New Polymer Syntheses. 67. Kevlar-Type Polyaramides of Monosubstituted Terephthalic Acids

Hans R. Kricheldorf,* Bernd Schmidt, and Rolf Bürger

Institut für Technische und Makromolekulare Chemie der Universität Hamburg, Bundesstrasse 45, 2000 Hamburg 13, FRG

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ABSTRACT: Polyaramides were prepared from 1,4-diaminobenzene and terephthalic acids with aromatic substituents of various lengths. Using phenoxyterephthalic acid as starting material, the synthetic approach was varied and the polycondensation of silylated 1,4-diaminobenzene with terephthaloyl chlorides was found to be the most satisfactory one. In addition to homopolyamides several copolyamides were prepared. Furthermore, the molecular weight and the end groups were varied. The polyaramides were characterized by elemental analyses, inherent viscosities, WAXS and DSC measurements, IR and NMR spectroscopies, optical microscopy, and thermogravimetric analyses. Despite relatively long substituents, meltable polyaramides were never obtained. However, two homo- and two copolyamides showed a good solubility in pure *N*-methylpyrrolidone and compatibility with poly(vinylpyrrolidone). Up to concentrations of 20 wt % in concentrated H_2SO_4, lyotropic solutions were not found.

Introduction

The poly(1,4-diaminobenzene–terephthalamide), Kevlar, is a polymer of great technical interest, because high-modulus fibers can be spun from lyotropic solutions. Shortcomings of this polyamide are its lack of meltability and its poor solubility which is restricted to concentrated sulfuric acid or a concentrated solution of inorganic salts in *N*-methylpyrrolidone (NMP). It is obvious that substitution of the terephthaloyl or diaminobenzene units may improve both meltability and solubility. One phenyl substituent[1,2] or one biphenyl side chain[2] neither imparts meltability nor significantly improves the solubility.

Also two methyl groups attached to the diaminobenzene unit do not change the properties basically.[3] Even two long alkoxy side chains per repeating unit render Kevlar-type polyaramides neither meltable nor soluble in nonprotic organic solvents.[4] In fact, four or six alkyl side chains are required per repeating unit to obtain a meltable and soluble Kevlar-type polyaramide.[5–7] An improved solubility is of particular interest for the preparation of blends with other matrix polymers from a suitable cosolvent. However, the long alkoxy chains are not thermostable above 300 °C and highly sensitive to oxidation even at temperatures below 200 °C. Furthermore, four or six alkyl side chains per repeating unit surround the polyamide backbone with a paraffin layer which prevents any compatibility with other polymers, perhaps with exception of polyethylene. In this connection the present and the succeeding work are aimed at synthesizing and characterizing polyaramides with a broader variety of aromatic substituents.

Experimental Section

Materials. The substituted terephthalic acids were prepared by nucleophilic substitution of dimethyl nitroterephthalate with phenols or thiophenols as described previously.[8–10] The corresponding terephthaloyl chlorides were prepared by means of refluxing thionyl chloride. One acid chloride not yet reported before is described below. 1,4-Diaminobenzene (gift of Bayer AG, Uerdingen, FRG) was silylated by means of chlorotrimethylsilane and triethylamine in refluxing toluene and isolated by distillation; mp 102–103 °C (lit.[11] mp 103–105 °C). 4-Methylbenzoyl chloride was purchased from Aldrich Co. and used without purification. 3,3′-Dimethoxybenzidine dihydrochloride was a gift of Bayer AG and was silylated without purification (see below). 3,5-Bis(azidosulfonyl)benzoic acid (mp 143 °C) was prepared according to the literature.[12] *N*-Methylpyrrolidone was purified by one distillation (in vacuo) over K_2CO_3 and two distillations over P_4O_{10}. Triphenyl phosphite and pyridine were purchased from Aldrich Co. (Milwaukee, WI) and purified by distillation.

2-[(4-Acetoxyphenyl)thio]terephthaloyl Chloride. 2-[(4-Hydroxyphenyl)thio]terephthalic acid (0.2 mol), acetic anhydride (0.3 mol), and pyridine (2 mL) were refluxed in dry 1,4-dioxane (1 L) for 5 h. The reaction mixture was then concentrated to a volume of ca. 300 mL, and the product was crystallized by cooling and portionwise addition of ligroin. The crude product was recrystallized from 1,4-dioxane/ligroin: yield 84%; mp 302–304 °C dec. Anal. Calcd for $C_{16}H_{12}O_6S$ (332.33): C, 57.83; H, 3.64; S, 9.65. Found: C, 57.50; H, 3.38; S, 9.50.

The dicarboxylic acid (0.15 mol) was refluxed in freshly distilled thionyl chloride (180 mL) for 3 h. Most of the thionyl chloride was then distilled off, and the residue was twice recrystallized from chloroform/ligroin: yield 94%; mp 98–100 °C. Anal. Calcd for $C_{16}H_{10}Cl_2O_4S$ (369.22): C, 52.05; H, 2.73; S, 8.68; Cl, 19.20. Found: C, 51.87; H, 2.66; S, 8.70; Cl, 19.35.

***N,N′*-Bis(trimethylsilyl)-3,3′-dimethoxybenzidine.** 3,3′-Dimethoxybenzidine dihydrochloride (0.2 mol) and chlorotrimethylsilane (0.42 mol) were dissolved (or suspended) in dry toluene (0.6 L), and triethylamine (0.84 mol) was added dropwise. The reaction mixture was then refluxed for 4 h, cooled, and filtered with exclusion of moisture. The product was isolated from the filtrate by distillation over a short-way apparatus in a vacuum of 10^{-3} mbar: yield 90%; mp 125–128 °C. Anal. