \pm 0.000\,008\ K\,mol\,J^{-1}$, a value very close to the previous fitted value. With these data one determines $\theta_1 = 397.5 \pm 13.4 K$ and, by using $\theta_3 = 67.4 K$, the error in heat capacity is also small, -0.38 ± 0.49. Obviously, compressibility, expansivity and low temperature heat capacity data are needed to improve the C_p assessment.

If we turn now to the new C_p–C_v conversion method[20] and use the universal A_0 value, $0.0039\ K\,mol\,J^{-1}$, with $\theta_1 = 419.8 K$ and $\theta_3 = 67.4 K$, the error is also unacceptable, $-9.56 \pm 2.46\%$, decreasing continuously from 230 to 300 K. This clearly indicates that it is better to choose the experiment-fitted value of A_0 for nylon 6[20], $0.008\,01\ K\,mol\,J^{-1}$. In fact, this decreases the discrepancy from the experiment to $-2.64 \pm 1.75\%$ $(230-300 K)$. The final recommended parameters for the C_p calculation using these data are listed in *Table 3*.

Nylon 12 (polylauryllactam)

Experimental heat capacity data for nylon 12 were measured with the method described in the experimental part and the data are listed in *Table 4*. Initially, for the conversion of C_v to C_p the value of A_0 from nylon 6[19] was used, adjusted for 14 heavy atoms, $0.000\,787\ K\,mol\,J^{-1}$. With $\theta_1 = 455.3 \pm 18.5 K$ (fitted from 230–300 K to the experiment) and $\theta_3 = 67.4 K$ (taken from nylon 6), the error was $-0.52 \pm 0.54\%$ $(230-300 K)$. The influence of θ_3 on the higher temperature results is only important for temperatures $>2\theta_3$ and cannot be determined without low temperature heat capacity data. From our experience with many other polymers[1-11], we observed, however, that molecules of similar chemical structure usually have very similar θ_3 values. This observation is the basis for the first guess that θ_3 for other nylons will be similar to the experiment-based value for nylon 6.

With the new C_p–C_v conversion method using $\theta_1 =$

$455.3 K$, $\theta_3 = 67.4 K$ and the universal A_0 value, the error is again unacceptably high, -7.62 ± 1.53 $(230-300 K)$. As in the case of nylon 11, this error indicates the need to use the experiment-fitted value for nylon 6, $0.008\,01\ K\,mol\,J^{-1}$. With these parameters, the final error is small, $-0.68 \pm 0.81\%$ $(230-300 K)$. The final recommended parameters are shown in *Table 3*.

Nylon 6.6 [poly(hexamethylene adipamide)]

For nylon 6.6 very low temperature experimental C_p data $(0.3-4.0 K)$ as well as higher temperature data $(230 K- T_g)$ exist in the ATHAS data bank[12]. The low temperature heat capacity data can be fitted to a Debye temperature and this calculation gives $\theta_D = 163.3 \pm 4.2 K$ from 0.5 to 4.0 K when 28 skeletal modes are used. Then, based on the relation $\theta_D = (\theta_1\theta_3^2)^{1/3}$ (References 16, 17), one can determine $\theta_1 = 613.7 \pm 8.1 K$ and $\theta_3 = 84.2 \pm 0.6 K$ by comparison with experiments from 230 to 280 K. Using the old method of C_p–C_v conversion and the experiment fit for A_0 for nylon 6, the discrepancy between measured and computed C_p is $0.55 \pm 1.13\%$ $(230-300 K)$.

If there had been no low temperature data, one could have determined θ_1 from the high temperature data and then, assuming a reasonable θ_3, calculated the difference from the experiment. In fact, θ_1 obtained by this method is only slightly different $(618.3 \pm 8.2 K)$. The value of θ_3 strengthens also the assumed values for the nylons for which no low temperature heat capacity data are available.

Using the full vibrational data[23] and the same θ temperatures, the error for the same temperature region is $-1.05 \pm 0.54\%$, also well within acceptable accuracy.

