Correspondence of lamellar thickness to melting point of nylon-6,6 single crystal

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The correspondence of lamellar thickness to the melting point of nylon-6,6 single crystal annealed in glycerol or without solvent was examined by hydrolysis in acids and by gel permeation chromatography (g.p.c.). The annealed samples showed a stepwise increase in lamellar thickness, which corresponded to the crystal thickness calculated from the observed melting point. Two lamellar thickening processes were observed for samples annealed in glycerol at high temperatures, an incomplete thickening process by half the length of one monomer unit and a complete thickening process evaluated to be about one and a half times the thickness of the former. The crystal thickness formed by the latter process corresponds to the thickness (and melting point) of solution-grown crystal isothermally crystallized under the same conditions. The large long spacings which led to approximately doubling or quadrupling of the lowest (main) crystal thickness were frequently observed, but they are, however, supposed to be only apparent long periods composed of the main crystal layers piled up in an arrangement like a bilayer or a pair of bilayers. The scale of lamellar thickness against melting point was assessed and it was concluded that the scale is probably reliable.

(Keywords: nylon-6,6 single crystal; annealing; lamellar thickening; melting point; hydrolysis; gel permeation chromatography)

INTRODUCTION

Lamellar thickening behaviour of several polyamides has been investigated previously, and it was proposed that the fold length increased in discrete jumps of one monomer unit and the layer thickness doubled in a discontinuous jump under critical annealing conditions[1-7].

For long enough repeat units of nylon-6,6 crystal, a stepwise increase in fold length should result. In previous papers[8,9], we reported that the layer thickness of a sample annealed in glycerol increases stepwise by half the length of a monomer unit. Simultaneously, another layer-thickening process of doubling (or quadrupling) the main crystal thickness was observed, which had been reported earlier by Dreyfuss *et al.*[1]. We found that melting points of the main crystal of annealed samples increase stepwise parallel to long spacings. Another melting point appearing at a temperature 10°C higher was observed. This was supposed to correspond to crystals with the above large layer thickness. However, the large layer thickness was larger than expected.

In the present paper, the correspondence of melting points to long spacings of samples annealed and/or hydrolysed with hydrochloric acid (HCl) is investigated precisely. To estimate the stem length of nylon crystal corresponding to the melting point, hydrolysis with an aqueous hydrochloric acid solution is effective in removing amorphous or semicrystalline components from the sample. This results in a reduction in molecular weight equivalent to the crystal thickness, which was estimated by means of gel permeation chromatography (g.p.c.). The reliability of the scale of lamellar thickness (monomer units per crystal thickness) against melting point is verified and a partial modification is made to the lamellar thickening model proposed by Dreyfuss *et al.*[1] to explain the thickening mechanism from the scale.

EXPERIMENTAL

Raw nylon-6,6 supplied by Toyo Rayon Co. Ltd was purified by the same procedure as described in their previous paper[9] ($\bar{M}_v = 18000$). The single crystal mat of nylon-6,6 was prepared from a 0.01% solution of the nylon in 60% aqueous formic acid (HCOOH) by dissolving at 95°C, isothermally crystallizing at 40°C and successively filtering at the same temperature, washing with fresh water, and vacuum drying to constant weight (this is called sample f). For comparison, a single crystal prepared by isothermal crystallization from a 0.05% solution of nylon-6,6 in glycerol at 190°C for 24 h was used (called sample g). These mats were annealed in glycerol or in nitrogen atmosphere without solvent, followed by quenching into methanol at room temperature (called wet and dry annealing, respectively).

The hydrolysed samples were prepared by treating with aqueous HCl solutions at 80°C for 24 h. Hydrolysis with aqueous HCOOH solution was also applied before the hydrolysis with HCl, though it is not as effective as HCl in cutting a molecular chain into lengths equivalent to the crystal thickness, but it is quite effective in removing amorphous and semicrystalline parts[9]. Since the wet-annealed and/or hydrolysed samples became porous and brittle, they were subjected in a hot press to a pressure of 100 kg cm^{-2} at 160°C.

The melting behaviour of a 3 mg sample was studied in a Perkin–Elmer DSC-II differential scanning calorimeter (d.s.c.) at a heating rate of 10°C min^{-1} under nitrogen. Small-angle X-ray scattering (SAXS) patterns were recorded photographically under conditions similar to those described in a previous paper[9]. G.p.c. chromatograms were recorded with an HLC-802A high performance liquid chromatograph (Toyo Soda Co.) equipped with 60 cm TSKgel G2000H and G3000H

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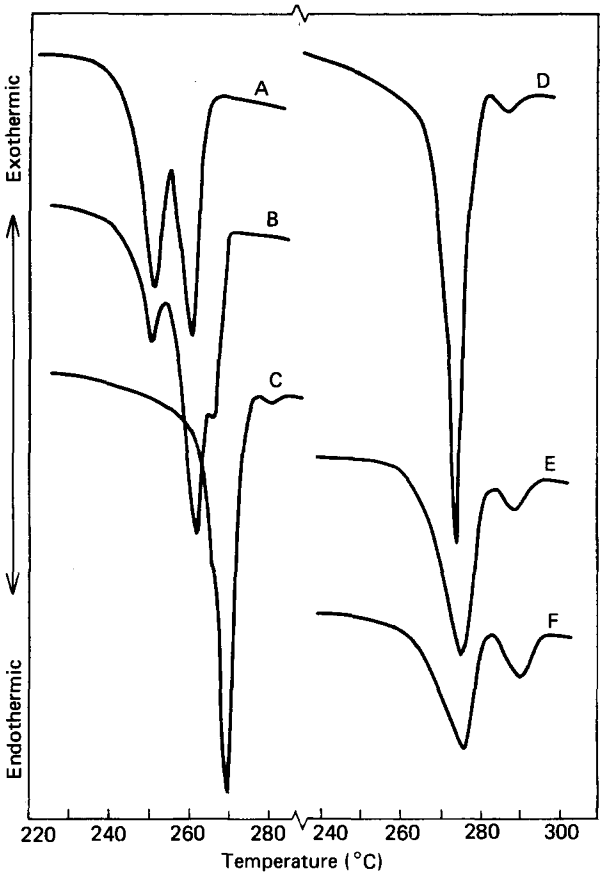

