Copolyamides of nylon-4,6 and nylon-4,T — **Source link** ⬈

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Copolyamides of Nylon-4,6 and Nylon-4,T

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Synopsis

Copolyamides of nylon-4,6 and nylon-4,T were prepared by a two-step method: (1) a prepolymerization in an autoclave (40 min at 210°C) and (2) a postcondensation in the solid state (4 h, 260°C). On these materials was studied the melting behavior with DSC, the crystalline structure with WAXS, the water absorption, and the mechanical properties with a torsion pendulum. In these copolyamides the order was found to remain high, but the crystalline structures of -4,6 and -4,T were not isomorphous. The torsion moduli increased with -4,T content both at RT and at 140°C.

INTRODUCTION

Random copolyamides have been of interest for a long time and special attention was given to the copolyamides with adipic acid and terephthalic acid. The length of the adipamide and terephthalamide units differ only little and isomorphous replacement seems possible.[1-6]

The melting temperature of adipamide/terephthalamide copolymers did not show a melting temperature depression but the temperature increase with composition was never linear.[1-3]

One of these copolyamide with adipamide and terephthamide units is nylon-4,6/-4,T. About this system little is known. Aubineau[4], synthesized a 50/50 copolymer starting from acid chlorides and found a melting temperature of 340°C. The syntheses of these copolymers is difficult, not only because of the high melting temperatures (T_m for -4,6 is 290°C[7] and for -4,T 427/475°C[8]) but also because of a side reaction, the cyclization of the diamine 1,4-diaminobutane to pyrrolidine.[7] For nylon-4,6 a synthesis from its salt has been developed.[7,9] Nylon-4,T could not be synthesized from its salt to a high molecular weight, but a synthesis with terephthaloylchloride was possible.[8,10] Both -4,6 and -4,T crystallize easily and form well ordered structures.[7-9] The mechanical properties of -4,6 are excellent particularly at higher temperatures.[9] For the -4,T polyamide no mechanical properties have been recorded.

We studied the synthesis of nylon-4,6/-4,T copolymers by a bulk method and evaluated some of their properties.

EXPERIMENTAL

Materials

Teterephthalic acid (TA), dimethyl terephthalate (DMT), adipic acid, and tetramethylene diamine (TMDA) were obtained from Aldrich (Europe). TMDA was distilled prior to use.

Nylon-4,6 salt was prepared in methanol[7] and had a pH of 7.2 (1% solution in water). Nylon-4,T salt was prepared in water and precipitated with ethanol[8]; it had a pH of 7.25.

Di(4-Amino butyl)terephthalamide (DABT)

To a dry reaction flask fitted with nitrogen bleed and distilling heads was added 99 g DMT (0.5 mol) and 132 g TMDA (1.5 mol). This mixture was warmed up in 60 min to 115°C and kept at that temperature for 2 h. At 65–75°C the mixture formed a homogeneous liquid and methanol started boiling off. After some time, precipitation started and when the temperature of 115°C was reached, the mass had solidified again. The reaction product was grinded and extracted with diethyl ether. In the IR spectrum of the material a strong amide I band at 1620 cm^{-1} was present and the ester band at 1720 cm^{-1} was absent.

Prepolymerization

A 100 mL stainless steel autoclave was either charged with 25 g of a mixture of nylon-4,6 salt and nylon-4,T salt, 1.25 mL water, and TMDA (8 mol% excess) or with a 25 g mixture of nylon-4,6 salt and DABT, 1.25 mL water, and so much adipic acid that the TMDA excess was 8 mol%.

The autoclave was flushed with nitrogen and was given a starting pressure of 5 bar. The autoclave was heated in 60 min to 210°C and kept at that temperature for 40 min.

Postcondensation in the Solid State

The powdered prepolymers were postcondensed in the solid state in a fluidized bed reactor in a stream of N_2 and steam (ratio 2 : 1), for 4 h at 260°C.

Characterization

Amine end groups were determined by potentiometric titrations in phenol/water at 22°C.[11] Carboxyl end groups were determined potentiometrically after dissolving the polymer at higher temperatures in o-cresol and diluting with benzylalcohol.[12] The 70/30, 50/50, and 0/100 polymers could not be analyzed as they did not dissolve.