Turning again to the new C_p–C_v conversion method and using the θ temperatures already determined and the experiment fit for A_0 for nylon 6[20], the error of the calculated C_p is $1.14 \pm 0.28\%$ $(230-320 K)$. The final recommended parameters are included in *Table 3*. *Figure 3* shows the heat capacities of nylon 6.6 (experimental and calculated) and *Figure 4* the error of the calculated C_p compared with the experimental C_p.

Nylon 6.9 [poly(hexamethylene nonanediamide)]

The heat capacity of nylon 6.9 was newly measured as described in the experimental section. With the old C_p–C_v conversion method and the A_0 value from nylon 6 adjusted for the different number of heavy atoms, $\theta_1 = 578.5 \pm 40.0 K$ was determined from 230 to 280 K. Using for θ_3 the value obtained from nylon 6.6, $84.2 K$,
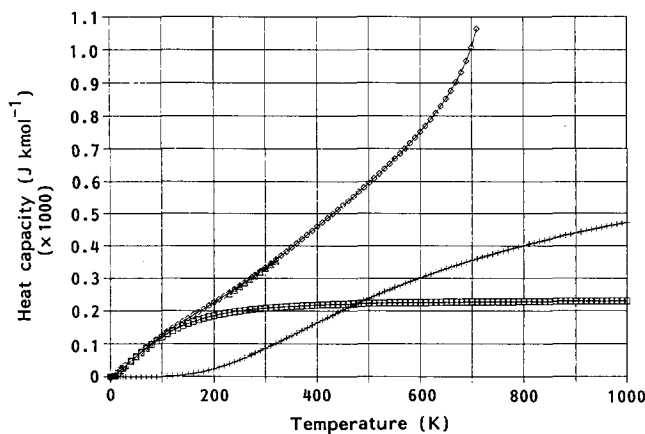

Figure 3 Heat capacity of nylon 6.6: □, skeletal vibration contribution; +, group vibration contribution; ◇, calculated C_p; △, experimental C_p
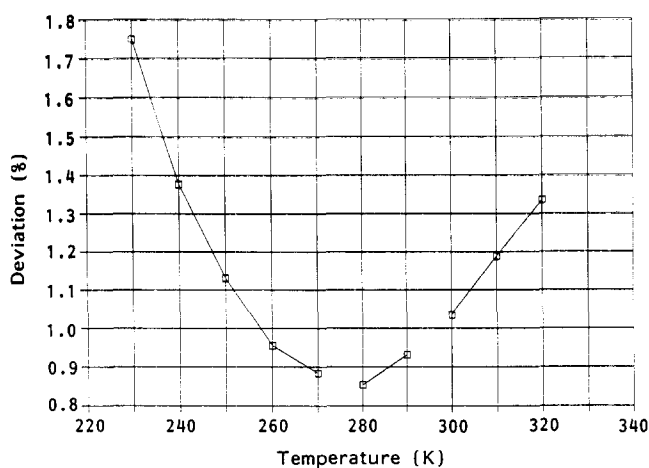
Figure 4 Heat capacity difference $C_{p,calc} - C_{p,exp}$ for nylon 6.6 as a function of temperature

the error was $0.66 \pm 2.19\%$ (230–310 K). The large spread of the θ_1 value reflected itself in the larger scatter of the error about its average value.

The new method of C_p–C_v conversion[20] with the same θ temperatures and the A_0 value given in the literature for nylon 6 gave an error of $1.20 \pm 1.00\%$ (230–310 K).

The recommended parameters are listed in *Table 3* and the experimental data in *Table 4*.

Nylon 6.10 [poly(hexamethylene sebacamide)]

The heat capacity of nylon 6.10 was newly measured as described in the experimental part. With the old C_p–C_v conversion method and the A_0 value from nylon 6 adjusted for the different number of heavy atoms, $\theta_1 = 542.8 \pm 24.6$ K was determined with data from 230 to 280 K. Using for θ_3 the value determined for nylon 6.6, 84.2 K, the error was $0.01 \pm 1.17\%$ (230–300 K).

