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Published on: 01 May 1985 - Journal of Polymer Science Part A (Wiley)

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The Synthesis and Some Properties of Nylon 4,T

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Synopsis

The synthesis of nylon 4,T from tetramethylenediamine and a terephthalic acid derivative was studied in a two step-process: prepolymerization, followed by postcondensation in the solid state (4 h, 290°C). The prepolymers were prepared by the nylon salt method, ester polymerization method, interfacial method, and a low temperature solution method. A maximum η_{inh} of 1.52 was obtained. From a solution in trifluoroacetic acid, films were cast and on these films we studied its IR spectrum, WAXS, and melting behavior with DSC. A boiled up sample had a double melting transition at 434 and 475°C and a ΔH_f of 130 J/g.

INTRODUCTION

Partial aromatic polyamides have a high glass transition temperature and a strong chain interaction.^{1,2} If this partial aromaticity is combined with a regular spacing of the amide groups in the chain, their crystallinities are also high. Fiber properties of these polymers are characterized as having a high initial modulus, good strength, and good high temperature properties.^{2,3} However, with this high order the melting temperatures are high—mostly too high for melt processing—and fibers have to be spun by a solution method.

One of these partial aromatic polyamides with a high amide content and a regular amide spacing is polytetramethyleneterephthalamide (nylon 4,T).

This polymer can be prepared from tetramethylenediamine and a terephthalic acid derivative. Nylon 4,T has a similar amide spacing as nylon 4,6 and poly-*p*-phenyleneterephthalamide. The synthesis of this polymer has been studied by an interfacial and a low-temperature solution method.

Shashoua and Eareckson² prepared the material by an interfacial method from terephthaloyl chloride (TCl) in methylene chloride (0.015 mol/L) and tetramethylenediamine (TMDA) (0.015 mol/L) with potassium hydroxide (0.030 mol/L) in water. The so obtained polymer had an η_{inh} of 1.20. In a Celanese patent⁴ the nylon 4,T syntheses has been described with TCl in xylene (0.1 mol/L) and TMDA (0.1 mol/L), MgO in water; their reported η_{inh} was 1.56.

Aubineau et al.⁵ studied the syntheses in solution. To a solution of TMDA (0.1 mol/L) and triethylamine (0.2 mol/L) in chloroform TCl (0.1 mol/L) was added. The precipitated polymer had an η_{inh} of 0.58.

As yet, no high temperature synthesis has been reported. At higher temperatures side reactions may take place such as the cyclization of TMDA to pyrrolidine, a cyclic monofunctional secondary amine. Nylon 4,T has a high crystallinity and a melting point as measured with DTA of 436°C.² The polymer is very insoluble and only sulfuric acid and trifluoroacetic acid are given as solvents.² Fibers could be spun from H₂SO₄ solutions and

they had a high initial modulus of 90 g/den combined with a good strength of 5.5 g/den. We had another look at the synthesis of this polymer and studied some of its properties.

EXPERIMENTAL

Materials

The materials terephthaloyl chloride (TCl), tetramethylenediamine (TMDA), hexamethylenephosphourostriamide (HMPT), *n*-methylpyrrolidone (NMP), and tetrahydrofuran (THF) and chloroform were distilled prior to their use. All other chemicals were used as received.

Polymerization

Nylon 4,T salt: To a solution of 106 g TMDA (1.2 mol) in 1000 mL of water was added 200 g terephthalic acid (TA) (1.2 mol). The temperature increased to 60°C and at some point the solution was virtually clear. After cooling the mass was precipitated by adding 2 L of ethanol. The salt was filtered, washed, and dried (287 g). A 1% solution in water had a pH of 7.25.

Salt polymerization: Ten grams of nylon salt and 3 g solvent were charged in a 100 mL stainless steel autoclave. After flushing with nitrogen, a starting pressure of 5 bar was given. The autoclave warmed up in 60 min to 210°C and remained at that temperature for 2 h.

Ester polymerization: Ten grams of Dimethylterephthalate (DMT) (0.051 mol) and 4.54 g TMDA (0.051 mol) were charged in a 100 mL stainless steel autoclave. After flushing with nitrogen a starting pressure of 5 bar was given. The autoclave warmed up in 60 min to 215°C and remained at that temperature for 2 h. The reaction mass was stirred with a magnetic stirrer.

Interfacial polymerization: To TMDA (0.01 mol) and KOH (0.02 mol) in 100 mL of water was added under vigorously stirring TCl (0.01 mol) in 100 mL of methylene chloride. The precipitated polymer was filtered, washed, and dried.

Solution polymerization: To TCl (0.015 mol) in 100 mL of THF cooled to -15°C was added TMDA (0.015 mol) and diisopropylethylamine (0.030 mol) in 20 mL of THF. The formed precipitate was filtered and washed with boiling water.

Solid state postcondensation: Three-gram samples of a prepolymer were postcondensed in the solid state in a fluidized bed reactor⁶ in a stream of dry nitrogen.

Characterization

Inherent viscosities (η_{inh}) were determined from 0.5% solutions in 96% sulfuric acid at 25°C. Films were cast from trifluoroacetic acid solutions. The melting behavior was studied with a duPont 990 Thermal Analyser DSC unit at a heating rate of 10°C/min. The peak temperatures were taken

as the melting points. For wide angle x-ray analysis (WAXS) a Kiessig pinhole vacuum camera was used.

RESULTS AND DISCUSSION

Synthesis

We studied the polymerization or prepolymerization of nylon 4,T with:

- the nylon 4,T salt, in an autoclave
- DMT-TMDA mixtures, in an autoclave
- TCl and TMDA, and a stirred interfacial method
- TCl and TMDA, and a solution method and on some samples a postcondensation in the solid state was conducted.

Nylon Salt

The prepolymerization of the nylon 4,T salt in an autoclave was studied at 210°C. This temperature was chosen because at higher prepolymerization temperatures cyclization of TMDA to pyrrolidine might take place. As this salt has a high melting temperature (286°C) and because prepolymerization in the liquid state is preferred, the effect of presence of solvent was studied. The results of these reactions are given in Table I.

In the experiment without a solvent the salt had not melted, but some polymerization had taken place. By the polymerizations in the presence of 30% solvent the salt had "melted" but the viscosities of products were low too. That only very low molecular weight prepolymers were obtained must be due to the low reactivity of the aromatic acid.⁷

DMT-TMDA Mixture

The polymerization with equimolar mixture of DMT and TMDA was studied without a solvent in an autoclave for 2 h at 215°C. The prepolymer had an η_{inh} of 0,10 which is only marginally higher than the viscosities of the prepolymers obtained by the nylon salt method.

Interfacial Polymerization

The polymerization was studied with TCl-solvent/TMDA-KOH-water system. The effect of varying the solvent is given in Table II. The viscosity

TABLE I
Nylon Salt Polymerization in an Autoclave for 2 h at 210°C

Solvent	η_{inh}
NO solvent	0.08
30% water	0.09
30% <i>m</i> -cresol	0.09
30% <i>p</i> -hydroxybiphenyl	0.09
30% glycol	0.08

TABLE II
Interfacial Polymerization at 0.1 mol/L

Solvent for terephthaloyl chloride	Acid acceptor	η_{inh}
Toluene	KOH	0.45
Methylene chloride	KOH	0.55
Chloroform	KOH	0.51
<i>o</i> -Xylene	MgO	0.45

of the polymer prepared with methylene chloride was somewhat higher than with chloroform or toluene and also higher than with xylene and MgO.

The effect of concentration was studied with methylene chloride (Fig. 1). As can be seen with decreasing concentration of the reactants the viscosities of the products increased. The extrapolated viscosities at extremely low concentrations are comparable to the results of Shashoua and Eareckson.¹

Solution Polymerization

The low temperature solution polymerization starting from TCL and TMDA was studied with varying the solvent system and the acid binder (Table III). With the solvents HMPT and NMP, the polymer precipitated after 5 min reacting; with THF, the polymer precipitated immediately. The polymers prepared in THF, however, had a higher molecular weight. More important than the type of solvent, seems to be the acid binder. The aliphatic diamines are strongly basic therefore only very strong tertiary amines are effective acid binders. The viscosities remained low with HMPT, TMDA, or TEA.

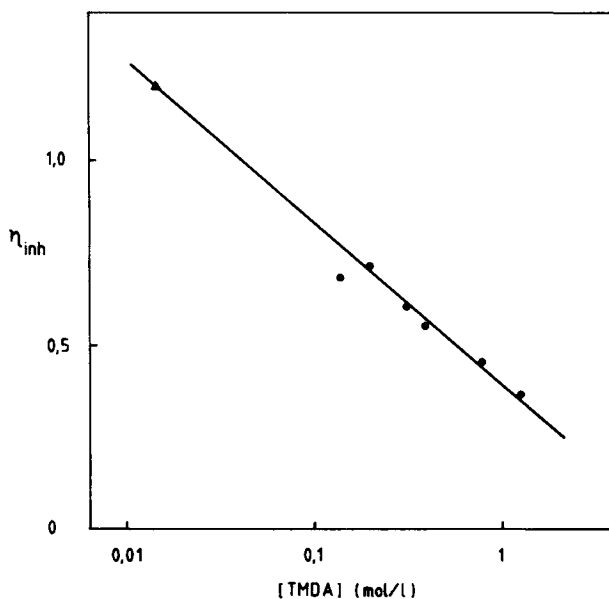


Fig. 1. Influence of TMDA concentration by the interfacial polymerization with the system TCL, methylenechloride and TMDA, KOH in water. (\blacktriangle) from Shashoua and Eareckson.¹

TABLE III
Low Temperature Solution Polymerization Influence of Solvent and Acid Binder

Solvent	Concentration (mol/L)	Acid-amine ratio	Acid binder	η_{inh}	Remarks
HMPT	0.1	1:1	—	0.10	Slow precipitation
HMPT	0.1	1:2	TMDA ^a	0.10	Slow precipitation
HMPT	0.1	1:1	TEA ^b	0.08	Slow precipitation
NMP	0.15	1:1	DMBA ^c	0.31	Slow precipitation
THF	0.15	1:1	DMBA ^c	0.34	Fast precipitation
THF	0.15	1:1	DIPEA ^d	0.39	Fast precipitation

^a TMDA = tetramethylenediamine.

^b TEA = triethylamine.

^c DMBA = dimethylbenzylamine.

^d DIPEA = diisopropylethylamine.

Higher viscosities could be obtained with *N,N'*-dimethylbenzylamine (DMBA) and *N,N'*-diisopropylethylamine (DIPEA).

Postcondensation in the Solid State

An effective way of increasing the molecular weight of a condensation polymer with a high melting temperature is postcondensation in the solid state.⁶ For nylon 4,T with a melting temperature of over 400°C¹ low solubility, and low reactivity, this polymerization method seemed suitable. We studied the solid-state postcondensation with a fluidized bed reactor (4 h, 290°C). The starting materials were prepolymers which preparation we have described earlier and the results are given in Table IV.

The prepolymer prepared by the low temperature solution method could be postcondensed to a high molecular weight. Of the other three prepolymers their viscosities increased only a little, possibly due to an imbalance of the reactive end groups.

PROPERTIES

Solubility

The solubility of nylon 4,T is known to be low.¹ The polymer is insoluble in benzyl alcohol, phenol, formic acid, or NMP-LiCl. It is soluble in very

TABLE IV
Postcondensation of Some Prepolymers in the Solid State for 4 h at 290°C

Method	Prepolymerization		η_{inh}	Postcondensation (4 h, 290°C)
	Conditions			
Nylon salt	No solvent, 2 h, 210°C		0.08	0.19
Ester	2 h, 215°C		0.10	0.23
Interfacial	Methylene chloride, KOH		0.62	0.70
Solution	THF, DMBA ^a		0.34	1.09
Solution	THF, DIPEA ^b		0.39	1.52

^a DMBA = dimethylbenzylamine.