Figure 1 Heating curves of single crystal mats annealed in glycerol at 204°C for various periods of time: A, unannealed; B, 30 min; C, 90 min; D, 12 h; E, 24 h; F, 70 h

columns and 30 cm TSKgel GMHXL (× 2) columns and an RI-8 differential refractometer at 25°C. The eluent was chloroform containing 20 vol % *m*-cresol and the flow rate was 1 ml min^{-1}. The number average molecular weight M_n was calibrated using a polyethylene glycol standard, whose curve fitted closely the molecular weights of nylon-6,6 monomer, oligomers and polymer. In this measurement, a count of 6000 corresponded to an elution volume of 46 ml.

RESULTS

Melting points and long spacings of the nylon-6,6 single crystal mat annealed in glycerol

Typical d.s.c. thermograms of the single crystal mat annealed in glycerol at 204°C for various annealing times are shown in *Figure 1*. The unannealed mat shows a doublet melting peak (both peaks are called peak 1). The lower temperature peak corresponds to the melting peak of the original crystal, while the higher temperature peak is presumed to be caused mainly by the reorganized crystal formed during the heating process[10,11]. The lower temperature peak (250°C) of the mat annealed for 30 min is smaller in area, whereas the higher temperature peak (260.5°C) is larger in peak area and is accompanied by a new peak at 266°C. For the sample annealed for 90 min, the peak at 250°C disappears and a sharp peak appears at 270°C accompanied by a shoulder peak at 266°C. A similar process is repeated for longer annealing times. The new peak (peak 2) appears at ~ 10°C higher than peak 1 for mats annealed for longer than 30 min, and it also shifts stepwise to higher temperature parallel to peak 1 and increases in peak area as annealing time increases. However, if the mat is annealed for too long (e.g. 70 h), the melting peaks become lower and broader, which reflects thermal degradation of the sample during annealing. The main long spacings estimated from SAXS patterns were: curve A, 57.2; curve B, 64.2; curve C, 75.6; curves D and E, 94.8; and curve F, 115 Å. The stepwise increase in the long spacings was observed parallel to the melting points. The annealing time effect was parallel to the temperature effect[8], which can be also applicable to this study.

In *Figure 2*, the melting points and long spacings of single crystal mats annealed at various temperatures for 4 h in glycerol are plotted against annealing temperature. The stepwise increase of melting points seen in peaks 1 and 2 is similar to but clearer than the previous results[9]. The dashed lines in *Figure 2* show the scale calculated in a previous paper[9] from the following equation[12]:

$$T_m = T_m^\circ(1 - 2\sigma_e/\Delta h_f l_c) \qquad (1)$$

where T_m and T_m° (=300°C[10]) are the observed and equilibrium melting points, σ_e is the end surface free energy, Δh_f the heat of fusion and l_c the crystal thickness (T_m=250°C, l_c=44.8 Å, for the unannealed mat). Close agreement is obtained between the calculated and observed melting points. Two series of long spacings similar to the previous results[9] (the highest one is not shown here) are seen. The lower (main) series (57–87 Å) closely corresponds to peak 1, but the higher series (120–

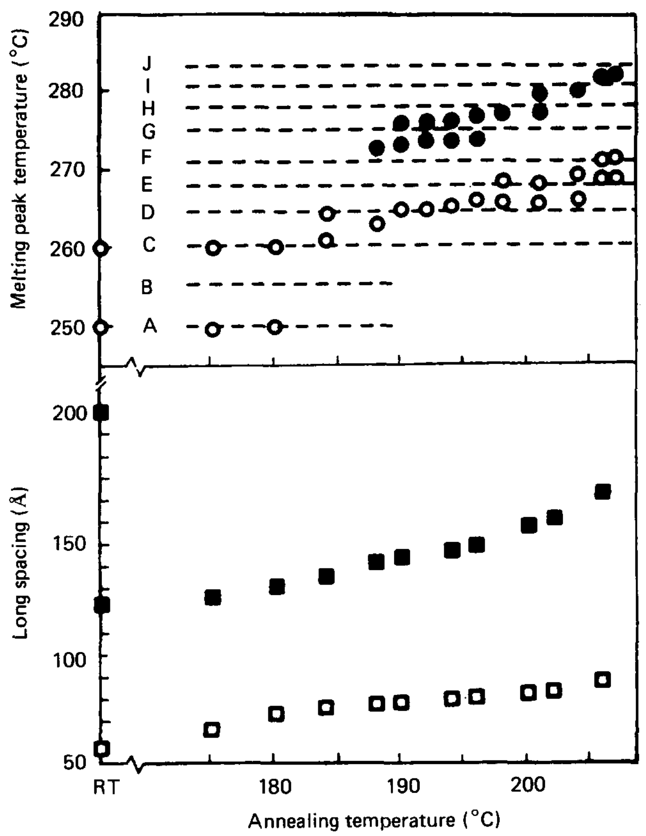

Figure 2 Plots of melting points and long spacings against annealing temperature. Plots of melting points are from peak 1 (○) and peak 2 (●), and long spacings are estimated from arc 1 (□) and arc 2 (■) for unannealed samples and samples annealed in glycerol for 4 h at various temperatures. Monomer units/crystal thickness: A, 3.5; B, 4; C, 4.5; D, 5; E, 5.5; F, 6; G, 7; H, 8; I, 9; J, 10

180 Å) is considerably larger than that estimated from peak 2 (the SAXS arc corresponding to the former is called arc 1, the latter arc is called arc 2).