With the new method and the same parameters as before, the error is $0.60 \pm 0.18\%$ (230–300 K).

The final, recommended parameters are listed in *Table 3* and the experimental data in *Table 4*.

Nylon 6.12 [poly(hexamethylene dodecanediamide)]

Experimental C_p data have already been discussed in the ATHAS data bank[12]. These data had been measured previously in this laboratory and were preliminary, unpublished results. They were fitted to the Tarasov equation from 230 to 280 K and yielded $\theta_1 = 617.5 \pm 16.5$ K. Using $\theta_3 = 84.2$ K taken from nylon 6.6 and applying the new method for the C_p–C_v conversion with A_0 derived from nylon 6, the error of the calculated data over the data bank values is $1.00 \pm 0.35\%$ (230–310 K). The measurements on nylon 6.12 were repeated in this research as outlined in the experimental section. The new data are consistently higher. The average and standard deviations between the two sets are $3.81 \pm 0.77\%$ (230–300 K), just outside the typical experimental error for different polymer samples[12]. Fitting the new data to the Tarasov equation from 230 to 310 K, $\theta_1 = 533.2 \pm 30.3$ K is obtained. With $\theta_3 = 84.2$ K and the same C_p–C_v conversion as before, the error is $-0.42 \pm 0.65\%$ (230–310 K).

To recommend a set of improved data, we compared all θ_1 values determined for $a.b$ nylons. Most confidence is placed on the value for nylon 6.6, since in that case low as well as high temperature measurements were

made. The θ_1 value obtained from the present experiments on nylon 6.12 fits the trend of θ_1 better. On this basis alone the new data were chosen as recommended experimental heat capacity and are listed in *Table 4*. The full set of recommended parameters is listed in *Table 3*.

Polymethacrylamide

In polymethacrylamide the amide group is located in the side chain. Trying to approximate its group vibrations, we used some of the frequencies of β-polyalanine (with an extended chain structure) described below, some of the frequencies known from propionamide[25] and vibrations from the frequency spectrum of polypropylene[26]. The group vibrations so derived are listed in *Table 5*. In selecting the number of skeletal vibrations as 11, the analysis of poly(methacrylic acid)[9]

Table 5 Group frequencies of polymethacrylamide (28)[a]

Assignment	Number of vibrators	Frequency (K)
From polypropylene (17)		
CH$_3$ asymm. stretching	1.00	4262
CH$_3$ asymm. stretching	1.00	4259
CH$_2$ asymm. stretching	1.00	4213
CH$_3$ symm. stretching	1.00	4147
CH$_2$ symm. stretching	1.00	4085
CH$_3$ asymm. bending	1.00	2107
CH$_3$ asymm. bending	1.00	2101
CH$_2$ bending	1.00	2094
CH$_3$ symm. bending	0.25	1987
	0.38	1987–1973
	0.37	1973
CH$_2$ wagging	0.18	1876
	0.43	1876–1842
	0.39	1846
CH$_2$ twisting	0.33	1791–1722
	0.55	1722–1695
	0.12	1695
C–C chain stretching	0.16	1685
	0.84	1685–1650
C–CH$_3$ stretching	0.44	1614–1568
	0.56	1614–1534
CH$_3$ rocking	0.55	1521–1453
	0.45	1453
CH$_3$ rocking	0.65	1393–1361
	0.21	1361–1333
	0.14	1336
CH$_2$ rocking	0.52	1295–1222
	0.48	1289
C–C chain stretching	0.17	1197
	0.55	1198–1167
	0.28	1167
From β-polyalanine (5)		
C–CO stretch	1.00	1402
Amide III	1.00	1771
Amide IV + VI	0.45	817–838
	0.28	838–895
	0.27	895–948
Amide V	0.21	902–926
	0.56	926–1043
	0.23	1043–1052
From propionamide (6)		
NH$_2$ asymm. stretching	1.00	4829
NH$_2$ asymm. stretching	1.00	4657
C–N stretching	1.00	2386
C=O stretching	1.00	2344
NH$_2$ bending	1.00	1426
NH$_2$ rocking	1.00	1164

