Preparation and properties of high molar mass nylon-4,6: a new development in nylon polymers

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(*Received 2 October 1984*)

The preparation, in a two-step process, of poly(tetramethylene adipamide) (nylon-4.6) has been studied. The first step involves precondensation of tetramethylene-diammonium adipate (nylon-4,6 salt) with water as solvent. A kinetic model is postulated that describes the prepolymerization by a second order amidation reaction with formation of pyrrolidine end-groups as a side reaction. In the second step, prepolymer powder is subjected to solid state polycondensation to achieve a sufficiently high molar mass. High molar mass nylon-4,6 (Stanyl[*]) exhibits a very high melting temperature (about 290°C) and high crystallinity, which makes it an attractive material for applications at high temperature where dimensional stability is a strict demand, such as applications in industrial yarns and engineering plastics.

(Keywords: poly(tetramethylene adipamide); nylon-4,6; prepolymerization; solid state aftercondensation; physical properties)

INTRODUCTION

Although from patents and publications it has long been known that poly(tetramethylene adipamide) (nylon-4,6) potentially offers attractive properties because of its high melting temperature and its high crystallinity, the material has not until now been produced commercially[1–3]. The reason for this is the difficulty of achieving a sufficiently high molar mass ($M_w > 40 \times 10^3$ g/mol) while preventing discolouration, as appears from patent literature[4].

Application of conventional nylon-6,6 techniques for making nylon-4,6, i.e. prepolymerization of a nylon salt solution in water at 210°–220°C and aftercondensation in the melt phase at 270°–280°C, will not lead to the desired product properties. Besides, as this aftercondensation temperature remains below the melting point of nylon-4,6, the reactor contents will solidify so that decharging is impossible.

A study by Gaymans *et al.*[5] describes the preparation of nylon-4,6 in a two-step process: first, a low molar mass prepolymer is formed at 215°C under autogenous pressure and then the prepolymer is postcondensed *in vacuo* in the solid state at 290°C or in the melt at 305°C.

In the paper presented here, a kinetic model for the prepolymerization is presented together with a number of features of the solid state aftercondensation and a number of properties of Stanyl®.

EXPERIMENTAL

Polymerizations

Prepolymerizations were carried out as described in an earlier publication[6]. The prepolymers were subjected to solid-state polymerization at 260°C in a horizontally rotating 0.5 l flask under a constant flow of nitrogen (24 n·l h^{-1}) and steam (3 g h). To this end, a 'Büchi Rotavapor' was used with the rotating flask situated in an electric furnace (Cenco Instruments).

Characterization

Prepolymers as well as high molar mass samples were dried before analysis. The amino end groups were determined by potentiometric titration of a nylon-4,6 solution in phenol with hydrochloric acid in a mixture of glycol and phenol at elevated temperatures. The carboxyl end groups were determined in a similar manner by potentiometric titration of a nylon-4,6 solution in a *o*-cresol/benzyl alcohol mixture with tetrabutylammonium hydroxide in a mixture of 2-propanol and methanol at elevated temperature. In addition, the pyrrolidine content was determined by g.l.c. after complete hydrolysis with hydrochloric acid and extraction with chloroform.

Relative viscosities were measured with an Ubbelhode capillary viscometer at a concentration of 1 g/100 ml in 96% sulphuric acid at 20°C.

Light scattering experiments were carried out with Sofica 42.000 apparatus ($\lambda = 546$ nm) with solutions of ≈ 0.005 g ml^{-1} in 2.0 mol l^{-1} KCl + 85% formic acid, which were freed from dust by centrifugation. High temperature g.p.c. measurements were executed at 110°C in *m*-cresol with M 150 C Waters g.p.c. apparatus equipped with two silanized Zorbax (Du Pont) bimodal columns (PSM 60 Å and 1000 Å). The column effluent was monitored by means of a differential refractometer. The concentration of the solutions amounted to 0.25–0.30 wt%; the injection volume was 100 μl and the flow rate was 0.5 ml/min.

N-trifluoroacetylation of nylon-4,6 and -6,6 was carried out according to the method developed by the organic chemistry department of Mainz university[7], however we used $C_2H_4Cl_2$ as solvent.

N-TFA-polyamide was dissolved in CH_2Cl_2 and injected into the g.p.c. type ALC 244 (Waters), equipped with three μ-Styragel columns with nominal pore sizes of 5×10^2 Å, 10^3 Å and 10^4 Å, respectively. The effluent (flow rate 1 ml/min) was monitored by means of a u.v. detector, adjusted at 254 nm.