The pyrrolidine end groups were determined in hydrolyzed samples by gas chromatography. To hydrolyze the polymer, 0.06 g material and 0.5 mL 6N HCl in a sealed tube under N_2 were heated for 10 h in an oil bath at 130°C. After cooling 0.2 mL of the supernatent liquid was withdrawn and treated with 0.7 mL 2N alcoholic sodium hydroxyde solution to free the amines. The gas chromatography analyses of 1 μL of this solution was carried out using a preconditioned chomasorb (RTM) 130 column 1.5 m $\times$ 0.6 cm. From the ratio of the TMDA and pyrrolidine peaks and a knowledge of the approximate TMDA concentration in the polymer, the pyrrolidine concentration can be calculated from:

$$\frac{[\text{pyrrolidine}]}{\text{TMDA}} \times \frac{1000}{\text{average mol. wt. repeat unit}}$$

The η_{inh} were determined using 0.5% solutions in 96% H_2SO_4.

The ground polymer, dried for 24 h at 100°C in a vacuum oven, was melt pressed at 10°C above its melting temperature and cooled at 20°C min^{-1}. DTA studies were conducted on a DuPont 990 Thermal Analyser at a heating rate of 20°C min^{-1}. Torsion pendulum analysis were conducted at a constant frequency of 0.215 Hz and a heating rate of 1°C min^{-1}, on samples 50 mm long, 10 mm wide, and 2 mm thick.

Conditioning: dry, 24 h at 100°C in a vacuum oven, 50% rh, 3 months in a desiccator at RT above a saturated solution of sodium bichromate, 100% rh, 3 months in a desiccator above water.
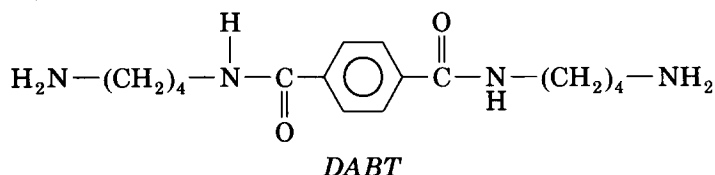
RESULTS AND DISCUSSION

Synthesis

With Nylon-4,T Salt

The results of the copolymerization with mixtures of nylon salts are given in Table I. With increasing -4,T content, the η_{inh} of the samples decreased. This is in line with the very low values reported for nylon-4,T.[8] The end group analysis of the copolyamides give low values for the pyrrolidine and amine groups and the acid concentration of the 90/10 and the 80/20 are higher than that of -4,6. This suggests that the decreasing molecular weights must be due to an increase in acid end group content. An explanation for this might be that due to the low reactivity of the aromatic acid[13] amine is lost before it has reacted.

With TMDA Substituted Terephthalic Acid

By the copolymerization, the terephthalicacid–TMDA reaction seems to be the rate determining step. In an attempt to obtain higher molecular weights the polymerization was carried out with the diamide di(4-amino butyl) terephthalamide (DABT).

$$H_2N-(CH_2)_4-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{\|}}{N-C}}-\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{}}{C-N}}-(CH_2)_4-NH_2$$

DABT

The copolymers (70/30 and 50/50) were synthesized by mixing DABT, adipic acid, and -4,6 salt and polymerizing using the salt procedure (Table II).

TABLE I
Nylon–Salt Mixtures Polymerization

Materials	$[-NH_2]$ (meq/g)	$[-COOH]$ (meq/g)	[Pyr] (meq/g)	η_{inh}
100/0	0.055	0.018	0.02	1.30
90/10	0.011	0.061	0.02	1.08
80/20	0.013	0.129	0.02	0.97
70/30	0.019	—	0.03	0.72
50/50	0.031	—	0.06	0.49
0/100(8)	—	—	—	0.19

TABLE II
Polymerization with DABT

Materials	$[-NH_2]$ (meq/g)	$[-COOH]$ (meq/g)	[Pyr] (meq/g)	η_{inh}
100/0	0.055	0.018	0.02	1.30
70/30	0.013	—	0.02	1.04
50/50	0.053	—	0.02	0.75

TABLE III
Melting Behavior

Materials	First run		Second run	
	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)
100/0	305	134	290	77
90/10	305	125	289	68
80/20	309	109	293	64
70/30	311/337	111	302	73
50/50	326/350	82	310	76
0/100[a]	—	—	428/475[a]	108[a]

[a]Solution cast film.[8]

These copolyamides had a lower η_{inh} than nylon-4,6 and the pyrrolidine and amine end groups were low; but compared to the corresponding copolyamides prepared from the mixtures of the nylon salts, they had a higher η_{inh}.

DTA

The postcondensed polymers were scanned up to 10°C past their melting transitions, cooled at 50°C/min, and scanned again. The observed melting transitions and heats of fusion are given in Table III.

The melting transition of the postcondensed powders was a single peak for nylon-4,6 and for the copolyamides 90/10 and 80/20 and a double peak for 70/30, 50/50, and 0/100.[8] After remelting, only the 50/50 had two endotherms of which the higher transition was small. A cast film of -4,T had also a double melting transition.

The main transitions were in the second run at a 15°C lower temperature than in the first run. The melting temperatures (second run, main endotherm) increased gradually with the terephthalic content (Fig. 1). The heats of fusion in the first runs are considerably higher than in the second runs (Table III). The heats of fusion of the copolyamides (second run) are somewhat lower than that of nylon-4,6 where the 80/20 composition seems to have the lowest order.

WAXS

The WAXS was studied on melt pressed films and a solution cast film for -4,T. The d_{010} values for -4,6 and -4,T are comparable but the d_{100} differ considerably (Table IV). The packing of the chains in the unit cell is thus
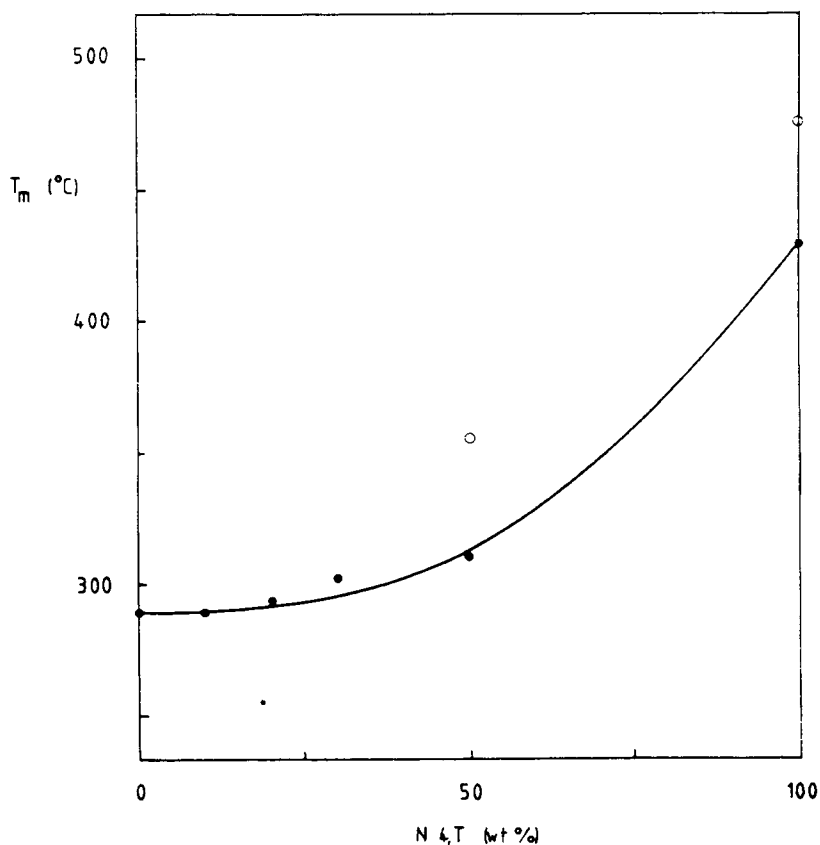
Fig. 1.   Melting temperatures, second run: (●) main peak, (○) second peak.

different. In the copolyamides the d_{010} and d_{100} of the -4,6 gradually amalgamate and the intensities of -4,T are very weak in 70/30 and weak in 50/50, but have values comparable to -4,T. In the compolyamides 70/30 and 50/50, two types of crystals are present and the packing density of the -4,6 part is reduced by the presence of the -4,T units.

