Preparation and Some Properties of Nylon-4,2

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Synopsis

An attempt was made to produce a new short-chain aliphatic polyamide nylon-4,2. This polyoxamide can be prepared by polycondensation of tetramethylene diamine and diethyl oxalate. A high molecular weight polymer ($\eta_{inh} = 1.9$ from 0.5% solutions in 96% sulphuric acid) has been obtained by employing a two-step polycondensation method; the precondensation was carried out in solution at low temperatures (20–140°C) and the postcondensation in the solid state at high temperatures (250–300°C). The effect of solvent composition and reaction temperature on the prepolymerization and the effect of reaction time and temperature on the postcondensation were studied. We also investigated the influence of moisture during washing, storing, and the solid-state reaction on the polymerizability by the postcondensation. Nylon-4,2 is soluble only in highly polar solvents such as trifluoroacetic acid (TFA), dichloroacetic acid, and 96% sulphuric acid. Films were cast from TFA. With these films we studied the IR spectrum, WAXS pattern, water absorption, and melting behavior. Nylon-4,2 was found to melt at 388–392°C, has a crystallinity of 70%, and a low water absorption (3.1% at 50% RH). The glass transition temperature of the dry sample was found to be at $\sim 120^\circ\text{C}$ and for the wet sample at -15°C .

INTRODUCTION

Polyamides with a high amide content have been of interest for apparel fiber applications because of their possible similarity to wool and silk. We studied the little-known nylon-4,2, a polyamide which can be prepared from tetramethylene diamine (TMDA) and oxalic acid ester.

Nylon-4,2 has the same amide content as nylon-3 and silk and it has special structural features. It is an even-even polyamide, where the dipole moments of the amide groups have alternating directions, which enhances the chain interaction,¹ and it possesses oxamide groups, which according to Morgan and Fletcher² have a trans structure. This means that in both crystalline and amorphous phase each oxamide group is coupled to just two other oxamide groups which implies a closer chain packing. Due to these special structural features we expect nylon-4,2 to have a well-packed crystalline phase, a high crystallinity, and possibly a better than average packed amorphous phase and consequently good fiber properties like high modulus, high glass transition temperature, and a low boiling water shrinkage.

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Polyoxamides have been studied for many years.²⁻¹² The synthesis from oxalic acid is not a favorable route as the oxalic acid decomposes at high reaction temperatures.¹³ High molecular weight polyoxamides can be prepared from oxaloyl dichloride,^{3,4} from ring-opening polymerization of cyclic oxamides,⁵ or from a diester of oxalic acid.⁶⁻¹⁰ The syntheses from the diester have been carried out in two steps. The first step is a low-temperature reaction in solution with a low molecular weight prepolymer precipitating out. This is followed by a second step, the postcondensation, at higher temperatures (250–300°C) to a high molecular weight polymer.

Depending on the temperature of melting the reaction in this second step is in the melt or in the solid state. With these syntheses catalysts sometimes employed.^{11,12} The polyoxamides (–6,2, –8,2, –10,2, and –12,2)⁷⁻¹⁰ are polyamides with high crystallinity and excellent fiber properties and are highly solvent resistant.

The aims of our study are to see whether nylon-4,2 can be synthesized in a high molecular weight and to study some of its properties.

EXPERIMENTAL

Materials

The materials tetramethylenediamine (TMDA), diethyl oxalate (DEO), 1,2,4-trichlorobenzene (TCB), and 2-pyrrolidone were distilled prior to use. Dimethyl oxalate (DMO) was sublimed before use and phenol was used directly after freeing from moisture. Petroleum ether and diethyl ether, technical grade, were used as received.

Polymerization

The polycondensation reaction of TMDA with DEO was conducted in two steps. The prepolymers were prepared in presence of a solvent and the polymers were obtained by solid-state polymerization (SSP) of these prepolymers.

Prepolymerization

To a dry nitrogen flushed 1-L flang flask, fitted with a mechanical stirrer, a nitrogen inlet, and a distilling head, 250 g phenol and 250 g TCB were added. To this solvent mixture, which had been warmed up to 65°C, 22.44 g (0.255 mol) TMDA and 36.5 g (0.250 mol) DEO were added. The solution was warmed up to 140°C in 30 min and maintained at this temperature for 2 h. During the polymerization ethyl alcohol was liberated and the initial homogeneous solution gradually turned cloudy and viscous. After 2 h the reaction mixture was cooled to about 80°C and poured into 2 L of petroleum ether. The precipitated polymer was washed twice with diethyl ether and dried in a vacuum oven.

Postcondensation

Small samples were postcondensed in the solid state in a fluidized bed reactor¹⁴ in a stream by dry nitrogen (e.g., for 4 h at 270°C). The solid-state polymer-

izations of larger batches were conducted in a tumble reactor, with nitrogen streaming over the reaction powder.