The d.s.c.-curves were recorded with a Perkin-Elmer DSC-II at a scan speed of 5°C min^{-1} for both heating and

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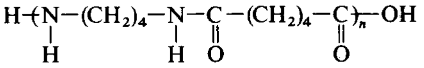
cooling, unless otherwise indicated. The peak temperatures were taken as the crystallization and the melting point.

Torsion pendulum experiments were executed at a constant frequency of 0.2153 Hz over a temperature range from −150°C to +200°C, at a heating rate of 1°C min^{-1}. The samples were thoroughly dried for 24 h *in vacuo* at 105°C under a nitrogen leak.

RESULTS AND DISCUSSION

Prepolymerizations

From a large number of experiments two series are selected to show the relation between the concentration of amino (*a*), carboxyl (*c*) and pyrrolidine (*p*) end groups and the polymerization time (*t*) for isothermal prepolymerization at 210°C at an initial -4,6 salt/water ratio of 93/7 (wt/wt) and 1.2 wt% excess 1,4-diaminobutane (DAB) with respect to -4,6 salt (see *Table 1*). The end groups measured on dry prepolymers were converted into actual reactor concentrations (dimension: eq kg^{-1}) taking into account the amount of amidation water. In *Table 1*, $t=0$ is defined as the point of time at which the polycondensation temperature is reached. P_n is defined as the number of half repeat units per chain, i.e. as $P_n = 2n$ for the structural formula

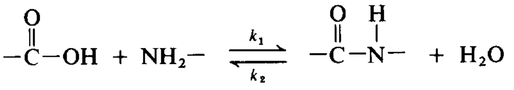


$$\text{H}\!\left(\underset{\text{H}}{\text{N}}-(\text{CH}_2)_4-\underset{\text{H}}{\text{N}}-\underset{\text{O}}{\overset{}{\text{C}}}-(\text{CH}_2)_4-\underset{\text{O}}{\text{C}}\right)_n\text{OH}$$

The amide-group and water concentrations are given as *x* and *w*, respectively. As can be seen from *Table 1*, a conversion of about 50% has already taken place during heating.

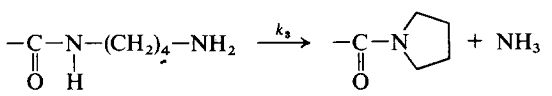
As expected for polycondensations, *a* and *c* decrease as a function of time. However, they do not decrease at the same rate, *a* sloping somewhat more sharply than *c*. In addition, pyrrolidine appears as a third end group, and its concentration *p* increases with time. In *Figure 1*, *p* and the unbalance in amino and carboxyl end groups ($a-c$), measured on dry prepolymers, are plotted as a function of polycondensation time (*t*) for all experiments carried out at 210°C. In spite of considerable scatter in the experimental points, it can be concluded that $a-c+p$ is constant. In our opinion this means that the additional loss in amine groups with respect to carboxyl groups is attributable to the formation of pyrrolidine by a 1 to 1 stoichiometry:

polyamidation (1)



$$-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{OH} + \text{NH}_2- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} -\overset{\text{O}}{\overset{\|}{\text{C}}}-\overset{\text{H}}{\overset{|}{\text{N}}}- + \text{H}_2\text{O}$$

pyrrolidine formation (2)



Results similar to those in *Figure 1* were obtained also at different reaction temperatures and different initial -4,6 salt/H_2O ratios.

The kinetic equations now become:

$$\frac{dx}{dt} = k_1 \cdot a \cdot c - k_2 \cdot x \cdot w$$

$$= k_1(a_{\text{initial}} - x - p)(c_{\text{initial}} - x) - k_2 \cdot x \cdot (x + w_{\text{initial}})$$

and

$$\frac{dp}{dt} = k_3 a$$

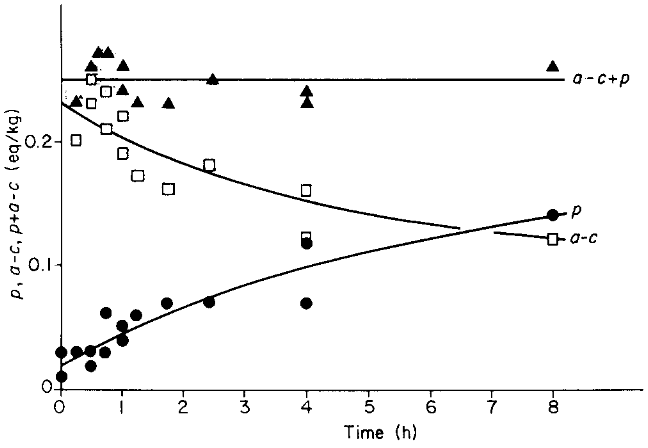


Figure 1 Pyrrolidine content (*p*) and unbalance in amino- and carboxyl end groups ($a-c$) as a function of reaction time, measured on dry prepolymers. $T=210$°C; initial-4,6 salt/H_2O ratio 93/7; excess DAB 1.2 wt% with respect to -4,6 salt. (●) *p*, (□) $a-c$, (▲) $a-c+p$

Table 1 Prepolymerization of nylon-4,6 salt at 210°C at a −4,6 salt/water ratio of 93/7 (wt/wt) and 1.2 wt% excess DAB with respect to −4,6 salt

Series	Exp. no.	Time (h)	End groups (dry prepolymers) (eq/kg)			Solution concentration (eq/kg)					P_n
			a	*c*	*p*	*a*	*c*	*p*	*x*	*w*	
Initial −4,6 salt/H_2O mixture			–	–	–	8.11	7.86	0.00	0.00	3.85	1.00
VII	517	0	4.77	4.08	0.01	4.09	3.51	0.01	4.35	8.20	2.10
(four samples		0.5	1.98	1.71	0.04	1.62	1.40	0.03	6.46	10.31	5.23
from one		1	1.26	1.03	0.06	1.02	0.83	0.05	7.03	10.88	8.41
experiment)		4	0.71	0.56	0.14	0.57	0.45	0.11	7.41	11.26	14.15
VIII	419	0.5	1.70	1.40	0.02	1.38	1.14	0.02	6.72	10.57	6.29
(separate poly-	414	0.75	1.43	1.14	0.03	1.16	0.92	0.02	6.94	10.79	7.59
condensations)	412	1	1.11	0.85	0.05	0.89	0.68	0.04	7.18	11.03	9.87
	416	4	0.71	0.51	0.08	0.57	0.41	0.06	7.45	11.30	15.36
	411	8	0.69	0.55	0.17	0.55	0.44	0.14	7.42	11.27	14.15

The best fit for the independent parameters k_1, k_2 and k_3 is estimated by computerized minimization of the sum of squares:

$$\Sigma s^2 = (a_{\text{calc}} - a_{\text{measured}})^2 + (c_{\text{calc}} - c_{\text{measured}})^2 + (p_{\text{calc}} - p_{\text{measured}})^2.$$

Application of this procedure to the data of series VII and VIII (*Table 1*) leads to a very good fit for the experimental points, as demonstrated in *Figures 2* and *3*, where the solid lines represent the calculated functions for a, c and p, respectively.

This procedure was applied to kinetic results at different temperatures as well. The results are summarized in *Table 2*. Provided the experimental errors in a, c and p are mutually independent, the last column of *Table 2* gives the standard deviation of the residuals. In this case, this standard deviation has the same order of magnitude as the experimental titration error, i.e. $\pm 0.01\,\text{eq}\,\text{kg}^{-1}$, which indicates a good fit of the experimental points with the applied model.

At first glance this result may seem surprising, because studies on the polycondensation kinetics of nylon-6,6 salt in the presence of water have shown that the foreward reaction rate constant for polyamidation (k_1) is dependent on the initial water concentration[8,9]. For our experimental conditions, however, the increase in water concentration caused by condensation is relatively small, as considerable conversion has already taken place during heating (see *Table 1*).

The absence of numerical values for low temperatures (180°–190°C) in *Table 2* is caused by solidification of the reactor contents by crystallization after a relatively short time. At high temperatures (230°C), no k-values can be given because conversion has already taken place to a major extent during heating and the system is in equilibrium soon after the reaction temperature is reached.

A least-squares analysis for $\ln k_1$ and $\ln k_3$ as a function of $1/T$ leads to following Arrhenius equations:

$$\ln k_1 = -9.76 \times 10^3/T + 20.2$$

and

$$\ln k_3 = -16.48 \times 10^3/T + 30.2$$

The Arrhenius equation for k_1 given above is only slightly different from the one published in a previous study, where no correction for the pyrrolidine formation was applied[6]. No clear relation between the equilibrium constant K and temperature can be observed, so it is uncertain whether the amidation reaction is exo- or endothermic under these conditons.

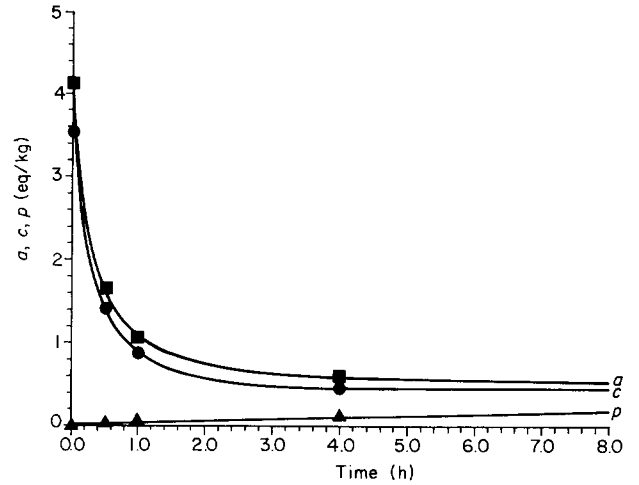


Figure 2 Amino (■), carboxyl (●) and pyrrolidine (▲) concentration as a function of reaction time for series VII of *Table 2*. Solid lines have been calculated with the model