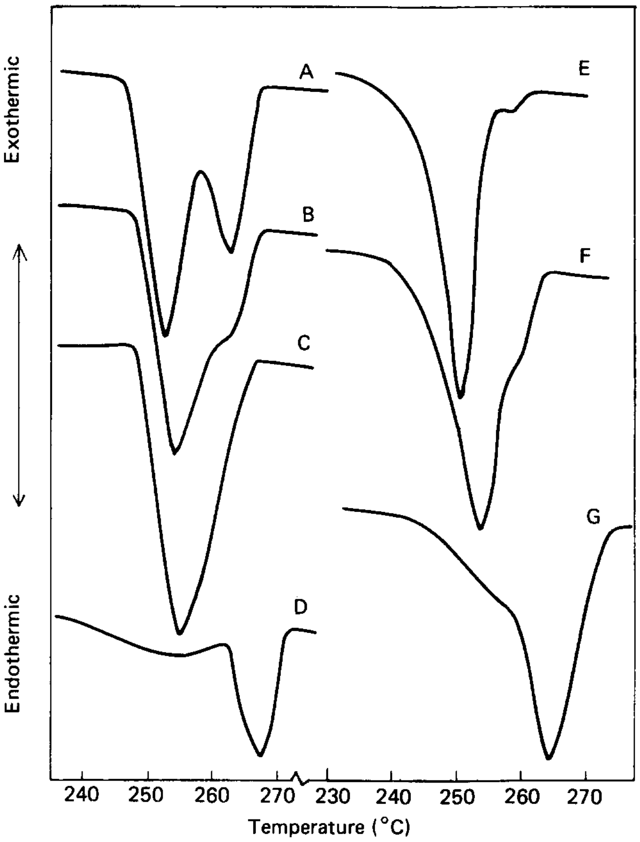

Figure 3 Heating curves of single crystal mats dry-annealed at 248°C for 5 min (A), 30 min (B) and 60 min (C), and the mat dry-annealed at 260°C for 30 min (D). Heating curves of respective samples hydrolysed with 10% HCl at 80°C for 24 h are shown on the right hand side: E, f-H; F, f248-H; G, f260-H

Dry annealing of the mats and hydrolysis with hydrochloric acid

Figure 3 shows d.s.c. heating curves of the mats annealed without solvents (dry annealing). For sample f annealed at 248°C (curves A, B and C), which is just below the lower temperature peak, the lower temperature peak increases in area accompanied by a decrease in area of the higher temperature peak with increasing annealing time. This supports the presumption of reorganization. The mat annealed at 260°C (curve D) (just below the higher temperature peak) for 30 min shows a single peak at 267°C, accompanied by a very broad melting peak at 255°C as a result of the partial melting of the original crystal (mats annealed at 248 and 260°C for 30 min will be denoted f248 and f260, respectively).

The above samples were first treated with 50% HCOOH at 95°C for 24 h (except for sample f) and then with 10% HCl at 80°C for 24 h. D.s.c. thermograms of these samples are also shown in *Figure 3* (the sample hydrolysed with HCl will be denoted f-H, etc.). Sample f-H shows a sharp lower temperature peak, while the peak at the higher temperature almost disappears because it could not reorganize. The other hydrolysed samples (f248-H and f260-H) show a broad single peak slightly shifted to lower temperatures. The broad peak of sample f260 due to the partial melting almost vanished for sample f260-H.

Figure 4 shows SAXS photographs of the above samples. Three long spacings of 57, 124 (double the former) and 210 Å (quadruple) are observed even for the unannealed sample f. On annealing at 248°C, a small increase in long spacings is seen, estimated from both arc 1 and arc 2, though this temperature must be ineffective for the larger long spacings (arc 2). Sample f260 shows only one vague long spacing of 148 Å. After hydrolysis, the large long spacings estimated from arc 2 (double and quadruple) for samples f and f248 vanished, while the lowest one estimated from arc 1 remained unchanged.