TABLE IV
Wide-Angle X-Ray Data of Melt Pressed Films

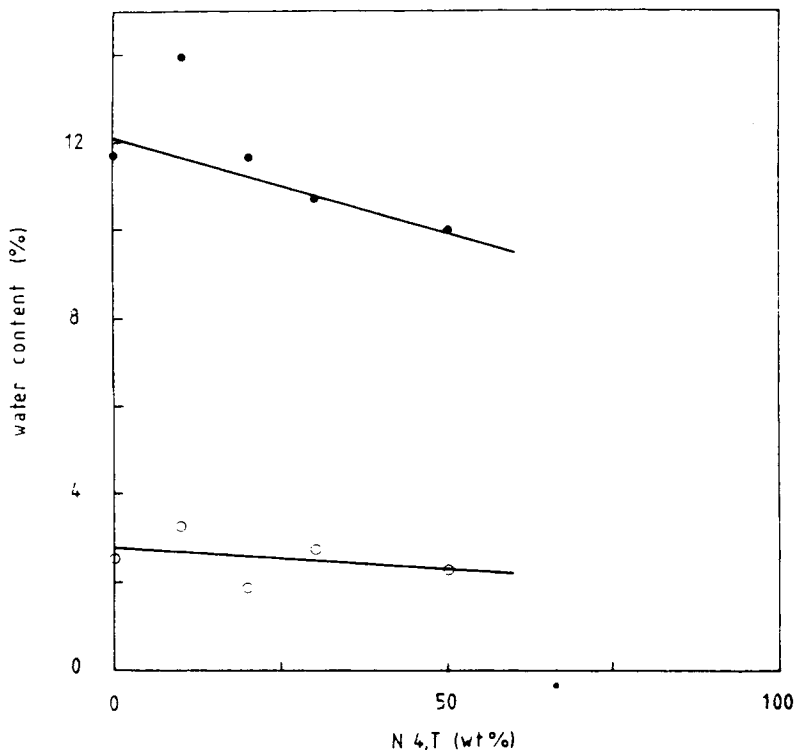| Materials	d_{010}			d_{100}	
	-4,T	-4,6		-4,6	-4,T
100/0		3.87		4.14	
90/10		4.02		4.14	
80/20			4.08		
70/30			4.20		4.86
50/50	3.86				4.90
0/100[a]	3.87				4.87

[a]Solution cast film.[8]

Fig. 2.   Water absorption: (○) 50% rh, (●) 100% rh.

Water Absorption

As nylons absorb water the properties of the material changes. The amount of water absorbed depends on the amide content, the aromaticity and the crystallinity.[14,15] The water absorption of the copolyamides (Fig. 2) decreases with increasing -4,T content both at 50% rh as 100% rh. As the crystalline order changes only marginally the decrease in water absorption with -4,T content must be due to the increase in aromaticity.

Mechanical Properties

The torsion properties were studied on melt pressed stips, dry and conditioned at 60 and 100% r.h. The glass transition (G''_{max}) was in all cases a single transition. The glass transition temperatures (temperature at G''_{max}) increased over the whole range linearly with the -4,T content (Fig. 3). This concentration dependence was stronger for the dry samples than the wet samples.

The torsion moduli (log G') of dry samples at 20 and 140°C are given in Figure 4. As can be seen the moduli both at 20 and 140°C increased considerably with -4,T content. That these copolyamides have at 140°C high moduli underlines the already observed DTA results that the order in these copolyamides remains high.