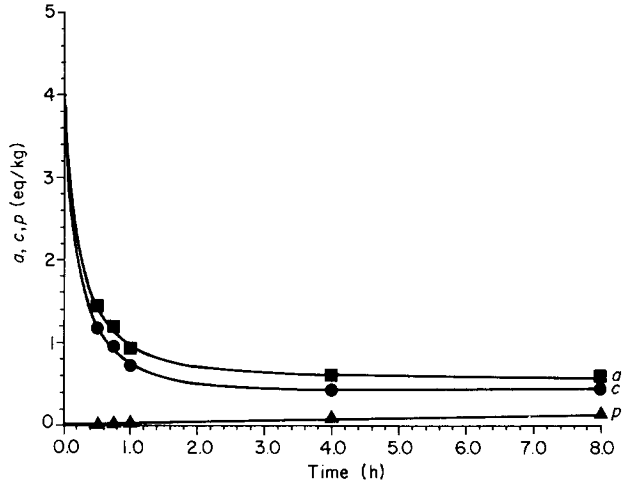


Figure 3 Amino (■), carboxyl (●) and pyrrolidine (▲) concentration as a function of reaction time for series VIII of *Table 2*. Solid lines have been calculated with the model

According to literature, the reaction enthalpy for the nylon-6,6 salt polycondensation changes from negative to

Table 2 Reaction rate constants for the amidation reaction and pyrrolidine formation for an initial -4,6 salt/H_2O ratio of 93/7 (wt/wt) and 1.2 wt% excess DAB with respect to -4,6 salt

Series	Exp. No.	Temp.	k_1 ($\text{kg}\,\text{h}^{-1}\,\text{eq}^{-1}$)	k_2 ($\text{kg}\,\text{h}^{-1}\,\text{eq}^{-1}$)	K	k_3 (h^{-1})	$\sqrt{\frac{\Sigma s^2}{n-1}}$
I	557-558	180	0.33	–	–		
II	525	180	0.25	–		0.003	
III	560	190	0.27	–		0.007	
IV	523	190	0.39	–		0.007	
V	407-429	200	0.66	0.0023	287	0.009	0.04
VI	534	200	0.64	0.0022	291	0.012	0.04
VII	517	210	0.81	0.0029	279	0.030	0.08
VIII	411-419	210	1.03	0.0030	343	0.021	0.03
IX	515	210	1.01	0.0042	240	0.020	0.05
X	532	220	1.58	0.0047	336	0.050	0.05
XI	524	230	–	–	220	0.060	

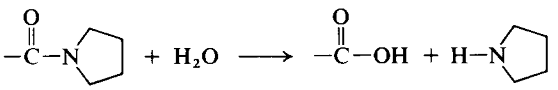
positive as the water content is increased and amounts to zero at a water content of about 18 wt% in the equilibrium situation, which is very close to the water content in our experiments. The average value of the equilibrium constant for nylon-4,6, i.e. 285, agrees quite well with a value of 300 for nylon-6,6 at comparable water content[9].

Solid state polycondensation (SSP)

Figure 4 shows the increase in relative viscosity (η_{rel}) during SSP at 260°C for a typical nylon-4,6 prepolymer. As a result of its high melting temperature, nylon-4,6 can be aftercondensed in the solid state at a much higher temperature than practised for nylon-6 and -6,6 and very high molar mass nylon-4,6 (M_w of about $100 \times 10^3\,g\,mol^{-1}$) can be obtained without the need to use accelerators.

One of the major factors affecting the rate of increase in molar mass during SSP is the excess of aminogroups with respect to carboxyl groups in the starting prepolymer $(a-c)_{PP}$. *Figure 5* shows the differences in SSP-velocity for a nearly balanced prepolymer (curve A); for an overcompensated prepolymer (curve B) and for a prepolymer with an appropriate excess of amino groups (curve C).

The amino excess in prepolymer is necessary because in our opinion pyrrolidine end groups are formed during SSP as well (reaction 2) and are subsequently stripped with water:



So, ultimately, amino-terminated chains turn into carboxyl terminated chains by the loss of pyrrolidine.

Properties of high molar mass nylon-4,6

Molar mass distribution. Table 3 summarizes the results of molar mass and molar mass distribution measurements of some nylon-4,6 samples, measured according to different techniques, i.e. light scattering, end group analysis and high temperature g.p.c. As can be seen from this Table, the ratio of M_w from light scattering to M_n from end group analysis amounts to approximately 2.2. However, large deviations from this value sometimes are observed, especially at high molar mass, due to uncertainty in the end group analysis. For this reason, we have more confidence in the g.p.c. analysis, which yields an M_w/M_n of 2.2–2.3 for most nylon-4,6 samples.

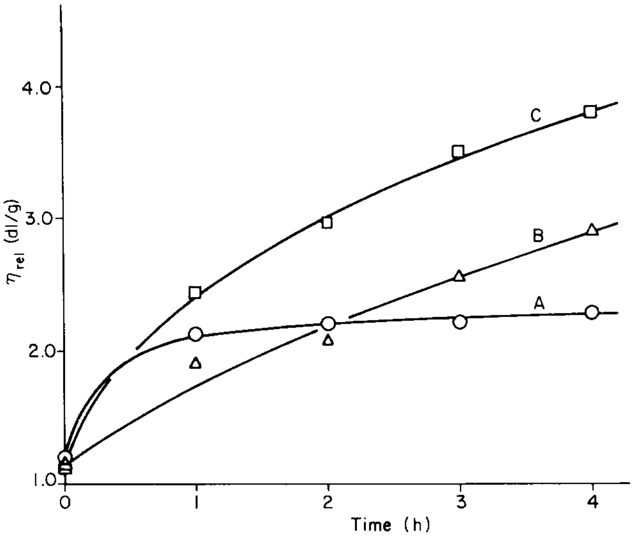


Figure 5 Increase in relative viscosity as a function of SSP time at 260°C for various prepolymers: curve A: (○) STA561 = $(a-c)_{PP}$ = 0.01 eq/kg; curve B: (△) STA566 = $(a-c)_{PP}$ = 0.64 eq/kg; curve C: (□) STA591 = $(a-c)_{PP}$ = 0.28 eq/kg

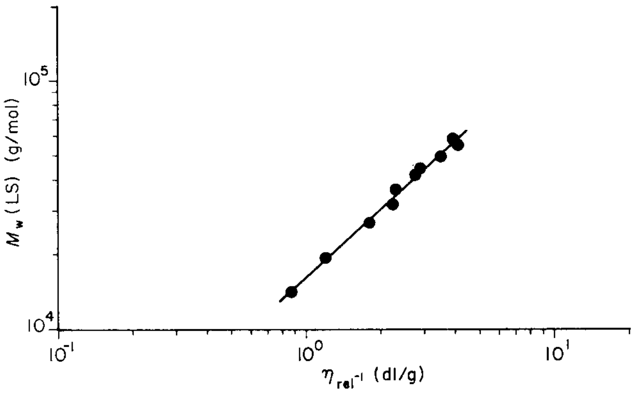


Figure 6 Relation between M_w from light scattering and relative viscosity for nylon-4,6

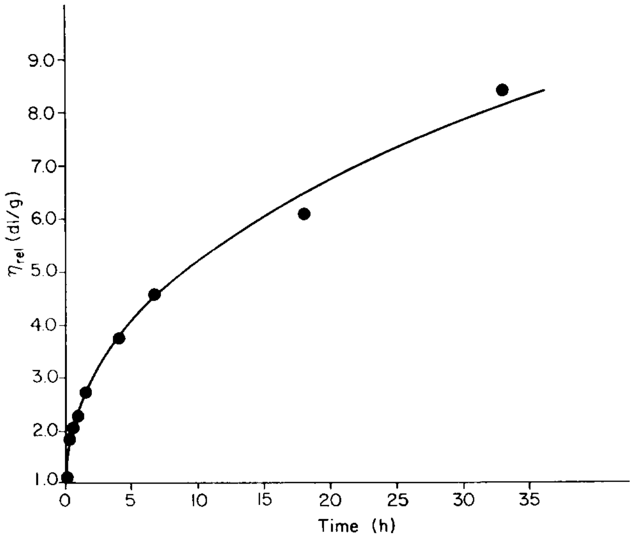


Figure 4 Increase in relative viscosity as a function of SSP time at 260°C for a typical nylon-4,6 prepolymer

Figure 7 presents high temperature g.p.c. chromatograms of Stanyl® (nylon-4,6) and Ultramid A4 (nylon-6,6), i.e. samples 11 and 12 from *Table 3*, showing a relatively narrow molar mass distribution for Stanyl® with respect to this particular nylon-6,6 sample. From a comparison of the low temperature g.p.c. chromatograms recorded in dichloromethane after trifluoroacetylation it can also be concluded that the molar mass distribution for Stanyl® is not broader than for this nylon-6,6 sample (see *Figure 8*). No significant change in the g.p.c. chromatogram for Stanyl® was observed after injection moulding at 315°C. This is an indication that in spite of the relatively high processing temperature, which is about 30°C higher

