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Whiskers. 10. Polycondensations of *N*-(4′-Aminobenzyl)lactams

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ABSTRACT: Three *N*-(4′-aminobenzoyl)lactams were prepared by condensation of 4-(sulfinylamino)-benzoyl chloride with *N*-(trimethylsilyl)-3-dimethylazetidinone-2, *N*-(trimethylsilyl)pyrrolidone-2, and *N*-(trimethylsilyl)azepinone-2. The polycondensation of the *N*-(4-aminobenzoyl)lactams was studied in various reaction media, such as *N*-phenylpyrrolidone, diphenyl sulfone, *m*-terphenyl, or Marlotherm-S, at temperatures ranging from 180 to 400 °C. With regard to molecular weights, the best results were obtained in Marlotherm-S at 300 or 350 °C ($\eta_{\mathrm{inh}} \sim 1.5$ dL/g). The ratio of polycondensation versus polyaddition (by ring opening) was determined by ^{1}H NMR spectroscopy. Up to 90% polycondensation was found for the β-lactam derivative, along with side reactions limiting the molecular weight. The pyrrolidone- and ϵ-caprolactam-based monomers yielded copolyamides containing 80−95% 4-aminobenzoyl units. The WAXD powder patterns exhibit the typical reflections of semicrystalline poly(4-aminobenzamide) with little influence of the reaction conditions. The morphology of the polyamides was examined by SEM and TEM. Aggregates of crystallites looking like shavings were obtained at reaction temperatures ≥275 °C.

Introduction

Poly(1,4-aminobenzamide) is an interesting polymer because it forms lyotropic solutions in both acidic and nonacidic solvents and allows the spinning of high modulus fibers from such solutions.[1−5] Several methods are reported for the synthesis of poly(1,4-aminobenzamide). The oldest method yielding a pure polyamide is based on the polycondensation of 4-aminobenzoyl chloride hydrochloride in polar aromatic solvents at low temperatures.[3−5] The needle-like crystals of this monomer were also polycondensed at high temperatures in the dry state, so that the needle-like morphology was maintained over the whole course of the polycondensation despite the evolution of 2 mol of HCl.[5] Another high-temperature polycondensation process is based on phenyl 4-aminobenzoate as monomer.[6] At 425 °C, a poly(1,4-aminobenzamide) with an inherent viscosity of 1.9 dL/g (in concentrated H_2SO_4) was obtained. An even higher viscosity was found for the polyamide prepared from 4-aminobenzoic acid and CS_2 via 4-(isothiocyanato)benzoic acid as reaction intermediate.[7] No information on viscosities or molecular weights is available for the polycondensation of *N,O*-bis(trimethylsilyl)-4-aminobenzoic acid with $ZnCl_2$ in DMF.[8,9]

Copolyamides rich in 4-aminobenzoyl units were obtained when *N*-(4′-aminobenzoyl)lactams were subjected to polycondensation in various liquid reaction media.[10−13] Depending on the reaction medium and the ring size of the lactam, the polycondensation (eq 1) prevailed more or less over the polyaddition process (eq 2). No polycondensation was conducted above 240 °C, and the temperature was said to have only a negligible influence on the course of the polymerization. However, it is also reported[14,15] that heating of alternating copolyamides above 300 °C results in liberation of lactams, so that a polyamide rich in 4-aminobenzoyl units is formed (eqs 3 and 4).[14,15] This elimination condensation mechanism was ascribed to the intermediate formation and reaction of *N*-(4-aminobenzoyl)lactam and 4-aminobenzoyl end groups. These results suggest that the polycondensation of *N*-(4′-aminobenzoyl)lactams at temperatures ≥300 °C might yield a nearly pure poly(1,4-aminobenzamide). In the connection the present work had two aims. Firstly, the polycondensation of three different *N*-(4′-aminobenzoyl)lactams of different ring size should be studied at temperatures in the range of 200−400 °C. Secondly, the morphology of the resulting polyamides should be determined. Whisker-like crystals of poly(1,4-aminobenzamide) might be of interest as reinforcing components of composites. The in situ formation of lengthy crystals of copolyamides from *N*-(4-aminobenzoyl)-ϵ-caprolactam in a melt of poly(tetrahydrofurandiol) was recently reported by Mülhaupt and co-workers.[16] Despite low aspect ratios (length/diameter < 10) and low molecular weights ($\eta_{\mathrm{inh}} < 0.1$ dL/g in H_2SO_4), a considerable mechanical reinforcement of the poly(urethane) matrix was found. Preformed polyamide whiskers of higher quality might give even better mechanical results in a variety of matrices and allow a comparison with in situ formed composites.