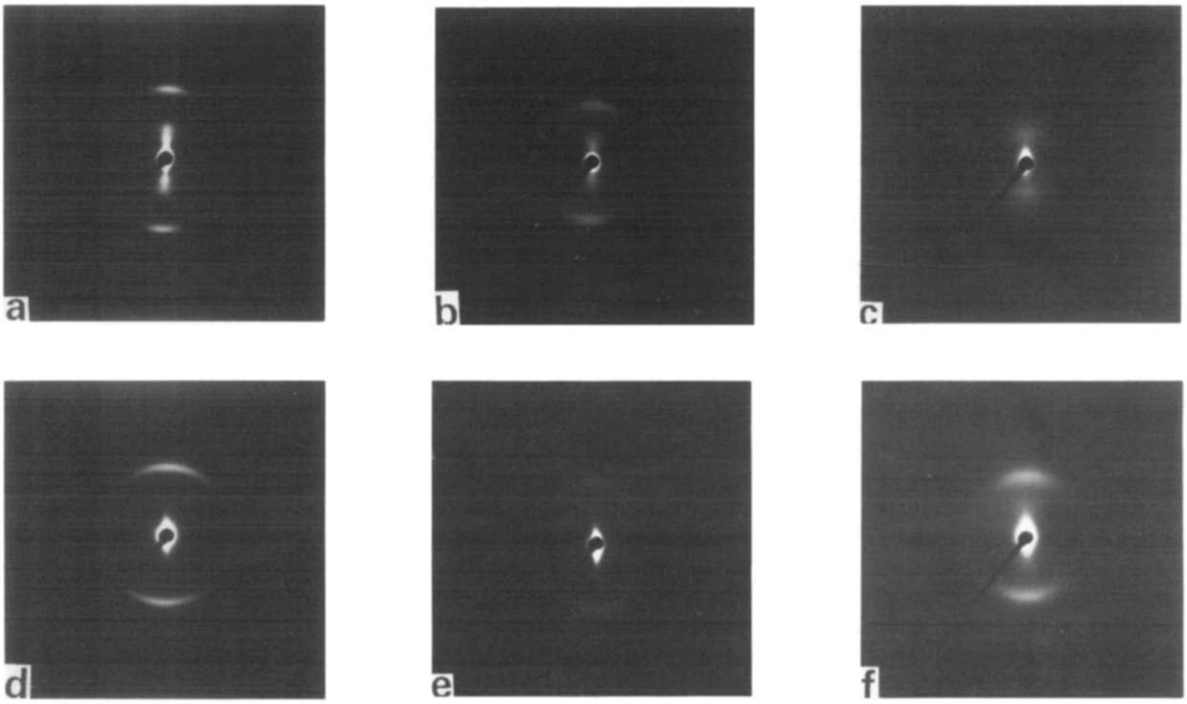

Figure 4 SAXS photographs of samples (a) f, (b) f248 and (c) f260 and hydrolysed samples (d) f-H, (e) f248-H and (f) f260-H

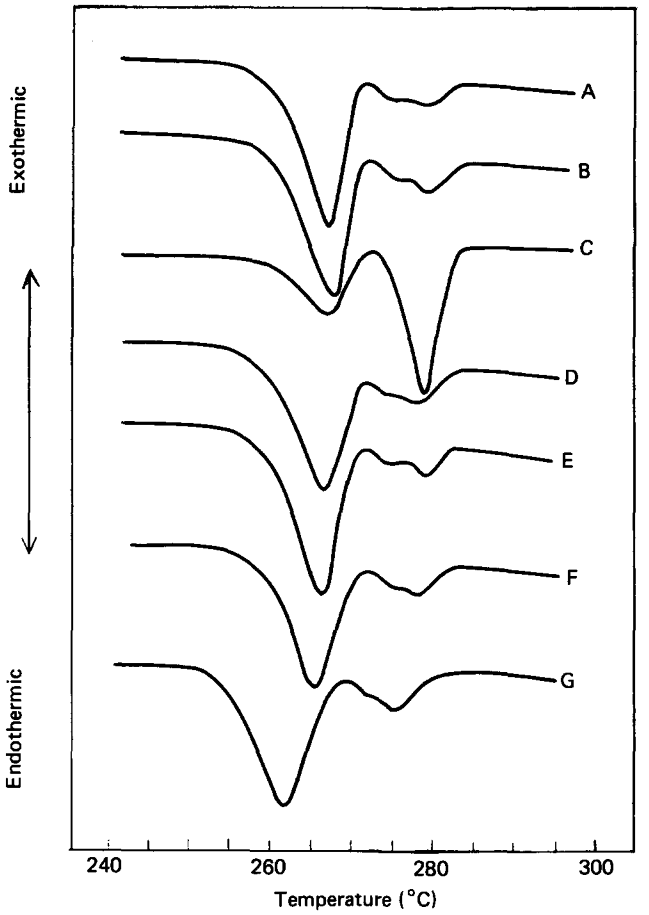

Figure 5 Heating curves of typical wet-annealed samples (at 195°C for 24 h) treated with 45% (B) and 58% HCOOH (C) at 100°C for 24 h and with 8% HCl (D) at 80°C for 24 h. A, Unhydrolysed. E, F, G, Hydrolysed with 10% HCl for 8, 24, 48 h, respectively

Sample f260-H shows a long spacing of 68 Å, which is far shorter than that of the unhydrolysed sample f260, but close to one half of it. This implies that the large spacings are apparent long periods composed of the main crystal layers piled up in an arrangement like a bilayer or a pair of bilayers; i.e. we cannot find melting peaks corresponding to these large spacings.

Hydrolysis of wet-annealed samples in aqueous formic acid and hydrochloric acid solutions

Figure 5 shows d.s.c. thermograms of typical wet-annealed samples, w, (at 195°C for 24 h) treated with various concentrations of aqueous HCOOH solutions at 100°C for 24 h and aqueous HCl solutions at 80°C for 24 h. As the concentration of HCOOH or HCl is increased, peak 2 grows larger, while peak 1 becomes smaller. D.s.c. thermograms of samples hydrolysed with 10% HCl at 80°C for various times are also shown in *Figure 5*. A considerable decrease in peak temperature is observed for the sample hydrolysed for 48 h (curve G). Nylon-6,6 crystal is the α form (triclinic)[13], and we could estimate a thickness increment of 12.8 Å, which is close to one monomer unit projected on the normal[10]. Long spacings and melting points of sample w unhydrolysed or hydrolysed with 45% HCOOH were 74.4 Å (corresponds to 5.5 monomer units), 98 Å (7.5 monomer units) and 268, 277°C, respectively. For sample w hydrolysed with 58% HCOOH the results are 102 Å and 278°C. If it is heated up to a temperature between two peaks (e.g. 272°C) and then quenched, it shows a sharp melting peak at 279°C accompanying a broad peak at *ca.* 250°C and only one long spacing of 100 Å. The long spacing of the sample hydrolysed with HCl hardly decreased, though the melting point decreased to 276°C (curve G) as a result of degradation of nylon. The weight loss of the sample hydrolysed with 55% HCOOH (100°C, 24 h) or 10% HCl (80°C, 24 h) was *ca.* 50%, which increased up to 90–99% under the severer condition. Therefore, an optimun treating time is around 24 h, after which a steep depression begins in the melting points, long spacings and molecular weights.