The β-transition at -80°C at 60% rh and the γ-transition t -145°C were found to be independent of the polymer composition.
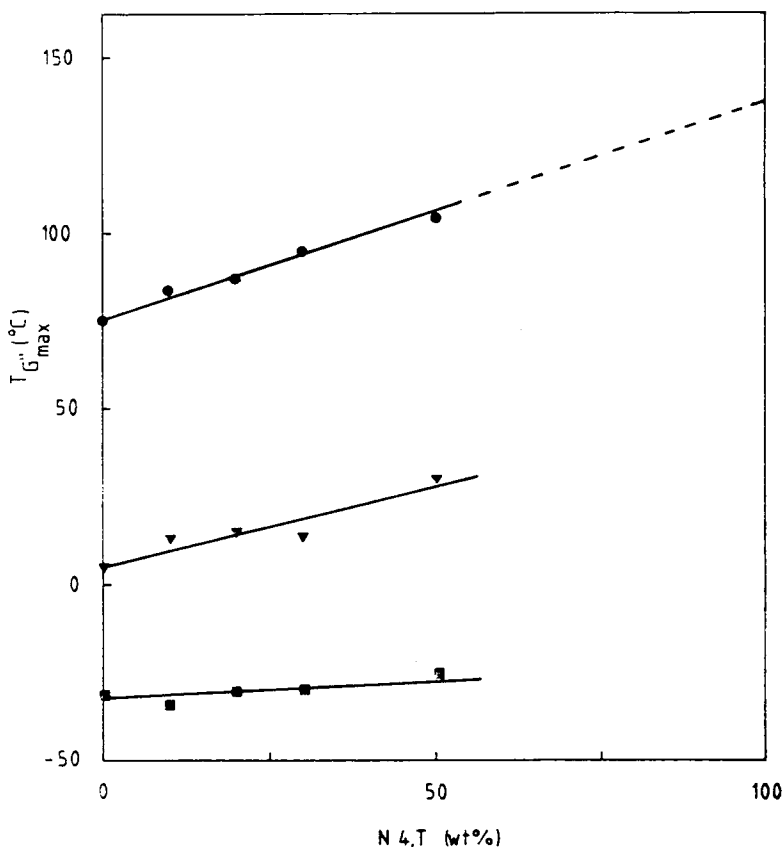
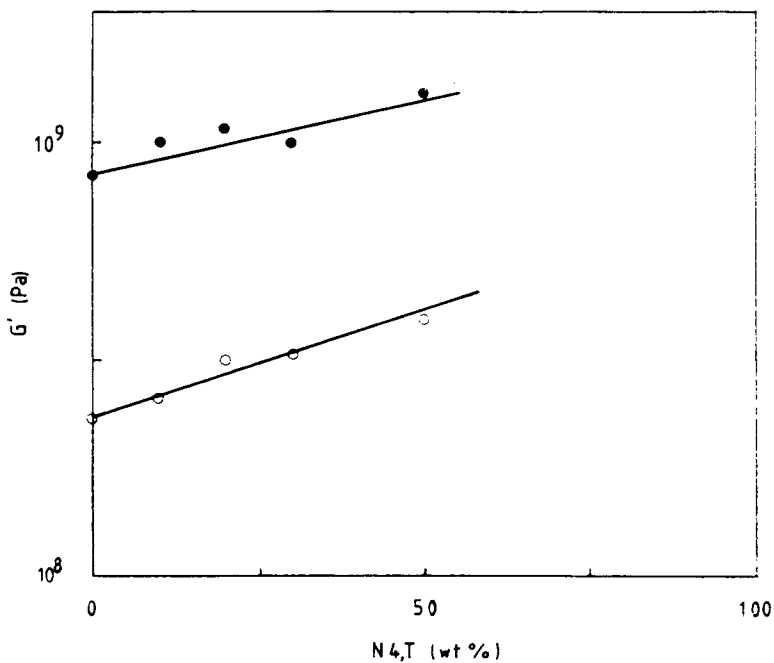Fig. 3.   Glass transition temperatures: (●) dry, (▼) 50% rh, (■) 100% rh.

Fig. 4.   Torsion pendulum moduli of dry samples: (●) 25°C, (○) 140°C.

CONCLUSIONS

The synthesis of copolyamides of -4,6 and -4,T is hampered by the low reactivity of the terephthalic acid. With DABT higher molecular weights could be obtained.

The order of the -4,6 cell structure in the copolymer is decreased and at higher -4,T concentrations, a separate -4,T phase is present. This combined with the somewhat lower heats of melting of the copolyamides suggests that there is no true isomorphous replacement in this system, but the disordering effects are minimal.

Due to this minimal loss of order in these copolymers, the shear moduli above the glass transition temperature remain high. The actual moduli of these materials are higher than those of nylon-4,6 at 20 and 140°C.

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