Characterization

Inherent viscosities (η_{inh}) were determined from 0.5% solutions in 96% sulphuric acid at 25°C. Films were cast from trifluoroacetic acid solutions. The infrared spectra were obtained from films. The melting behavior was studied with a du Pont 990 Thermal Analyzer 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

Since it is known that the monomers TMDA and DEO are quite unstable at high temperatures, mild polymerization conditions are preferred. In accordance with the methods used for other polyoxamides^{7,10} a precondensation in solution at low temperatures (20–140°C) and a postcondensation in the solid state at 250–300°C were chosen.

Solution Prepolymerization

We studied the effect of the type of diester, the solvent, and the reaction temperature on the inherent viscosity of the polymer.

Type of Ester

The solution polymerization in TCB was conducted with two types of oxalic esters: dimethyl oxalate (DMO) and diethyl oxalate (DEO). In both cases a suspension was readily formed and after 2 h at 100°C the reaction was stopped. The precipitated polymers were analysed and the polymer from DMO had an η_{inh} of 0.128 and that from DEO of 0.132. As DEO was cheaper and easier to handle it was chosen for further study.

Solvent and Temperature

The solution polymerization was studied by carrying out the reaction in a number of solvents and at several temperatures. The results are presented in Table I.

If the reaction was carried out at 25°C in toluene precipitation started in 10 min and the powder was a low molecular weight polymer. The solubility of the prepolymer in toluene at 25°C was apparently very low. In an attempt to increase the solubility the reaction temperature was raised to 100°C but this made little difference to the viscosity η_{inh} of the precipitated polymer. A good solvent for polyamidation of esters¹⁵ has been reported to be TCB, however, the use of this solvent gave little improvement. Pyrrolidone-2, which is a solvent sometimes used for the polyamidation reactions, did in our case keep the prepolymer in solution longer, but this had only a minor effect on the η_{inh} . A very strong solvent for polyamides is phenol and during a reaction in phenol the solution

TABLE I
Effect of Prepolymerization Conditions on Inherent Viscosity

Solvent	Time (h)	Temperature (°C)	Remarks	η_{inh}
Toluene	24	25	Precipitate in 10 min	0.119
	2	100	Precipitate in 10 min	0.126
Pyrrolidone-2	2	100	Precipitate in 30 min	0.150
TCB	24	25	Precipitate in 10 min	0.128
	2	100	Precipitate in 10 min	0.132
TBC/phenol 1:1	2	70	Gel	0.122
	2	130	Gel	0.146
	2	140	Gel	0.160
TBC/phenol 1:4	2	140	Solution	0.140
Phenol	2	140	Solution	0.091

remained clear, but the η_{inh} of the prepolymer was found to be very low. Mixtures of TCB and phenol gave gelled reaction products and their viscosities were somewhat higher.

None of these solution polymerizations gave polymers of sufficiently high viscosities to be suitable for film making or fibre spinning, but these products can be used as starting material for further polymerizations. As the TCB-Phenol 1:1 solvent system gave the highest η_{inh} this method was used for preparing samples to study the postcondensation in the solid state.

Solid-State Postcondensation

Nylon-4,2 is expected to have a high melt temperature $T_m > 350^\circ\text{C}$,⁷ therefore the postcondensation cannot be carried out in the melt without strong degradation. In earlier studies on polyoxamides^{7,10} high molecular weight samples could be prepared with the postcondensation in the solid state.

In our case is in a fluidized the method of postcondensation bed reactor with nitrogen or steam as fluidizing gas. We studied the postcondensation at different temperatures for different times and looked at the effect of water.

Reaction Temperature and Time

The SSP in nitrogen for 4 h at the temperatures 270, 283, and 290°C (Table II) showed a steady increase in inherent viscosity with temperature. Increasing the reaction time (Table II) also increased the viscosity. Under these reaction

TABLE II
Influence of Reaction Temperature and Time by the Solid-State Postcondensations in Nitrogen

Temperature	Time (h)	η_{inh}	Appearance
270	4	1.93	Yellow
283	4	2.08	Light brown
290	2	2.26	Light brown
290	4	2.40	Light brown
290	16	2.70	Light brown

TABLE III
Influence of Washing and Storing Conditions on the Viscosity after Postcondensation in the Solid State (290°C, 4 h, Nitrogen)

	η_{inh} after SSP
Prepolymer washed with ether and directly used	2.3
Prepolymer washed with water and directly used	0.71
Prepolymer washed with ether and stored for 6 months at 25°C, 50% RH	0.59

conditions samples with a very high molecular weight can be synthesized. A high molecular weight is necessary for solution spinning. All the samples were found to be coloured, the polymer prepared at the lowest temperature somewhat less than the others.