Both the single crystal mat crystallized isothermally in glycerol at 190°C for 24 h (sample g) and sample f wet-annealed at 190°C for 24 h (sample w) were dry-annealed for 30 min at just below the melting points and then hydrolysed with HCl. Their d.s.c. heating curves are shown in *Figure 6*. Sample w shows two melting peaks (peaks 1 and 2), whereas sample g shows a single melting peak. The peak of sample g closely corresponds to peak 2 of sample w. Sample w dry-annealed at 263°C (w263) shows a sharp peak 1 at a slightly higher temperature, which shifts to lower temperature after the hydrolysis, while peak 2 is unchanged. Both samples g and w dry-annealed at 270°C (g270 and w270) show a single peak at 277°C and a broad peak at an extremely low temperature (*ca.* 255°C) caused by the crystal recrystallized from a partially molten component. Hydrolysed samples g270-H, w263-H and w270-H show sharp melting peaks

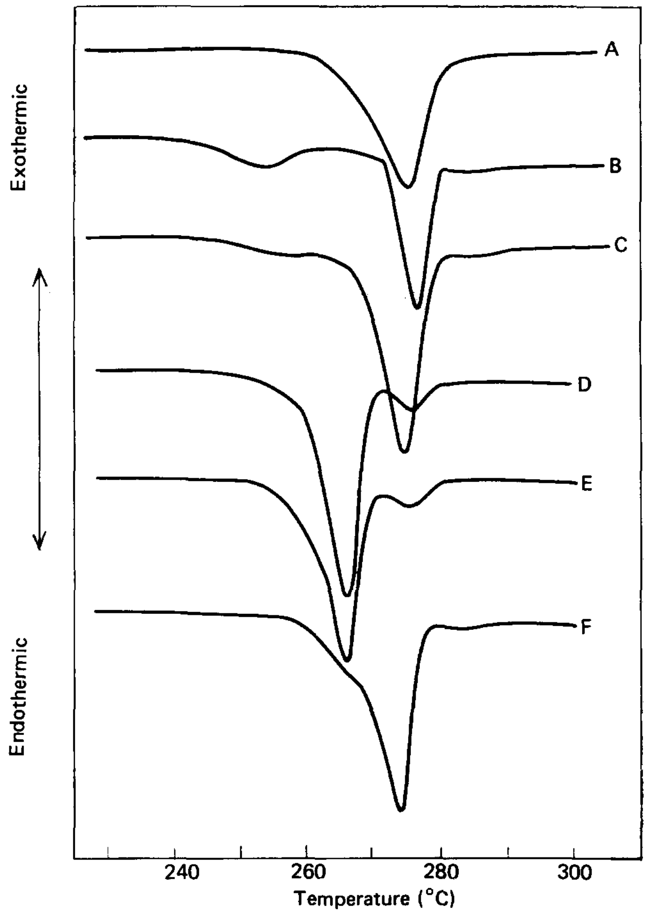

Figure 6 Heating curves of samples g and w dry-annealed at 263 or 270°C for 30 min and then hydrolysed with 10% HCl at 80°C for 24 h. A, sample g; B, g270; C, g270-H; D, w; E, w263-H; F, w270-H

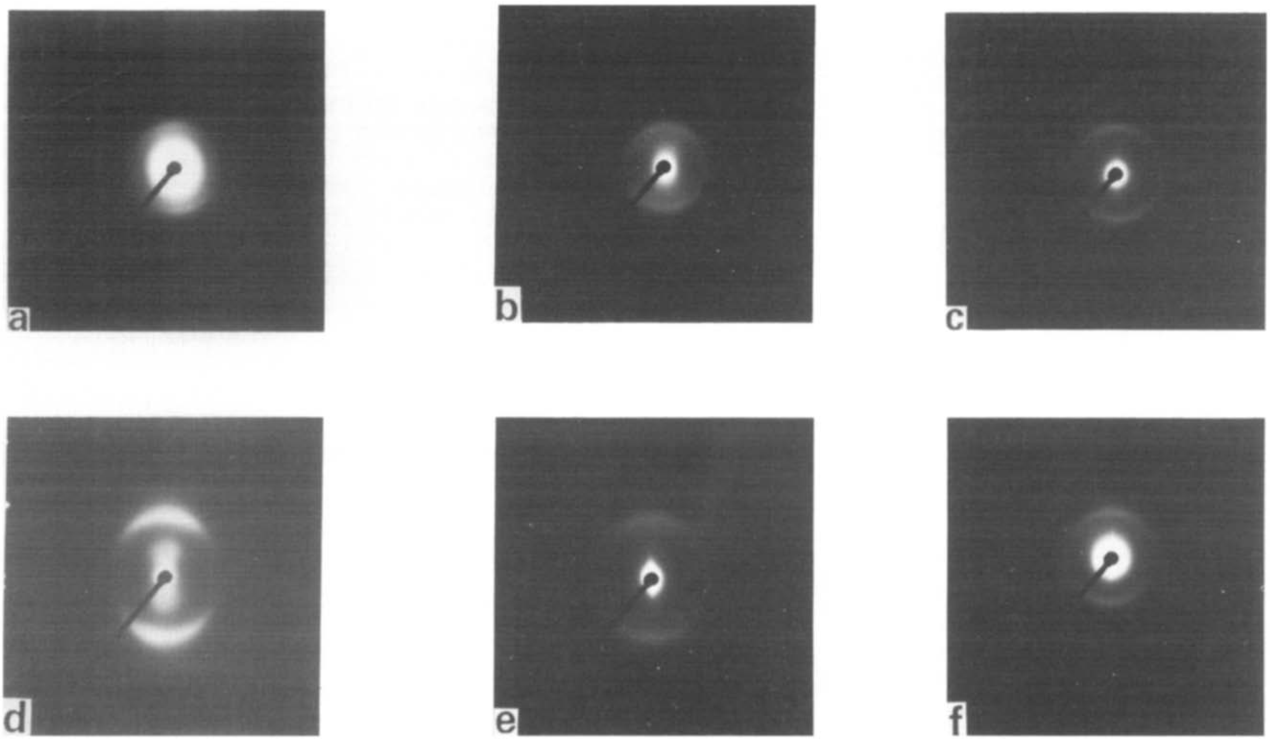

Figure 7 SAXS photographs of (a) sample g, (b) g270, (c) g270-H, (d) w, (e) w263-H and (f) w270-H