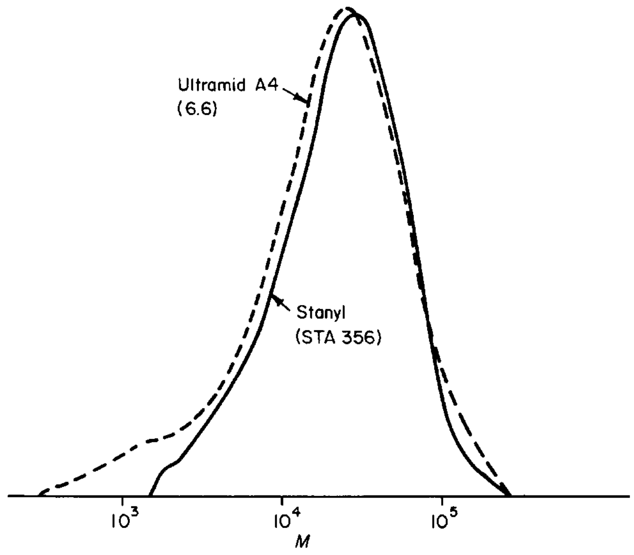


Figure 7 High temperature g.p.c. chromatograms of Stanyl® (nylon-4,6) (——) and Ultramid A4 (nylon-6,6) (– – – –)

than for nylon-6,6, no crosslinking or gel formation occurs in Stanyl®. A least-squares analysis for the relation between $\ln M_w$ and $\ln(\eta_{rel} - 1)$ for the nylon-4,6 samples from *Table 3* results in:

$$M_w = 16.24 \times 10^3 (\eta_{rel} - 1)^{0.926}$$

This relation is plotted double-logarithmically in *Figure 6*. We found that nylon-6 samples with η_{rel} in between 2.5 and 3.5 meet this relation as well.

Rate of crystallization

From a theoretical point of view, the best way to compare rates of crystallization of nylon-4,6 with those of nylon-6 and nylon-6,6 is to measure isothermally the radial growth rate of spherulites as a function of temperature. From a practical point of view, however, this approach is not very suitable. A different way to compare relative rates of crystallization is to measure the supercooling ($T_m - T_c$) as a function of cooling rate in repeated d.s.c. scans. The results of these measurements are shown in *Figure 9*; obviously, ($T_m - T_c$) is smaller for Stanyl® than for nylon-6,6 and -6, especially at high cooling rates.

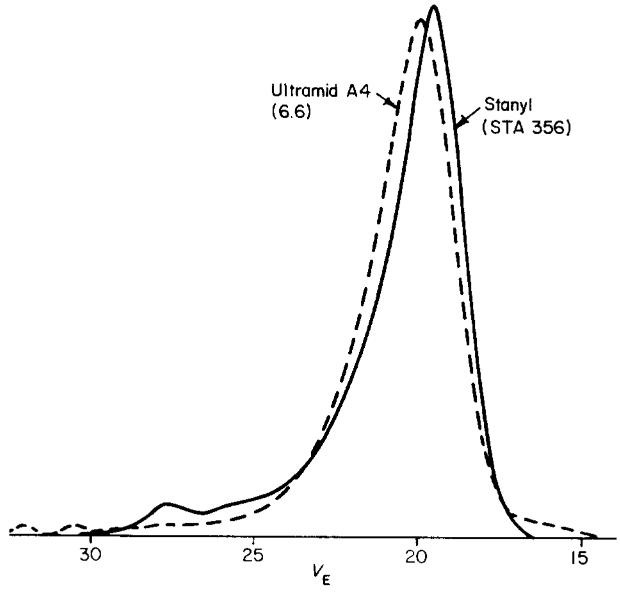


Figure 8 Low temperature g.p.c. chromatograms after trifluoroacetylation of Stanyl® (nylon-4,6) (——) and Ultramid A4 (nylon-6,6) (– – – – –)

The phenomenon points to a higher rate of crystallization of Stanyl® with respect to -6 and -6,6, which can be ascribed to the higher symmetry of the nylon-4,6 molecule[5].

Melting point and degree of crystallinity

In *Figure 10*, typical d.s.c.-curves are presented for a nylon-4,6 sample after 4 h SSP. The first heating curve shows a high melting point of 293°C and a high enthalpy of fusion (ΔH_f) of $138\,J\,g^{-1}$, or $27\,kJ\,mol^{-1}$. The second melting point, recorded after cooling at the relatively slow rate of $5°C\,min^{-1}$ from 315°C and subsequent heating from 220°C, is observed at 290°C with $\Delta H_f = 98\,J\,g^{-1}$, or $19.4\,kJ\,mol^{-1}$. Under the same d.s.c. conditions, ΔH_f of nylon-6 and -6,6 amounts to 63 and $77\,J\,g^{-1}$, or 7.1 and $17.4\,kJ\,mol^{-1}$ respectively.

If we assume that the enthalpy of fusion for completely crystalline nylon-4,6 and nylon-6,6 (ΔH_f^0) has the same value as for nylon-6, the latter one being $230\,J\,g^{-1}$[10] than Stanyl®, nylon-6,6 and nylon-6 would have degrees of crystallinity of about 43%, 33% and 27%, respectively.

Table 3 Molar mass distribution of a number of nylon-4,6 samples

		Light scattering and end group analysis			High temperature g.p.c.		
Sample no.	Rel. visc. (dl/g)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
1	1.87	14	6.1	2.30	6	13	2.3
2	2.20	19	9.3	2.04	9	20	2.3
3	2.81	27					
4	3.20	32	16.9	1.95	16	37	2.3
5	3.24	36					
6	3.70	43	21.7	2.00	15	44	2.9
7	3.82	44					
8	4.49	48					
9	4.90	58	24.4	2.37	19	58	3.1
10	4.99	55					
11	3.46	–	21.5	–	14	32	2.2
12[a]	3.18	–	16.7	–	8	31	3.8

[a] Ultramid A4 (BASF, W. Germany)

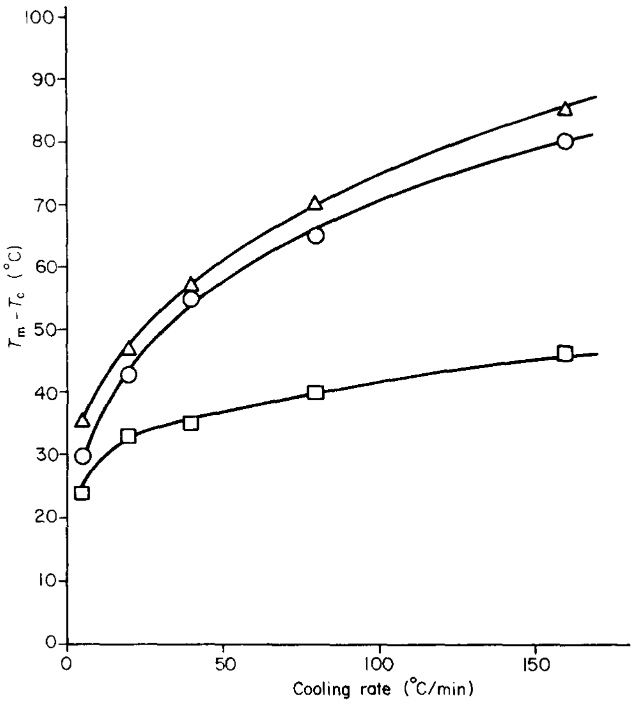


Figure 9 Supercooling ($T_m - T_c$) as a function of cooling rate in d.s.c. apparatus for Stanyl^R (nylon-4,6) (□); Ultramid A4 (nylon-6,6) (○) and nylon-6 (△)

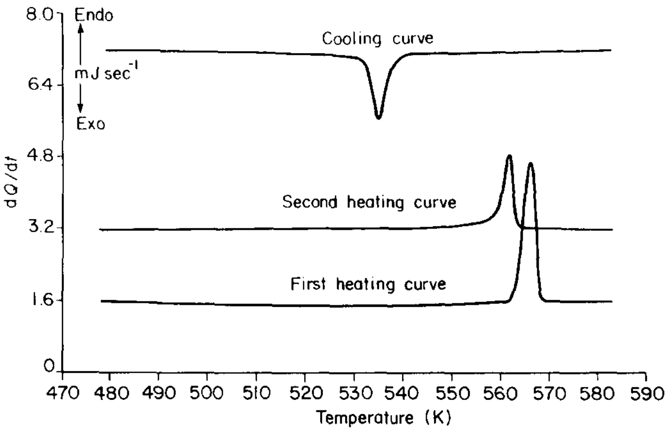


Figure 10 D.s.c. curve of Stanyl®. Heating rate 5°C min^{-1}; cooling rate: 5°C min^{-1}