Water

By conducting the polymerization on a larger scale, some batches could not be postcondensed to high molecular weights. One of the reasons for this might be the hydrolysis of the ester groups in the prepolymer. In order to study the susceptibility of the prepolymer ester endgroups to hydrolysis we varied the washing procedures, the effect of the storing conditions, and the presence of steam during SSP on the postcondensation of a prepolymer. We also studied the effect of steam on an already postcondensed sample.

If a prepolymer is prepared in a TCB/phenol mixture the reaction mass is a solid gel. The prepolymer can be obtained by precipitating the gel with petroleum ether and washing twice with ether. It was found that the resulting polymer still contained some phenol. To get rid of this last phenol it had to be washed a few extra times and this could be done with either ether or water. The effect of this last washing step was studied and the results are given in Table III. As can be seen the ether-washed sample was excellent postcondensable while the water-washed sample did not postcondense well. This suggests hydrolysis of the ester end group in the prepolymer to the less reactive acid end group.

Normally the prepolymers were postcondensed soon after they were obtained. If, however, a prepolymer was stored for 6 months at atmospheric conditions (20°C, 50% RH) it did not postcondense well (Table III). Again ester hydrolysis might be the cause.

Sometimes the SSPs on nylons are carried out with steam instead of nitrogen in order to prevent the formation of gel^{16,17} and color.¹⁸ A SSP of our prepolymer

TABLE IV
Effect of Steam (1 Bar) by the SSP

	Gas (1 bar)	SSP reaction conditions Temp. (°C)	Time (h)	η_{inh} (before SSP)	η_{inh} (after SSP)	Remarks
Prepolymer	N ₂	290	4	0.163	2.3	Light brown
Prepolymer	H ₂ O	290	4	0.163	0.28	White
Polymer	H ₂ O	290	0.5	2.3	0.47	—
Polymer	H ₂ O	290	2	2.3	0.43	—

TABLE V
Solubilities

Solvent used	Solubility
Trifluoroacetic acid	Soluble
Dichloroacetic acid	Soluble
Sulphuric acid 96%	Soluble
Hot SbCl_3	Soluble
Formic acid 90%	Insoluble
Hot, aqueous phenol	Insoluble
Dimethylacetamide	Insoluble

with steam as fluidizing gas resulted in a colorless product but the molecular weight had not increased (Table IV).

If a high molecular weight sample was steam treated at 290°C in the reactor (Table IV) the viscosity decreased strongly.

To obtain a high molecular weight material water contact should be avoided during precipitation, washing, storing, and SSP of the prepolymer. At 290°C the polymer itself also seems to be easily hydrolyzed.

STRUCTURES AND PROPERTIES

Solubility

The solubility of a polymer with a well-packed crystalline phase tends to be low. The results of the solubility tests are given in Table V. At room temperature the polymer dissolved with relative ease in trifluoroacetic acid and dichloroacetic acid and slowly in concentrated sulphuric acid. At higher temperatures it dissolved in SbCl_3 too. The polymer did not dissolve or even swell in formic acid and hot aqueous phenol. This is a notable feature as nylon-3 is said to dissolve readily in both formic acid and hot aqueous phenol.¹⁹ Nylon-4,2 is clearly very resistant to solvents. This also means that the analysis from solutions is difficult and that solution spinning is limited to only a very few solvent systems.

Film Formation

Films up to 0.5 mm thick were formed from 5% solutions of polymer in trifluoroacetic acid. The color of the film was light brown. Films could be formed from viscosities over 0.6, but for films of good strength and flexibility a viscosity of at least 1.9 was needed.

Infrared Analysis

The infrared spectrum of a polymer film sample is identical with that reported in the literature (Fig. 1).²⁰ The assignments of the respective bands are given in Table VI. The position of the N-H stretching frequency at 3300 cm^{-1} is notable. This band position depends on the amide distances²¹ and as it has the same frequency as most other aliphatic polyamides the amide distance of -4,2 is not expected to differ from the other polyamides.

Fig. 1. Infrared spectrum of a solution cast film.

X-Ray Analysis

Nylon-4,2 is an even-even polyamide with an oxamide group. As the oxamide groups are *trans* according to Morgan and Pletcher² a good chain interaction in both the amorphous and the crystalline phase and a high crystallinity are expected. For this study we used a solvent cast film, which was boiled up in water for 1 h. The diffraction pattern showed several sharp bands and of these the interplanar spacings are given in Table VII as well as those of some other polyamides. The d_{010} (the distance between the amide planes) of -4,2 is smaller than that of the other nylons.