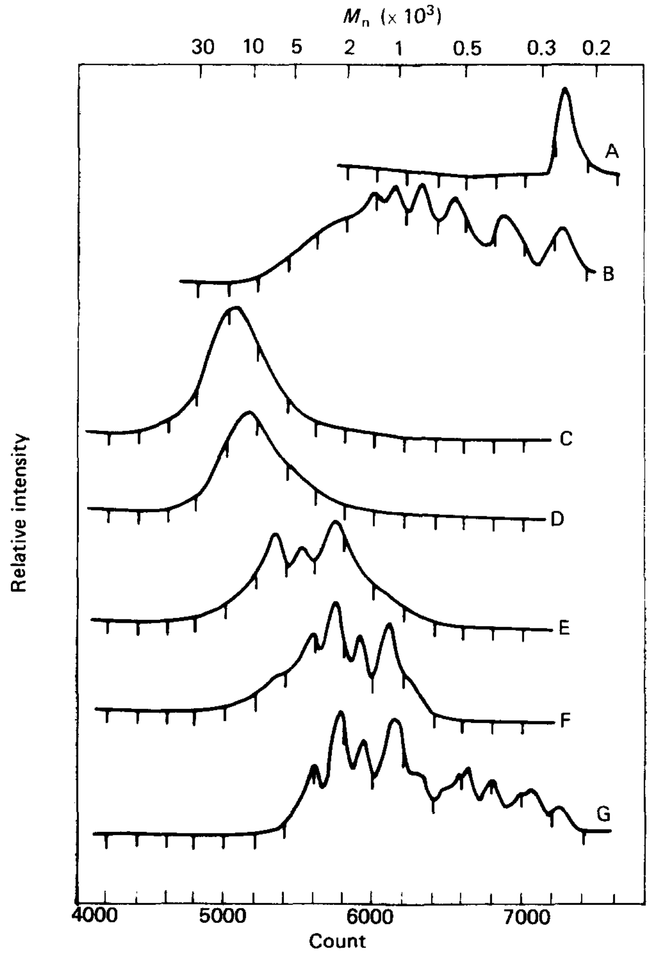

Figure 8 G.p.c. chromatograms of nylon-6,6 monomer (A) and oligomers (B), and those of wet-annealed samples (at 195°C for 24 h) hydrolysed with 10% HCl for various periods of time: E, 8 h; F, 24 h; G, 48 h. C, Unhydrolysed; D, hydrolysed with 55% HCOOH at 100°C for 24 h

slightly shifted to lower temperatures, where the broad melting peaks at 255°C almost vanished, implying that the recrystallized crystals were removed.

Typical SAXS photographs of hydrolysed samples are shown in *Figure 7*. Sample g shows a long spacing of 96 Å, which increases slightly to 98 Å after dry-annealing at 270°C, and then decreases to 94 Å after hydrolysis. Sample w, however, shows four long spacings, estimated from arc 1 (the same as that of sample g and the lowest one of 74 Å), and arc 2 (double or quadruple the lowest). The larger long spacings (arc 2) vanished if the sample was hydrolysed enough.

Estimation of average molecular weight of hydrolysed samples by g.p.c. chromatograms

G.p.c. chromatograms of the adipic acid–hexamethylenediamine salt (monomer) and nylon-6,6 oligomers (obtained by dry-annealing the salt at 208°C for 10 min) are shown in *Figure 8*, curves A and B, respectively. The monomer shows a peak at a count of 7260 ($M_n = 244$), while the oligomers show peaks corresponding to monomer numbers 1, 2, 3, 4, 5 and 6, monomer numbers increasing toward lower counts. This is precisely reported elsewhere[14]. G.p.c. chromatograms of the wet-annealed sample (at 195°C for 24 h) hydrolysed with 10% HCl at 80°C for various treating times are also shown in *Figure 8*. The unhydrolysed sample (curve C) and the sample hydrolysed with 55% HCOOH (curve D) show a single peak at a count of ~5000 ($M_n = 12\,000$–$14\,000$), which means that hydrolysis with HCOOH solution is not as effective as with HCl in cutting a molecular chain. The sample treated with HCl for less than 8 h (curve E) shows incomplete hydrolysis, while the sample treated for 24 h (curve F) shows a clear reduction in molecular weight, which reflects sufficient hydrolysis. However, the sample hydrolysed for 48 h (curve G) shows