Experimental Section

Materials. 3,3-Dimethylazetidinone was a gift of Hoechst AG (Hoechst, FRG), whereas pyrrolidone and ϵ-caprolactam were gifts of Bayer AG (Leverkusen, FRG). The lactams were used without further purification. 4-Aminobenzoic acid was also a gift of Bayer AG. The 4-(sulfinylamino)benzoyl chloride was prepared from 4-aminobenzoic acid in refluxing thionyl chloride and isolated by distillation in a vacuum[mp 31 °C (lit.[3] mp 31.0−31.5 °C)]. Marlotherm-S is a commercial solvent of Hüls AG (Marl, FRG). Like *m*-terphenyl (purchased from Aldrich Co.) and Santotherm (Therminol-66; purchased from Monsanto), it was distilled in vacuo prior to use. *N*-Methylpyrrolidone-2 and *N*-phenylpyrrolidone-2 were all purchased from Aldrich Co. (Milwaukee, WI) and purified by distillation (in vacuo) over dry K_2CO_3 and P_4O_{10}. Diphenyl sulfone was purchased from Merck Co. (Darmstadt, FRG) and distilled over P_4O_{10} in vacuo.

***N*-(Trimethylsilyl)-3,3-dimethylazetidinone.** 3,3-Dimethylazetidinone (0.75 mol) and chlorotrimethylsilane (0.8 mol) were refluxed in 1 L of dry tetrahydrofuran. Triethylamine (0.8 mol) was added dropwise with stirring over a period of 20 min. The heating was continued for 0.5 h; the reaction mixture was then cooled with ice, diluted with ligroin (200 mL), and filtered under exclusion of moisture. The filtrate was concentrated in vacuo, and the product was isolated by distillation at 100−102 °C/12 mbar. Yield: 89%. n_D^{20} = 1.4462. ^{1}H NMR ($CDCl_3$/TMS): δ 0.22 (s, 9H), 1.38 (s, 6H),

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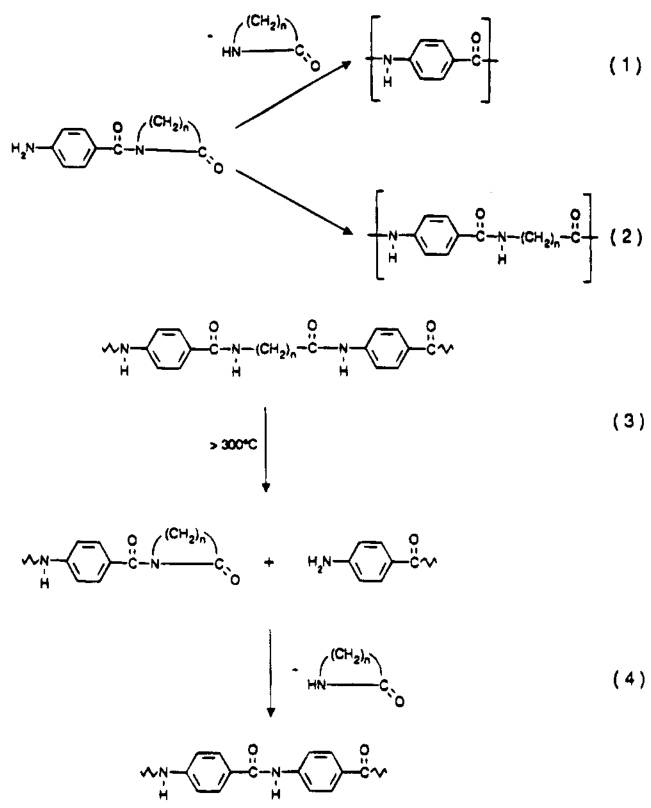


2.72 (s, 2H). Anal. Calcd for $C_8H_{17}NOSi$ (171.31): C, 56.09; H, 10.00; N, 8.17. Found: C, 55.94; H, 10.16; N, 8.45.

***N*-(Trimethylsilyl)pyrrolidone-2** was prepared analogously. Yield: 87%. n_D^{20} 1.4690 (lit.[17] n_D^{20} = 1.4620).

***N*-(Trimethylsilyl)azepinone-2** was also prepared analogously. Yield: 79%. n_D^{20} 1.4710 (lit.[18] n_D^{20} = 1.4700).

***N*-(4′-Aminobenzoyl)-3,3-dimethylazetidinone-2 (1).** 4-(Sulfinylamino)benzoyl chloride (0.5 mol) was dissolved in dry carbon tetrachloride (600 mL), and *N*-(trimethylsilyl)-3,3-dimethylazetidinone (0.55 mol) was added dropwise with stirring and cooling with ice. The reaction mixture was stirred for 20 h at 20 °C and concentrated in vacuo to approximately 50% of its original volume. The crystallized *N*-[4′-(sulfinylamino)benzoyl]-3,3-dimethylazetidinone-2 was filtered off and washed with cold, dry CCl_4 (100 mL). This crude intermediate was stirred for 3 h in a mixture of diethyl ether (250 mL) and ethanol (250 mL). The white product which precipitated from this solution was isolated by filtration and recrystallized from dry ethanol. Yield: 72%. Mp: 138−140 °C. ^1H NMR ($CDCl_3$/TMS): δ 1.70 (s, 6H), 2.84 (s, 2H), 4.03 (s, broad, 2H), 6.64 (d, 2H), 7.80 (d, 2 H). Anal. Calcd for $C_{12}H_{14}N_2O$ (218.3): C, 66.04; H, 6.47; N, 12.84. Found: C, 66.21; H, 6.28; N, 12.67.

***N*-(4′-Aminobenzoyl)pyrrolidone-2 (2a)** was prepared analogously. Yield: 84%. Mp: 166−168 °C (lit.[12] mp 162 °C).

***N*-(4′-Aminobenzoyl)azepinone-2 (2b)** was prepared analogously. Yield: 91%. Mp: 154−155 °C (lit.[13] mp 156−158 °C).

Polycondensations. (A) In Marlotherm-S, *m*-Terphenyl, Santotherm, and Diphenyl Sulfone. The solvents were heated under a slow stream of nitrogen up to the final reaction temperature (see Tables 1−3). The monomer was added at once, so that a concentration of 0.1 M was obtained. The temperature was maintained for 6 h. After cooling, the polyamide, which had precipitated from the reaction mixture, was isolated by filtration, extracted with hot CH_2Cl_2, and dried at 120 °C in vacuo.

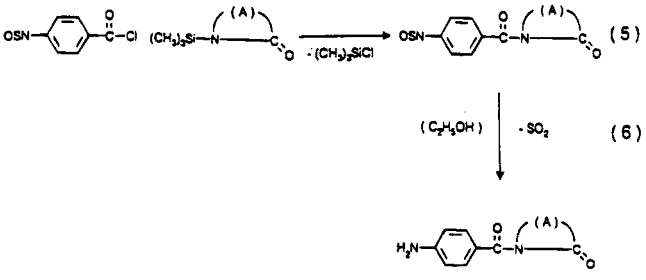
(B) In *N*-Methylpyrrolidone-2, *N*-Cyclohexylpyrrolidone-2, and *N*-Phenylpyrrolidone-2. The solvent and dry LiCl (50 g/L) were stirred at 80 °C under a slow stream of nitrogen until the salt had dissolved. The monomer was then added at once, so that a concentration of 0.2 M was obtained. The reaction mixture was rapidly heated to the final reaction temperature (approximately 10 min). A part of the resulting polyamide precipitated at higher conversions. After cooling, the reaction mixture was poured into methanol, and the precipitated polyamide was filtered off, washed with methanol, and extracted with hot CH_2Cl_2.

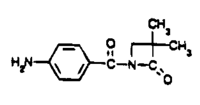
Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25 °C. The 100 MHz ^1H NMR spectra were recorded on a Bruker AC-100 FT spectrometer in 5 mm o.d. sample tubes using D_2SO_4 as solvent and TMS (trimethylsilyl sulfate in reality) as shift reference. The 25.4 MHz ^{13}C NMR spectra were recorded on a Bruker AC-100 FT NMR spectrometer in 10 mm o.d. sample tubes. The WAXD powder patterns were measured with a Siemens D-500 diffractometer by means of Ni-filtered Cu K_α radiation. The SEM micrographs were recorded with a Leitz AMR 1600 T instrument using electrons accelerated with 10 kV. The samples were sputtered with gold by means of a Balzers SC-040 instrument. The TEM micrographs were taken on a Philipps 400 T instrument with an acceleration voltage of 100 kV. The samples were prepared by drying a suspension in methanol on a carbon-coated copper net.

Results and Discussion

Synthesis of Monomers. Three synthetic methods of broader applicability are known for the preparation of *N*-(ω-aminoacyl)lactams. The first method is based on the acylation of *N*-(trimethylsilyl)lactams with ω-isocyanatoacyl chlorides followed by the addition of an alcohol which yields an acid sensitive urethane group. The acidolytic cleavage of the urethane group yields the amino group. This approach is applicable to both aliphatic and aromatic amino acids. The second approach consists of the acylation of free lactams by (sulfinylamino)benzoyl chlorides in the presence of a tertiary amine followed by the cleavage of the sulfinyl group with ethanol. The third approach uses nitrobenzoyl chlorides for the acylation of the lactams and requires hydrogenation of the nitro group as the final step. The second and third approaches are limited to the introduction of aromatic amino acyl residues.

After some preliminary studies of the second and third methods, a combination of method one and two was found to be most satisfactory when lactams of different ring size and reactivity should be involved. 4-(Sulfinylamino)benzoyl chloride was reacted with *N*-(trimethylsilyl)-3,3-dimethylazetidinone, *N*-(trimethylsilyl)pyrrolidone-2, or *N*-(trimethylsilyl)azepinone-2. The acylation of the silylated lactams is a smooth, clean, and almost quantitative reaction when conducted in an inert reaction medium. The resulting *N*-[4′-(sulfinylamino)benzoyl]lactams were pure enough to allow a direct transformation into *N*-(4′-aminobenzoyl)lactams by means of ethanol (eqs 5 and 6). Whereas the pyrrolidone and ϵ-caprolactam derivatives **2a,b** were described in the literature,[12,13] *N*-(4′-aminobenzoyl) derivatives of β-lactams have never been reported before.

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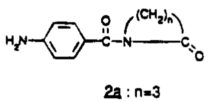

2a : n=3
2b : n=5

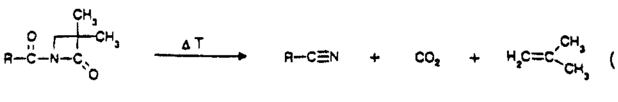
Table 1. Polycondensation of *N*-(4′-Aminobenzoyl)-3,3-dimethylazetidinone

exp no.	reaction medium	time/temp (h/°C)	η_{inh}[a] (dL/g)	condens[b] (%)	compos[c] (%)	yield (%) theor[d]	yield (%) real[e]
1	Marlotherm-S	6/200				0	0
2	Marlotherm-S	6/230	0.11	81	84	30	47
3	Marlotherm-S	6/250	0.11	95	95	52	91
4	Marlotherm-S	6/270	0.13	96	96	38	68
5	Marlotherm-S	6/300	0.10	98	98	4	7
6	diphenyl sulfone	6/270	0.20	98	98	4	7
7	*N*-methylpyrrol + 5% LiCl	18/180				0	0
8	*N*-phenylpyrrol + 5% LiCl	6/250				0	0

[a] Measured at 25 °C in H_2SO_4 with $c = 2$ g/L. [b] The difference to 100% represents the extent of polyaddition. [c] Mole fraction of 4-aminobenzoyl units in the isolated polyamide. [d] Calculated for 100% polyaddition. [e] Calculated on the basis of the experimental polycondensation/polyaddition ratio.

Polycondensations of *N*-(4′-Aminobenzoyl)-3,3-dimethylazetidinone. The polycondensations of monomers **1** and **2a,b** were studied in four or six different solvents to elucidate the influence of the reaction medium. Marlotherm-S was preferentially used as nonpolar solvent because it allows reaction temperatures up to 400 °C, which had proven to be useful for the synthesis of whisker-like crystals of various aromatic polyesters.[19,21] Furthermore, three polar solvents, diphenyl sulfone (DPS), *N*-methylpyrrolidone-2 (NMP), and *N*-phenylpyrrolidone-2 (NPP), were used as polar reaction media. Moreover, lithium chloride was added to these amide-type solvents to keep the oligo- and polyamides in solution. Last but not least, the temperature was varied over a broad range, with 180 °C being the lowest temperature.

Since no experience existed with the polymerization of *N*-(4′-aminobenzoyl)-β-lactams, and because a relatively high reactivity was expected for such a monomer, the polycondensations of monomer **1** were started at relatively low temperatures (nos. 1 and 7 in Table 1). Surprisingly, no polyamide was formed in either experiment. When the temperature was raised in Marlotherm-S, copolyamides were obtained in moderate or high yields. The yields passed a sharp maximum at 250 °C (no. 3, Table 1). In the polar solvents DPS and NPP + LiCl, the yields were close to zero despite temperatures <300 °C. Furthermore, the inherent viscosities were low in all cases. All these results together suggest that the polymerization of **1** involves considerable side reactions. This suggestion is confirmed by IR spectra of the isolated polyamides. A weak band is detectable at 2226 ± 1 cm^{-1} (Figure 1) which increases in intensity with higher reaction temperatures. An absorption in this range and the thermostability suggest that nitrile groups were formed by elimination of CO_2 and isobutylene (eq 7). However, a detailed study of this side reaction was not intended in this work. Despite the low molecular weights, the polycondensation of **1** is interesting because the polycondensation (eq 1) prevails largely over the polyaddition (eq 2). Obviously, the geminal methyl groups are a severe steric hindrance for the nucleophilic attack onto the carbonyl of the β-lactam.



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Polycondensations of *N*-(4′-Aminobenzoyl)pyrrolidone-2. The polycondensations of monomer **2a** were conducted in six different solvents (Table 2). Marlotherm-S was used as reaction medium for six experiments with variation of the temperature (nos. 1–6, Table 2). The evaluation of both yields and inherent viscosities indicate that raising the temperature from 200 to 300 °C favors the entire polymerization process, whereas higher temperatures, particularly temperatures above 350 °C, are unfavorable, obviously due to thermal degradation. Other reaction media did not give higher yields or higher molecular weights. The inherent viscosity of the sample prepared at 300 °C in Marlotherm-S (no. 4, Table 2) is the highest value of this work and also higher than all viscosities published previously by other research groups for polycondensations of *N*-(4′-aminobenzoyl)lactams. In other words, reaction temperatures around 300–320 °C and Marlotherm-S as reaction medium are favorable for high molecular weights.

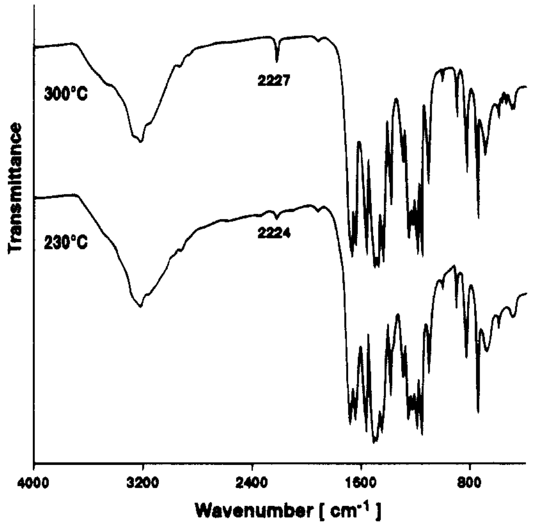


Figure 1. IR spectra of polyamides obtained from monomer 1: in Marlotherm-S at 300 °C (no. 5, Table 1) and in Marlotherm-S at 230 °C (no. 2, Table 1).

On the other hand, a neat poly(4-aminobenzamide) free of γ-aminobutyryl units was never obtained regardless of the reaction conditions. The molar compositions found at low temperatures (≤250 °C) certainly reflect the competition between polycondensation (eq 1) and polyaddition (eq 2). However, the compositions obtained at ≥350 °C are obviously influenced by the elimination of pyrrolidone from preformed polyamides. The existence and mechanism of this process were previoulsy demonstrated and studied (eqs 3 and 4).[14,15] Therefore, the question remains as to why the elimination of pyrrolidone-2 was not quantitative at temperatures ≥350 °C. An interesting finding is the higher percentage of aromatic units resulting from polar reaction media, when compared to Marlotherm-S at identical temperatures (e.g., nos. 9 and 11, Table 2). It seems that the crystallization and precipitation of oligo- and polyamides (observed in all experiments) buries γ-aminobutyryl units in positions which prevent the elimination of pyrrolidone-2 for steric reasons. A higher solubility of oligo- and polyamides favors a quantitative elimination.

In this connection, the NMR spectroscopic methods used for the determination of the molar composition need a short discussion. The data listed in Tables 1–3 are based on ^1H NMR spectra measured in D_2SO_4. Most spectra showed the expected intensity ratios of the aliphatic protons, as illustrated by Figure 2. However,

Table 2. Polycondensations of N-(4′-Aminobenzoyl)pyrrolidone-2 (2a)

exp no.	reaction medium	time/temp (h/°C)	η_{inh}[a] (dL/g)	polycond[b] (%)	compos[c] (%)	yield (%) theor[d]	yield (%) real[e]	elem anal. C	elem anal. H	elem anal. N
1	Marlotherm-S	6/200	0.22	82	85	40	59	69.52	5.10	11.05
2	Marlotherm-S	6/250	0.30	82	85	54	75	69.96	5.46	10.42
3	Marlotherm-S	6/275	0.36	85	87	58	84	69.04	5.06	10.95
4	Marlotherm-S	6/300	1.50	82	85	59	86	69.98	4.84	11.95
5	Marlotherm-S	6/350	0.86	85	87	57	83	69.13	4.76	11.68
6	Marlotherm-S	6/400	0.38	95	95	43	62	70.54	4.65	11.53
7	Santotherm	6/300	0.68	93	93	55	81	70.32	4.85	12.02
8	*m*-terphenyl	6/300	0.61	82	85	59	88	69.56	5.12	12.10
9	diphenyl sulfone	6/300	0.90	92	93	51	75	66.15	5.37	12.45
10	*N*-methylpyrrol + 5% LiCl	16/180	0.25	80	83	42	63	69.58	4.98	12.85
11	*N*-phenylpyrrol + 5% LiCl	6/250	0.47	93	93	52	74	70.23	4.69	12.05

[a] Measured at 25 °C in H_2SO_4 with $c = 2$ g/L. [b] The difference to 100% represents the extent of polyaddition. [c] Mole fraction of 4-aminobenzoyl units (margin or error ~±2%). [d] Calculated for 100% polyaddition. [e] Calculated on the basis of the experimental polycondensation/polyaddition ratio.

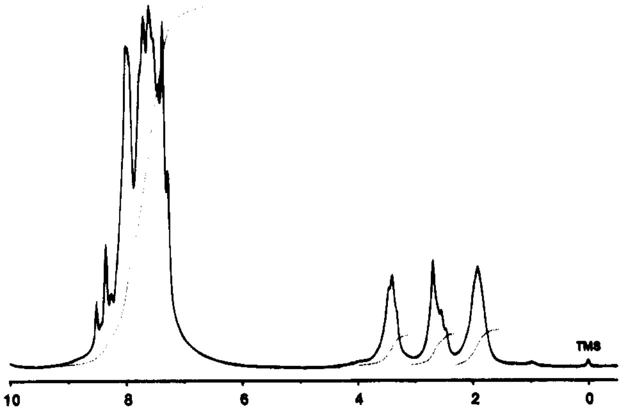


Figure 2. 100 MHz ^1H NMR spectrum (in D_2SO_4) of the polyamide prepared from monomer **2a** in Marlotherm-S at 300 °C (no. 4, Table 2).

Table 3. Polycondensations of N-(4′-Aminobenzoyl)azepinone-2 (2b)

exp no.	reaction medium	time/temp (h/°C)	η_{inh}[a] (dL/g)	polycond[b] (%)	compos[c] (%)	yield (%) theor[d]	yield (%) real[e]
1	Marlotherm-S	6/200	0.22	78	82	43	69
2	Marlotherm-S	6/250	0.41	81	83	52	85
3	Marlotherm-S	6/275	0.75	81	83	54	87
4	Marlotherm-S	6/300	1.12	76	81	57	89
5	Marlotherm-S	6/350	1.42	80	83	55	90
6	Marlotherm-S	6/400	gel	89	90	40	70
7	diphenyl sulfone	6/300	0.22	91	92	29	53
8	*N*-methylpyrrol + 5% LiCl	16/180	0.03	66	75	20	29
9	*N*-phenylpyrrol + 5% LiCl	6/250	0.38	97	97	45	82

[a] Measured at 25 °C with $c = 2$ g/L in concentrated H_2SO_4. [b] The difference to 100% represents the extent of polyaddition. [c] Mole fraction of 4-aminobenzoyl units in the isolated polyamide. [d] Calculated for 100% polyaddition. [e] Calculated on the basis of the experimental polycondensation/polyaddition ratio.

in some cases the signal intensities of β- and γ-CH_2 groups were neither equal nor identical with the intensity of the α-CH_2 group (2.7 ppm). Similar inconsistencies were observed in the case of polyamides prepared from monomer **2b** (Table 3). The broad signal of the β-, γ-, and δ-CH_2 groups (1.5 ppm) was in most cases more intensive than expected on the basis of the α-CH_2 signal. For instance, an intensity ratio of 4:1 was found, in the case of Figure 3, instead of the expected 3:1. These discrepancies may have two origins. Either the stronger signals result from overlapping with signals of unknown byproducts and residual solvent or the α-CH_2 signal is weakend by H/D exchange. Therefore, freshly prepared polyaramide solutions were measured four times with variation of time. However, the intensity ratios of the aliphatic signals remained constant. No evidence for an H/D exchange was found. Therefore, the signal of the α-CH_2 groups was evaluated in all cases and served as the basis for the data in Tables 2 and 3.

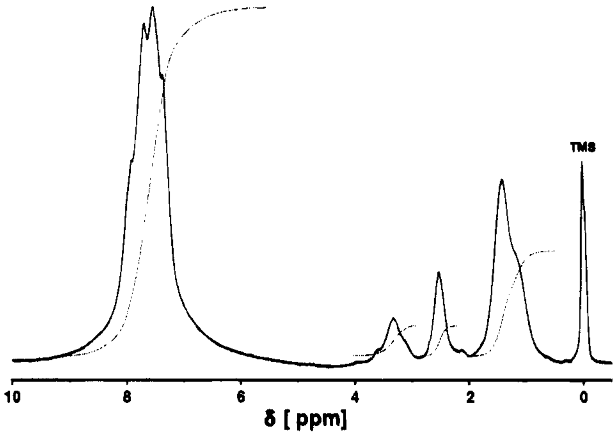


Figure 3. 100 MHz ^1H NMR spectrum (in D_2SO_4) of the polyamide prepared from monomer **2b** in Marlotherm-S at 300 °C (no. 4, Table 3).

This analytical procedure is justified by the following additional observations. Firstly, the results (molar compositions) are consistent when compared in one series (e.g., Table 2) or when the polycondensations of **2a,b** are compared with each other. Secondly, the quantification of the ^{13}C NMR signals (albeit less accurate) showed a satisfactory agreement with the ^1H NMR data (Figure 4). Thirdly, a satisfactory agreement with the WAXD powder patterns was found (discussed below). In this connection, it should be mentioned that other research groups[10-13] did not discuss their analytical methods and did not publish NMR spectra of the polyamides.

Polycondensations of N-(4′-Aminobenzoyl)azepinone-2. The polycondensations of monomer **2b** were conducted analogously to those of **2a**, but without Santotherm and *m*-terphenyl (Table 3). Again a series with increasing reaction temperature was studied in Marlotherm-S as reaction medium (nos. 1−6). The results agree with those obtained from polycondensations of **2a** in that the highest yields and viscosities were found at temperatures of 300 and 350 °C. In contrast to **2a**, the highest viscosity was obtained at 350 °C (no. 5, Table 3). Again the highest fraction of 4-aminobenzyl units was observed for the samples prepared at 400 °C in Marlotherm-S or the more polar solvents (nos. 7 and 9). Remarkable also is the constancy of the composition

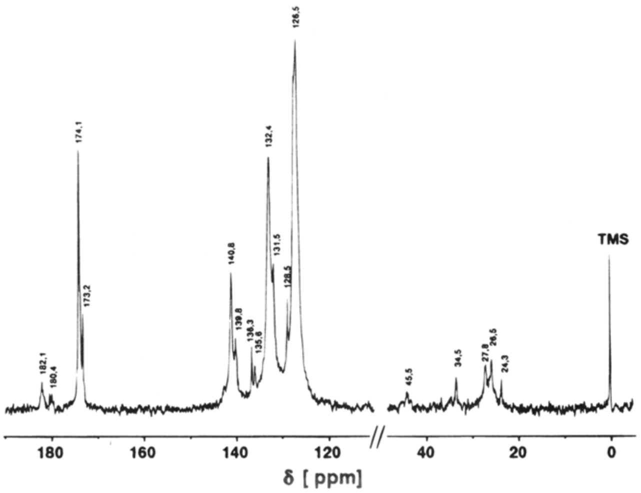


Figure 4. 25.4 MHz ^{13}C NMR spectrum (in D_2SO_4) of the polyamide prepared from monomer **2b** in Marlotherm-S at 350 °C (no. 5, Table 3).

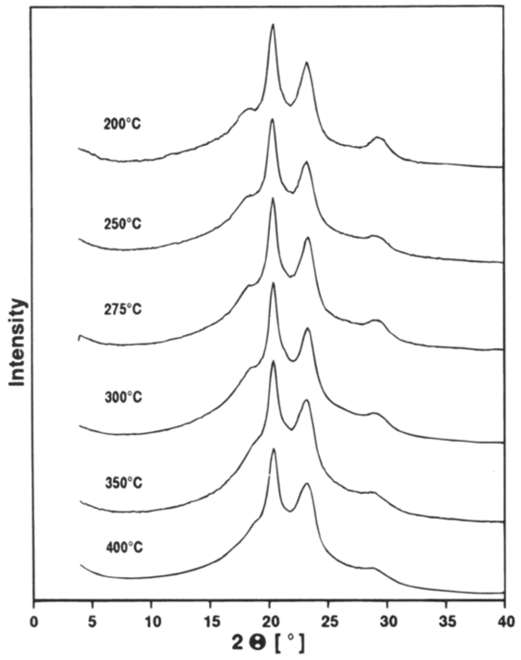


Figure 5. WAXD powder patterns of the polyamides prepared from monomer **2b** in Marlotherm-S with variation of the reaction temperature (nos. 1−6, Table 3).

upon variation of the temperature in Marlotherm-S. In this connection, it should be mentioned that also in this series a precipitation of oligo- or polyamides occurred in all experiments.

IR spectra of the isolated polyamides prepared from either monomers **2a** or **2b** were almost identical and invariant when the reaction temperature was varied. Furthermore, the WAXD powder patterns are typical for semicrystalline poly(4-aminobenzoic acid), and they do not vary with the reaction temperature (Figure 5) regardless of whether monomer **2a** or **2b** was used. This invariance of both IR and WAXD patterns agrees well with the constancy of the molar compositions as determined by ^1H NMR spectra.

Morphology of the Polyamides. The morphology of all polyamides prepared from monomers **2a,b** were examined by scanning electron microscopy (SEM) (Figures 6−10). Several analogies and few differences were found between both series of polycondensations (Tables 2 and 3). The polyamides prepared at temperatures below 275 °C formed small particles of irregular shape. However, at temperatures in the range of 275−350 °C, lengthy particles were formed which look liked shavings (Figures 6, 8, and 9). These "shavings" typically have lengths of 10−20 μm and vary in the width over a broad range. Even within one and the same sample, a considerable variation of size and length/diameter ratio was observed. Figure 6 represents the standard situation, whereas Figure 7 exhibits the relatively broad shavings obtained from **2a** at 300 °C in *m*-terphenyl.

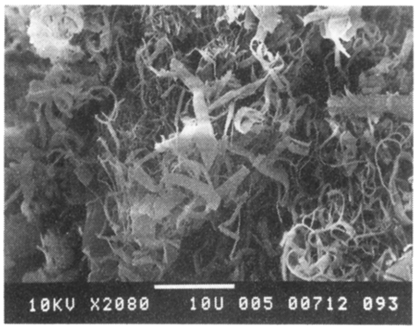


Figure 6. SEM micrograph of polyamide exp no. 4, Table 2 (the white bar represents 10 μm).

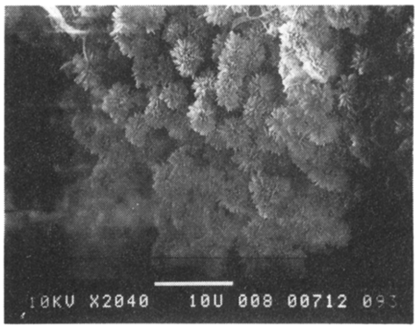


Figure 7. SEM micrograph of polyamide exp no. 6, Table 2 (the white bar represents 10 μm).

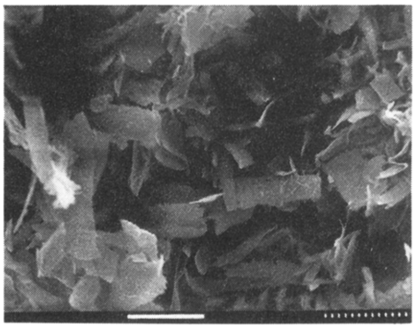


Figure 8. SEM micrograph of polyamide exp no. 9, Table 2 (the white bar represents 10 μm).

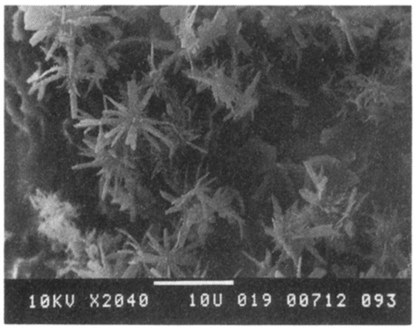


Figure 9. SEM micrograph of polyamide exp no. 5, Table 3 (the white bar represents 10 μm).