The 4.26-Å spacing, which is a shoulder on the 4.60-Å spacing, we have designated as the d_{100} and the 460-Å spacing as d_{hk2} . The d_{100} of -4,2 is smaller than that of the other nylons and this suggests that either the amide bond distance is smaller or that the angle between d_{010} and d_{100} is smaller. From the

TABLE VI
Infrared Data

Bands at wavenumbers (cm ⁻¹)	Intensity of the band	Assignment
3300	Very strong	N-H band
3070	Medium	N-H band
2960	Shoulder	CH ₂ band
2870	Medium	CH ₂ band
1640	Very strong	Amide I (C=O) band
1500	Very strong	Amide II (C-H; N-H) band
1460	Strong	Unidentifiable; unique to polyoxamides
1370	Strong	
1330	Strong	
1240	Strong	Complex vibration of the amide group and -CH ₂ chain
1190	Strong	
990	Medium	Amide IV band
780	Shoulder	Amide V band
560	Medium	Amide VI band
450	Medium	Amide VII band

TABLE VII
Wide-Angle X-Ray Data of Nylon-4,2 and Other Nylons

	-4.2	-4.6 (22)	-6.6 (23)	-6.2 (10)	-8.2 (10)	-10.2 (10)	-3 (23)
d_{010}	3.56	3.74	3.73	3.75	3.79	3.81	3.78
d_{100}	4.26	4.30	4.34	4.48	4.44	4.62	4.36

TABLE VIII
Water Absorption

	Humidities	
	50% RH	100% RH
Cast film	3.1	14.1
Cast film heat pressed (10 min, 240°C)	2.8	9.3

TABLE IX
Melting Behavior

	Melting temperature (°C)		Heats of fusion	
	Minor	Major	ΔH_f (J/g)	x_c (%)
Prepolymer (powder)	382	392	136	66
Postpolymer (powder)	380	391	148	72
Postpolymer (film)	—	388	154	75

infrared analyses we expected the amide bond not to differ from the other nylons. From this it seems that the lower d_{100} value must be due to a smaller angle between the d_{010} and the d_{100} planes. These results certainly indicate that -4,2 has a well-packed crystalline phase.

Water Absorption

The water absorption was measured on a solvent cast film. Care should be taken with the interpretation of these results as cast films can give much higher absorption values than melt pressed films. Therefore we studied the water absorption on both a cast film and a film which had an additional solid-state pressing (10 min at 240°C). The results are given in Table VIII. Though the polymer is hydrophilic (due to its high amide content) relative low water absorption values were obtained. The heat pressed film has lower values than the other. This might indicate that a melt pressed film would have even lower values. These results compare well with the results on nylon-3,¹⁹ for which a water absorption of 7–9% at 65% RH was reported.

Melting Behavior

The melting temperatures of polyamides depend on the amide content, the structural regularity, and the thermal history of the sample. With DSC the melting behavior was studied and the results are given in Table IX.

From the heats of fusion and an estimated value for a 100% crystalline sample of (205 J/g)²⁴ a rough idea of the crystallinity could be obtained. The melting

temperature of the major endotherm for the prepolymer and polymer powder was 392°C and for the film 388°C. These temperatures are high compared to the 340°C of nylon-3.¹⁹ The calculated crystallinities were all three in the order of 70% which is very high too. These high melting temperatures will make melt polymerization and melt processing impossible.

Glass Transition

As with other polyamides no glass transition was observed with DSC. One of the ways of obtaining a T_g is by studying the damping behavior with temperature. For this we used a torsion pendulum apparatus which is not really suited for films. For a dried sample the T_g was 120°C, for a sample conditioned at 50% RH the T_g was 70°C, and for a wet sample the T_g was -15°C.

The dry glass transition is high for an aliphatic polyamide, but for some other short-chain polyamides very high glass transitions have also been reported,^{20,25} for example, for nylon-3 a temperature of 180°C. On wetting the T_g drops enormously. But the sample conditioned at 50% RH has a T_g well above room temperature. For textile fibre applications this high T_g at 50% RH is desirable.

CONCLUSIONS

Nylon-4,2 can be synthesized to high molecular weights starting from oxalic esters by a two-step process, the polymerization in solution at low temperatures and the SSP at 250–300°C.

Nylon-4,2 has a very good crystalline packing and its crystallinity is high.

Although the material has a hydrophilic structure the water absorption is low and so is the solubility in several typical nylon solvent systems. The high glass transition temperature even of conditioned samples (at 50% RH) combined with a high crystallinity suggests that -4,2 might have excellent fiber properties like high initial modulus, small drop of modulus on wetting, good recovery properties, and possibly a low boiling water shrinkage.

If nylon-4,2 could be synthesized colourless and spun easily, it would be a potential interesting fiber material.

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