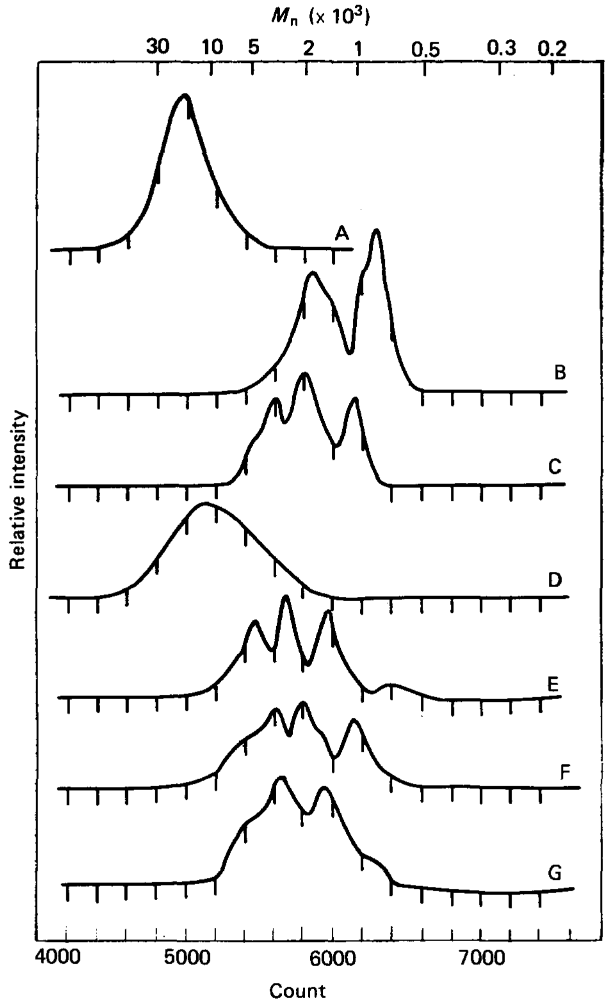

Figure 9 G.p.c. chromatograms of samples hydrolysed with 10% HCl at 80°C for 24 h. A, sample f; B, f-H; C, f260-H; D, g; E, g270-H; F, w263-H; G, w270-H

the same peaks as those of curve F and the extra peaks of oligomers similar to curve B (accompanied by extra middle peaks corresponding to 2.5 and 1.5 monomer units). This means that the molecular chain is cut further as the hydrolysing time increases. Therefore, the optimum hydrolysing time with 10% HCl is around 24 h.

Figure 9 shows g.p.c. chromatograms of samples of f, g and w hydrolysed with 10% HCl at 80°C for 24 h. The single crystal (curve A) shows a single peak at a count of 4930 ($M_n = 17400$), which shifts to lower molecular weight after hydrolysis (curve B). The hydrolysed sample f260-H (curve C) has three peaks shifted to slightly higher molecular weight than those of sample f-H. Sample g shows a broad peak at a count of 5130 ($M_n = 11800$), which is similar to that of the unhydrolysed sample w, reflecting thermal degradation during crystallization or annealing. The total number-average molecular weights of hydrolysed samples f-H, f260-H and w263-H are low enough, between 1500 and 2000, to be resolved into two or three peaks, which shift to slightly higher molecular weight with increasing dry annealing temperature (g270-H and w270-H). For hydrolysed samples, the higher molecular weights estimated from the resolved peaks are very close to multiples of the lowest, i.e. two or three times the main crystal thickness caused by hydrolysis at random on fold surfaces. If the higher molecular weights were a result of hydrolysis of the thicker crystals with large long spacings, M_n values of two and *four* times the main crystal should be found instead of three times.

Table 1 shows the observed melting point T_m, long spacing L and number-average molecular weight M_n corresponding to the count of each resolved peak, numbers of monomer units N_m and N_L per crystal thickness calculated from observed melting points[9] and long spacings, respectively, and the number N_G estimated from each M_n for g.p.c. curves. Good agreement between N_m and N_G is observed for all hydrolysed samples. N_L estimated from the long spacing of hydrolysed samples (f260-H, g270-H, w263-H and w270-H) is very close to the N_m and N_G values, while the N_L of hydrolysed samples f-H and f248-H are slightly larger, and the N_L of unhydrolysed samples (f, g and w) are far larger than the above numbers, reflecting insufficient degradation of the sample.

DISCUSSIONS AND CONCLUSIONS

It is inferred that the layer thickness of nylon-6,6 single crystal grown in solution or dry annealed cannot be estimated directly from the long spacing of SAXS patterns unless the sample is hydrolysed with acids; but the layer thickness can be estimated from the observed melting point using equation (1), as shown in *Figure 2*. The crystal layer thickness, which seems to be lowest (3.5 monomer units, $l_c = 44.8$ Å) for a solution-grown crystal[1], increases stepwise by half the length of a monomer unit with increasing annealing temperature. The single crystal mat shows two series of melting points (peaks 1 and 2), and two (or three) series of long spacings with wet annealing, i.e. the lowest long spacing (arc 1), and the larger long spacings (arc 2) which correspond closely to double (or quadruple) the main crystal thickness. The crystal thickness estimated from peak 2 increases by one monomer unit length, and is close to one and a half times that estimated from peak 1 (e.g. $N_m = 8$ (peak 2) is about 1.5 times 5 (or 5.5) estimated from peak 1, for the mat annealed at 198°C for 4 h). Peak 2 increased in peak area, while the larger long spacings vanished after hydrolysis. Moreover, the larger long spacings are observed even for the unannealed mats. Therefore, the main long spacing (arc 1) corresponds to peak 1, whereas the larger long spacings do not correspond to peak 2 or show any melting peak, so the larger long spacings are supposed to be only apparent.

Sample g showed a melting peak at 275°C, which closely corresponds to peak 2 of sample w. The melting points of samples isothermally crystallized at other temperatures also corresponded to peak 2 of samples wet-annealed at the same conditions. The long spacing of sample g (96 Å) closely corresponds to the main long spacing (inside arc of arc 1) of sample w (100 Å), while the long spacings of hydrolysed samples g270-H and w270-H are 93 and 91 Å, respectively. The lowest values of N_G (monomer units per crystal thickness) of samples g270-H and w270-H are close to 7 (the N_m and N_L values are also *ca.* 7). Therefore, two different processes of lamellar thickening can be considered for the wet-annealled sample, an incomplete thickening process by half the length of one monomer unit corresponding to peak 1 and a complete thickening process, about one and a half times the former. It is difficult to obtain nylon-6,6 crystals by isothermal crystallization at temperatures above 192°C

Table 1 Comparison of the number of monomer units per crystal thickness N_m, N_L and N_G estimated from melting point T_m, long spacing L and M_n in the g.p.c. curve, respectively