[a] Total of 28 group and 11 skeletal vibrations. Of the group vibrations, 17 were taken from polypropylene, 5 from β-polyalanine and 6 from propionamide

was followed. The equilibrium melting point used, 590 K, is a gross estimate, obtained by the use of the $T_m = \frac{3}{2} T_g$ empirical rule on a T_g extrapolated from T_gs of higher polyalkylacrylamides. Heat capacity data existed in the ATHAS data bank[12] from 60 to 300 K. Additional reported data from 10 to 50 K were not used since they were obtained by extrapolation.

Only the new C_p–C_v conversion method was used in this case, with the universal A_0 value. First $\theta_1 = 580.8 \pm 20.8$ K was determined in the temperature range 70–260 K. Then θ_3 was determined at the lowest possible temperatures (60–90 K) and was found to be 142.6 ± 19.3 K. The influence of θ_1 even at these low temperatures was considerable. The final error in comparison with the experimental results was only $0.20 \pm 1.62\%$. When using an A_0 value that was experiment-fitted for nylon 6, the error was higher, so that the universal A_0 value was retained for the computations. The recommended parameters are listed in *Table 3*.

Polyglycine

Polyglycine (PG) is the simplest member of the poly(amino acid) family and can also be thought of as the first member of the nylons (nylon 2). There exist two polymorphs, polyglycine I (extended β-sheets) and polyglycine II (α-helix).

For PGII, low temperature C_p data (1.4–20 K) as well as high temperature data (150–370 K) were reviewed in the ATHAS data bank[12]. A detailed dispersion curve of the vibrational spectrum also exists[27]. An equilibrium melting point of 555 K was extrapolated from higher nylons since no relevant data seem to exist. The low temperature data can be fitted with $\theta_D = 169.7 \pm 20$ K. Subsequently, by using the universal A_0 (out of the old method) and six skeletal vibrations, $\theta_1 = 528.1 \pm 34.9$ K and $\theta_3 = 96.4 \pm 3.3$ K can be determined for the temperature range 12–20 K. For all other temperatures the skeletal C_v is higher than the Dulong–Petit limit, a clearly impossible result, and no θ_1 or θ_3 can be determined. When the heat capacity is calculated with these θ temperatures, the 150–370 K temperature range has consistently an average error of -25 to -35%, with an r.m.s. deviation of only 3–5% from its average value. At the low temperatures, however, the fit is good, compared with the usual errors in such low temperature ranges. Using the new C_p–C_v method and the universal A_0 value, the error of the calculated compared with the experimental C_p is $-1.78 \pm 4.01\%$ (1.6–10 K). The choice of C_p–C_v conversion is of little consequence at these low temperatures and was made only for consistency of data treatment. The error is shown in *Figures 5* (1.6–10 K) and *6* (150–370 K). Judging this fit as satisfactory and observing the narrow range of the error at the high temperatures, we chose $\theta_1 = 528.1$ K and $\theta_3 = 96.4$ K as recommended parameters for the calculation of C_p. The large systematic deviation in the high temperature data will be addressed in the discussion section below.

For PGI C_p data from 150 to 370 K are reviewed in the ATHAS data bank[12]. Detailed dispersion curves of the vibrational spectrum also exist[22], referring to an infinite, isolated chain. These PGI vibrations are the ones used to construct the approximate group vibrations for the higher nylons, as discussed above. An initial attempt to fit the C_p data to θ temperatures failed since, as in PGII, the remaining skeletal contribution to the heat capacity after subtraction of the group vibrations from

the experimental data was higher than the classical Dulong–Petit limit. Attempts to use more than six skeletal vibrations by adding the amide VI mode to the skeletal vibrations for the fit to the experiments did not improve the analysis.

Calculating C_p using the θ temperatures determined from the fit to the low temperature data of PGII resulted in average errors of -30 to -35% at high temperature with a r.m.s. spread of 1.5–3.5%. All preliminary recommended parameters for PGI and PGII are also included in *Table 3* and discussed below.