^b DIPEA = diisopropylethylamine.

strong acids such as con. sulfuric acid, trifluoroacetic acid (TFA), and dichloroacetic acid.

Film Formation

Films up to 0.1 mm thick were formed from 5% solutions in trifluoroacetic acid. From solutions in H_2SO_4 films could be cast by precipitating in water, but these films had a high void content.

Infrared Analyses

The infrared spectrum of a polymer film (form TFA sol.) was recorded and in Table V the assignments of these bands are given. Crystalline bands are at 1160 and 730 cm^{-1} and an amorphous band at 1200 cm^{-1} .

X-Ray Analyses

The wide angle x-ray analyses of a film sample gave two sharp rings at 3.87 and 4.87 Å. These are both larger than the d_{010} and d_{100} of nylon 4,6 (3.71 and 4.30)⁸ and 6,6 (3.73 and 4.34).⁹

DSC

No second-order transition was observed with DSC. The melting transition had two endothermic peaks. A double melting transition is for polymers quite common and has been explained as a melting–recrystallization–melting effect¹⁰ and the temperature of the first endotherm is sensitive to the thermal history of the sample. The effect of thermal history was studied and the transition temperatures and the heats of melting are given in Table VI. After a crystallization treatment the first transition (T_1) rises from 427

TABLE V
Infrared Spectrum

Wave number (cm^{-1})	Intensity	Assignments
3310	vs	ν (N—H)
3070	m	2 \times amide II
2940	m	$\nu_a(CH_2)$
2870	w	$\nu_s(CH_2)$
1625	vs	Amide I, (C=O)
1540	vs	Amide II, δ CHN
1490	s	ν (C=C) arom.
1440	vw	$\delta_s(CH_2)$
1370	vw	$\gamma_w(CH_2)$
1315	s	$\gamma_w(CH_2)$
1290	s	Amide III?
1240	w	$\gamma_s(CH_2)$
1195	m	ν (a-c)
1155	m	
1110	m	δ_i (CH) arom.
1015	m	δ_i (CH) arom.
800	s	π -band
730	m	Amide IV
650	s-broad	Amide V

TABLE VI
DSC Analysis of Films

Film	T_I (°C)	T_{II} (°C)	ΔH_m (J/g)
As cast (TFA)	427	475	108
1 h, 100°C, H ₂ O	434	475	129
1 h, 166°C, DMAC	434	475	167
1 h, 20°C, 42% H ₂ SO ₄	432	475	140
10 min, 300°C in press	435	475	163

to 435°C. The second endotherm (T_{II}) is at 475°C. This is 40–50°C higher than the first transition.

The heats of melting (ΔH_m) rises with crystallization treatment too. With the data of Van Krevelen¹¹ an estimate of the heat of melting of a 100% crystalline material was calculated to be 200 J/g. With this figure the degree of crystallinity, x_c , were found to be 50–80%—which is high.

CONCLUSIONS

The synthesis of nylon 4,T to a high molecular weight can either be accomplished by interfacial polymerization at very low concentrations 0.015 mol/L (η_{inh} 1.20),¹ or a two-step process whereby first a prepolymer is made by a low temperature solution reaction followed by a postcondensation in the solid state at high temperatures (η_{inh} 1.52). Nylon 4,T has a high amide content and a regular spacing of the amide groups. The polymer is highly crystalline and has a high melting transition. A new look at its film and fiber properties would be of interest.

The author wishes to thank Jr. A. Beekhof for his contribution and Prof. Jr. J. Schuijjer for his active interest.

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Received July 27, 1984

Accepted October 25, 1984