Sample	T_m (°C)	L (Å)	M_n	N_m	N_L	N_G
f	250 (260.5)[a]	57.2	17 400	3.5 (4.5)[a]	4.46	(76.9)[b]
		123.9			9.68	
		210.5			16.5	
f248	255	69.4		3.9	5.42	
		151.6			11.8	
		258.4			20.2	
f260	267	148.0		5.4	11.5	
f-H	250 (257)	57.9	860	3.4 (4.2)	4.52	3.73
			1720			7.53
f248-H	254	62.8	940	3.9	4.91	4.09
			1890			8.26
f260-H	264	68.2	1190	4.9	5.33	5.18
			2510			11.0
			3660			16.1
g	275	96.4	11 800	7.0	7.53	(52.1)
g270	277	98.0		7.5	7.66	
g270-H	274	93.4	1610	6.9	7.30	7.04
			3370			14.8
			5120			22.6
w	266	75.9	12 400	5.2	5.93	(54.8)
	276	99.8		7.2	7.80	
		152.3			11.9	
		276.4			21.6	
w263	267	76.4		5.4	5.97	
	276	98.9		7.2	7.73	
w270	277	105.6		7.5	8.25	
w263-H	266	66.9	1120	5.2	5.23	4.88
	276	91.4		7.2	7.14	
			2360			10.4
			3580			15.8
w270-H	274	91.4	1630	6.9	7.14	7.13
			3410			15.0

[a] The higher temperature peak
[b] An unresolved peak

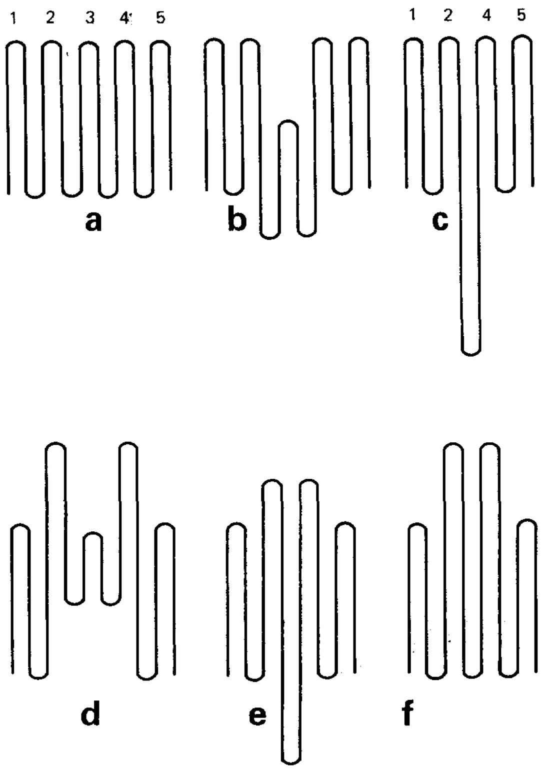

Figure 10 (a)–(c) Lamellar thickening model of doubling proposed by Dreyfuss *et al.*[1] and (f) the modified model of one and a half times thickening with two intermediate stages (d) and (e) proposed in this work. Numbering of the fold parts is shown in (a) and (c)

from a glycerol solution, whereas a sample is easily obtained by annealing in glycerol even at higher temperatures up to 206°C. Examining the validity of the T_m–l_c scale, we find that it is very reliable. If we suppose that $\Delta h_f = 45\,\mathrm{cal\,g^{-1}}$ (reference 15), we can obtain $\sigma_e = 4.6\,\mu\mathrm{J\,cm^{-2}}$ using equation (1), which closely corresponds to other published results[16].

A lamellar thickening mechanism for nylon-6,6 was proposed by Dreyfuss *et al.*[1], who said that it is not affected by crystallization temperature and solvent, and that the crystal layer thickness corresponds to 3.5 monomer units, but under critical conditions the layer thickness doubles in a discontinuous jump on annealing. They attributed these characteristics to the hydrogen bonding between molecular chains. Their lamellar thickening models from single to double fold length are illustrated in *Figure 10a–c* (shown in part). However, they need to be modified, because the crystal thickness estimated from peak 2 is about one and a half times that estimated from peak 1. Good correspondence of N_m to N_L and N_G is observed for the dry- and wet-annealed samples hydrolysed completely, based on which two crystal thicknesses corresponding to peaks 1 and 2 are also assessed.

The modified model from threefold to twofold, which results in one and a half time thicker crystal, is shown in *Figure 10(f)*. Some processes can be considered to arrive at stage (f) by repeated dislocation or fluctuation of the fold part. For example, if a dislocation of fold part 3 occurs, stage (b) results. At the next stage, (d), other dislocations of fold parts 2 and 4 occur to the upper side and then fold part 3 folds out to the bottom, which results in stage (f). Another example is from stages a to c, passing through stage b, then dislocating fold parts 2 and 4 to the upper side, e, and finally stage f. One of these processes occurred during partial melting and strong swelling in glycerol. The nucleus of crystallites corresponding to the complete thickening process is born in this manner and followed by recrystallization on it. The crystal component formed by the complete thickening process is stable in glycerol at the annealing temperature, whereas the crystal formed by the incomplete thickening process is metastable in hot glycerol. Therefore, the latter crystal is formed in insufficiently swollen parts, because it swells and melts predominantly if fine nylon powder is used (instead of the mat) and dispersed completely in glycerol. However, the gelation between the molecular chains occurs and proceeds during the annealing[17], which partly prevents the crystal component corresponding to peak 1 from dissolving. Long spacings corresponding to peak 2 are not usually detected by the SAXS method because the fraction in the sample is too small, but they can be detected if it is dry-annealed at temperatures between peak 1 and 2, and hydrolysed as demonstrated above.

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