Polyalanine

Polyalanine (PA) also has two polymorphs: α-polyalanine (α-helix) and β-polyalanine (corrugated sheets). Detailed dispersion curves exist for both α-PA[28] and β-PA[29]. Heat capacity data exist for both in the temperature range 1.6–300 K in the ATHAS data bank[12]. In all calculations, nine skeletal vibrations were assumed, based on the experience gained with polypropylene[1]. In that case it was found that the addition of a methyl group to a polyethylene backbone could best be described by the addition of three more skeletal, experiment-fitted vibrations. An equilibrium melting temperature of 573 K was used based on the PG value and taking into consideration the added methyl group.

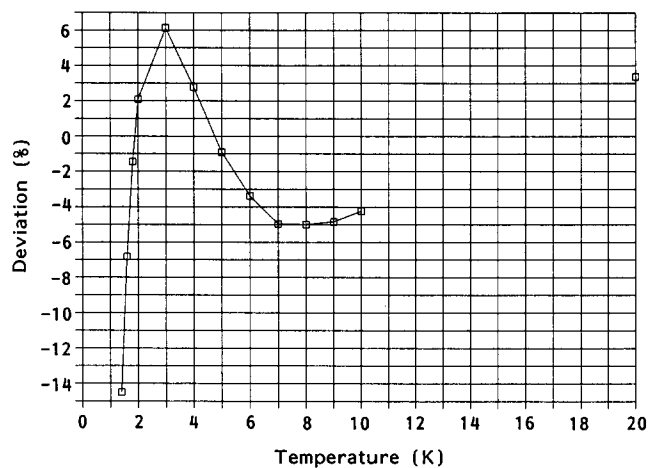For α-PA, $\theta_D = 133.7 \pm 4.3$ K was determined from the

Figure 5 Heat capacity difference $C_{p,calc} - C_{p,exp}$ of polyglycine II as a function of temperature (low temperature region)
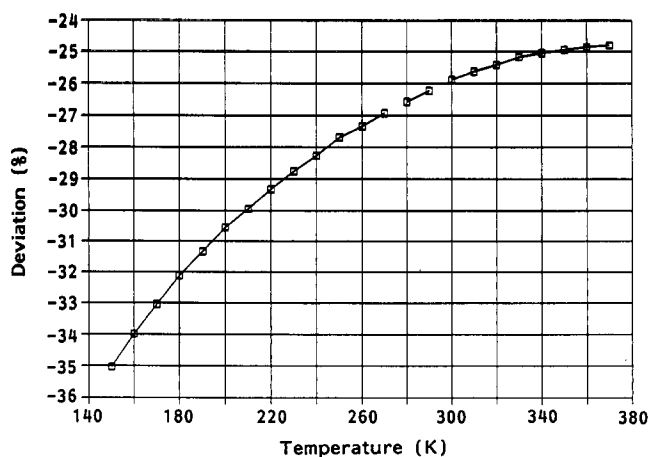

Figure 6 Heat capacity difference $C_{p,calc} - C_{p,exp}$ of polyglycine II as a function of temperature (high temperature region)
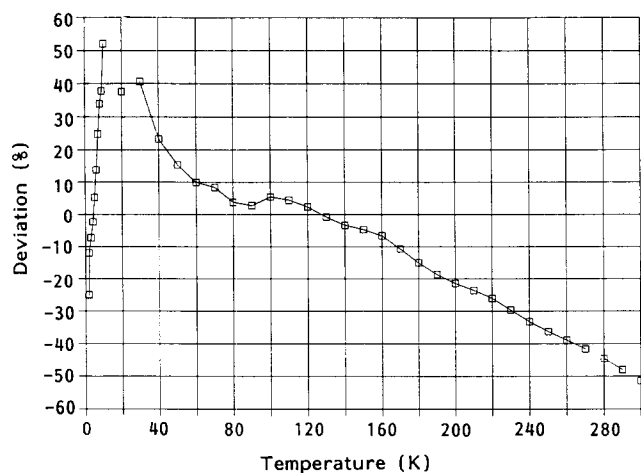
Figure 7 Heat capacity difference $C_{p,calc} - C_{p,exp}$ of α-polyalanine as a function of temperature