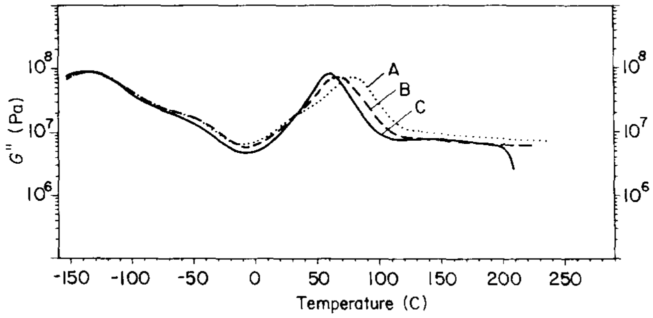


Figure 11 Loss shear modulus (G'') of dry Stanyl^R (nylon-4,6): (curve A); Ultramid B3 (nylon-6): (curve B); and Ultramid A3 (nylon-6,6): (curve C)

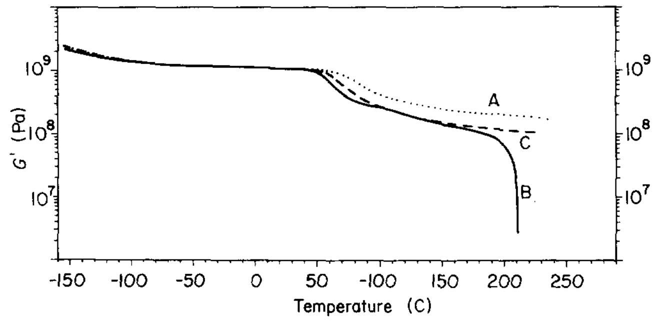


Figure 12 Storage shear modulus (G') of dry Stanyl^R (nylon-4,6): (curve A); Ultramid B3 (nylon-6): curve B); and Ultramid A3 (nylon-6,6): (curve C)

Longer solid state polycondensation not only results in higher molar mass but also in increasing melting temperature and heat of fusion. A ΔH_f of 178 J g^{-1} (or 35.2 kJ mol^{-1}) was observed at a melting temperature of 310°C after 33 h SSP at 260°C, indicating a degree of crystallinity of about 77%.

Visco-elastic behaviour

The glass transition temperatures of nylon-4,6, -6 and -6,6 were measured by torsion pendulum at 0.2153 Hz after thorough drying. The maximum of the loss shear modulus G'' indicates a T_g of 78°C for nylon-4,6, 66°C for nylon-6,6 and 59°C for nylon-6 (see *Figure 11*). From *Figure 12*, it can be seen that nylon-4,6 exhibits a smaller drop in storage shear modulus G' at T_g with respect to nylon-6,6 and -6, resulting in a higher storage modulus above T_g. This phenomenon probably stems from the higher crystallinity of nylon-4,6 with respect to nylon-6,6 and nylon-6[11].

Summary of the most relevant physical properties of Stanyl^R

The physical properties of nylon-4,6, -6 and -6,6 are summarized in *Table 4*. The high storage modulus as well as the low loss factor $tg\,\delta(G''/G')$ above T_g for Stanyl® potentially offer attractive mechanical properties such as,

Table 4 Major differences in physical properties between nylon-4,6, nylon-6,6 and nylon-6

	D.s.c. (5°C min^{-1})				Torsion pendulum				Gradient column
	T_m second scan (°C)	T_c (°C)	ΔH_f (J g^{-1})	Crystallinity (%)	T_g (dry) (°C)	G'^a (Pa)	G''^a (Pa)	$tg\,\delta^a$	Density (kg m^{-3})
Nylon-4,6 (Stanyl^R)	290	264.5	98	43	78	2×10^8	8.6×10^6	4.3×10^{-2}	1180
Nylon-6,6	262	218	77	33	66	1.3×10^8	7×10^6	5.4×10^{-2}	1140
Nylon-6	222	173	63	27	59	1.1×10^8	7×10^6	6.4×10^{-2}	1140

^{a} At 180°C

respectively, high dimensional stability and low creep rate.

The T_m's and T_g's of Stanyl® offer better retainment of the mechanical properties at elevated temperatures for both yarn and engineering-plastic applications. The higher crystallinity of Stanyl® with respect to nylon-6 and -6,6 offers better solvent resistance at room temperature as well as at elevated temperature.

The high crystallization temperature and the high rate of crystallization of Stanyl® offers the possibility to achieve shorter cycle times with respect to nylon-6 and nylon-6,6 for injection moulding applications.

ACKNOWLEDGEMENTS

The authors are grateful for the permission from the DSM Management to publish this work. The authors also express their appreciation to Ir P. J. de Jong (DSM Mathematical Department), Dr V. Mathot (DSM Fundamental Polymer Research Department), Dr R. Pikaart (DSM Analytical Department), Dr C. Vonk (DSM Physical Department) and many other colleagues for their support. Finally, the authors wish to thank Dr R. J. Gaymans (University of Twente) for stimulating discussions.

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