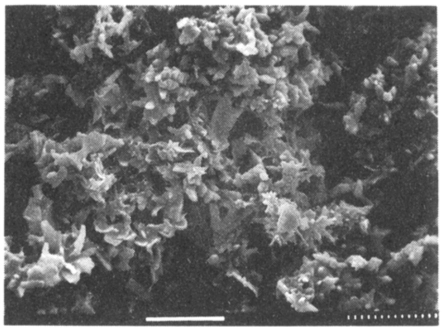
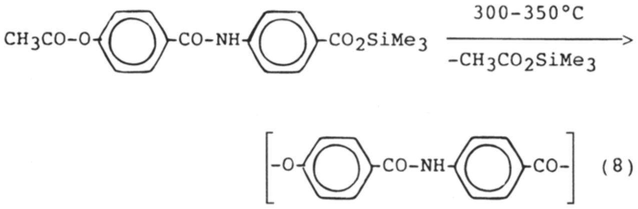


Figure 10. SEM micrograph of polyamide exp no. 6, Table 3 (the white bar represents 10 μm).

With increasing temperature, smaller and thinner "shavings" were formed (Figure 9). At 400 °C, neither **2a** nor **2b** yielded "shavings" (Figures 7 and 10). Whereas star-shaped bunches of cylindrical crystals were obtained from **2a** (Figure 7), small particles of irregular shape resulted from the polycondensation of **2b**.

Clearly, the highest temperature does not favor the formation of whiskers or long "shavings" in contrast to the polycondensation of 4-acetoxybenzoic acid.[19,20] Interestingly the morphology of poly(ester amide)s prepared according to eq 8 is almost identical with the



(8)

shavings displayed in Figures 6 and 9.[21] Obviously the influence of 4-aminobenzoic acid dominates the crystal growth also in the case of these poly(ester amide)s.

Albeit this work was mainly designed as a preparative study, the question of interest was whether the "shavings" are single crystals or aggregates of smaller crystallites and particles. Therefore three samples were examined by transmission electron microscopy. Due to thickness of the "shavings", the results are not unambiguous. Nonetheless, Figure 11 suggests that the sample obtained from **2a** at 300 °C in Marolotherm-S is a disordered aggregate of smaller particles. In contrast, the "shavings" obtained from **2b** under the same conditions look at first glance like a bundle of fibrous crystallites (Figure 12). At higher magnification (×60000), an almost isotropic distribution of tiny whiskers (lengths ~ 50−150 nm) was observable. Yet, it remained unclear if these "whiskers" were exclusively located on the surface of the "shaving" or if they represent its building blocks. Regardless if **2a** or **2b** were used as monomers, it is difficult to understand how an isotropic or irregular aggregation of small whiskers or crystallites can generate the characteristic anisotropic shape of the "shavings". At first glance it seems that the crystal growth of polyamides or poly(ester amide)s derived from 4-aminobenzoic acid is completely different from that of poly(4-hydroxybenzoic acid) or poly(6-hydroxy-2-naphthoic acid).[22,23]

Conclusion

Whereas the polycondensation of *N*-(4′-aminobenzoyl)-3,3-dimethylazetidinone does not yield polyamides of high molecular weight, polycondensations of *N*-(4′-aminobenzoyl)pyrrolidone-2 or -azepinone-2 are more satisfactory. The optimum temperature range for both yield and molecular weight is 300−350 °C. Regardless of the reaction conditions, a poly(4-aminobenzoic acid) absolutely free of aliphatic monomer units was never obtained. Nonetheless, the resulting polyamides are semicrystalline materials with the characteristic morphology of "shavings". These "shavings" are seemingly aggregates of smaller crystallites and not single crystals in contrast to whiskers of aromatic polyesters prepared and analogous reaction conditions. The crystal growth of these "shavings" is currently under investigation and

Figure 11. TEM micrograph of polyamide exp no. 4, Table 2 (the black bar represents 0.5 μm; magnification: 28 × 10³).

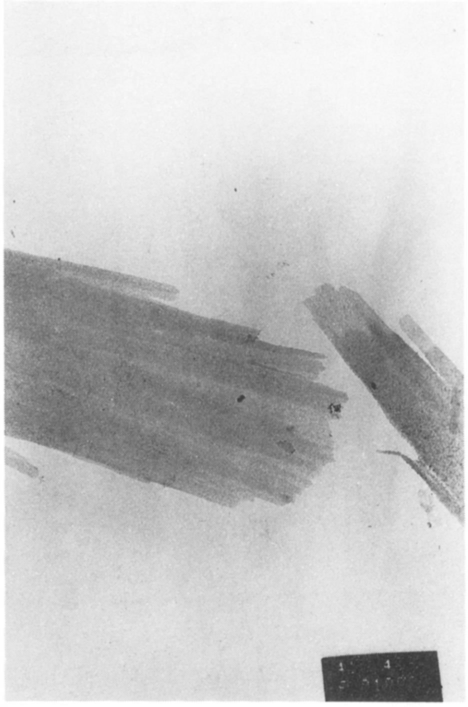


Figure 12. TEM micrograph of polyamide exp no. 4, Table 3 (the black bar represents 1.4 μm; magnification: 10 × 10³).

will be discussed in more detail in a future part of this series.

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