heat capacities between 2 and 6 K. Next, $\theta_1 = 626.6 \pm 45.6$ K and $\theta_3 = 61.9 \pm 2.4$ K were obtained from heat capacities from 60 to 160 K. As in the case of PG, the skeletal experimental C_v becomes larger than the Dulong–Petit limit, but only above 200 K. The experimental C_p below 10 K can also not be fitted well to the calculation. It results in errors ranging from -25 to $+55\%$ in the temperature range 1.6–10 K. At intermediate temperatures the situation improves somewhat.

From 60 to 160 K, with the universal A_0 value according to the new C_p–C_v method, the error is $2.00 \pm 5.31\%$. At higher temperatures the error increases again, gradually reaching -50% at 300 K. The θ temperatures determined are recommended as preliminary and are included in *Table 3*. The deviation of the calculated from the experimental C_p is shown over the whole temperature range in *Figure 7*.

For β-PA the situation is analogous. $\theta_D = 148.2 \pm 2.8$ K is obtained from 2 to 6 K and then $\theta_1 = 632.7 \pm 60.3$ K and $\theta_3 = 72.0 \pm 3.5$ are determined from 40 to 110 K. As in α-PA, the low temperature data cannot be predicted, the error ranging from -25 to $+25\%$ from 1.6 to 10 K. In the range 40–110 K, which was actually fitted to the θ temperatures, the error is smaller. With the universal A_0 value (new method) the error is $1.43 \pm 8.84\%$. These preliminary parameters are again recommended with the same words of caution used for α-PA and are included in *Table 3*.

DISCUSSION AND CONCLUSIONS

The skeletal heat capacities of the synthetic nylons could be fitted successfully to Tarasov parameters, while for the polypeptides the success was limited. Since no special consideration was given to the H bonding, this suggests that the thermodynamic properties of the nylons linked to the vibrational spectrum are not affected as much as other properties by the hydrogen bonding. Only the much larger value of A_0 than the average of other polymers may be linked to the different structure of the nylons. This effect is taken care of by use of the experiment-fitted A_0 value, but is in need of further experimental verification for polyamides other than nylon 6.

The adjustment of A_0, a method previously used in this laboratory, was proved to be justified by the calculations outlined. Its significance is more that of a

third adjustable parameter, since adjusting the universal value brings it closer to the experimentally fitted value and thus permits a comparison of the θ temperatures between different classes of polymers.

Since, for nylon 6 and nylon 6.6, both complete (calculated) and approximate (constructed) dispersion curves were available, our method of approximation of frequency spectra could be checked. It was seen that as long as the curves are constructed with caution, the approximation turns out to be valid. In addition, the example of polymethacrylamide showed that it is even permissible to transfer group vibrations from the backbone to the side groups. The behaviour of the amide group as a side group does not seem to change θ_1 appreciably, since it remains in the range of the values determined for the nylons. The θ_3 value seems to increase, however, being higher than the usual values determined. To verify this observation, experimental data below 60 K are needed. In general, the similar treatment of amide groups in the backbone and in the side chain seems to be justified.

Attempting to compare the θ values determined for the various nylons, one must realize that it is difficult to compare parameters obtained from different temperature ranges. A starting point for the discussion should be nylon 6.6, where the very low temperature (0.3–4 K) C_p data give confidence in the θ_3 temperatures determined. Increasing the number of methylene groups in the repeating unit, one sees that θ_1 decreases in the sequence nylon 6.6, nylon 6.9, nylon 6.10, nylon 6.12 and approaches, as expected, the value for polyethylene $(519 \text{ K})^2$. Turning to the nylon a type, one sees that θ_1 of nylon 6 is also close to that of polyethylene, but no trend can be established for the other nylons. In fact, θ_1 for nylon 6 obtained from the same narrow temperature ranges as for nylon 11 and 12 is 50–100 K lower (see *Table 3*). These observations clearly point towards the need for more precise heat capacity measurements, covering wider and lower temperature ranges. Overall, it is of interest to observe that the major differences between the nylon and polyethylene heat capacities result from differences in group vibrations and not from skeletal vibrations.

For the poly(amino acids) polyglycine and polyalanine we were not able to predict C_p over the whole temperature range where experiments exist. For polyglycine II the fit was good at very low temperatures (1.6–10 K), while for both α- and β-polyalanine we were able to obtain a satisfactory fit in an intermediate temperature range. Similar difficulties were encountered by Daurel *et al.*[30] and Finegold *et al.*[31]. The former researchers[30] were able to interpret their experimental data only up to 100 K for polyalanine using an analysis similar to the one presented here. They treated β-polyalanine as a two- and three-dimensionally coupled structure, taking into account its pleated sheet nature. The θ values they determined were $\theta_1 = 470$ K, $\theta_3 = 44$ K for α-polyalanine and $\theta_2 = 169$ K, $\theta_3 = 48$ K for β-polyalanine. The parameters obtained by Finegold *et al.*[31] from their own data from 1 to 20 K were $\theta_1 = 321$ K, $\theta_3 = 51$ K (α-polyalanine) and $\theta_2 = 156$ K, $\theta_3 = 35$ K (β-polyalanine). Their assumption of a small mole fraction of Einstein oscillators superimposed on the continuous modes has, however, no physical explanation. Moreover, the agreement with the calculated C_p of Daurel *et al.* is only qualitative. In neither case was it possible for these two research groups to predict heat

Table 6 Deviation of calculated C_p from experimental C_p of polyglycine (PG) and polyalanine (PA) in terms of water content[a]

T (K)	PGI	PGII	α-PA	β-PA
150	30.7	31.5	3.0	22.5
160	30.8	29.9	4.4	26.4
170	30.8	28.5	7.4	28.9
180	30.7	27.2	10.8	31.2
190	30.6	26.1	11.6	34.0
200	30.5	25.0	16.5	36.9
210	30.1	24.0	18.5	39.6
220	29.9	23.2	20.9	43.5
230	29.6	22.4	24.9	49.2
240	29.2	21.8	29.3	54.5
250	28.9	21.1	33.2	57.6
260	28.5	20.6	36.9	60.4
270	28.1	20.1	41.0	64.1

[a] Results obtained from using equation (3)

capacity at higher temperatures. To explain this discrepancy, some peculiarities of the polypeptides have to be pointed out. The possibility of hydrogen bonding at two out of three backbone atoms could complicate the separation of group and skeletal vibrations and lead to increased deviations from treating the system as linear (but see also the failure using two- and three-dimensional analyses). These factors should, in addition, be corrected to some degree by fitting to the three-dimensional θ_3 temperature. Also, the normal mode calculations used for the dispersion curves seemed to be in agreement with the experimental neutron-scattering frequencies.

These considerations tend to imply that perhaps the experimental C_p data contain systematic errors. Problems of water content in biopolymers are notorious and have plagued experimental measurements. To analyse this possibility, one can perform a simple speculation: assuming that the difference between experimental and calculated heat capacity is totally due to water, one can estimate what percentage of water in the sample would account for the deviation. The equation used was:

$$w/w\% \text{ of } H_2O \approx \frac{C_{\text{p,calc}} - C_{\text{p,exp}}}{C_{\text{p,}H_2O}} \times \frac{MW_{H_2O}}{MW_{\text{repeat unit}}} \times 100$$

(3)

Since most of our data were below 273 K we used the heat capacity for ice[32]. The results of this calculation are shown in *Table 6*. Given the approximate nature of the calculation, it is seen that water contents of this magnitude are not impossible and the relative constancy of the calculated amounts may indicate, especially for polyglycine, a reasonable explanation for the discrepancy. Although this is not proof of our contention, it points towards the urgent need for further measurements, planned in our laboratory in the near future.

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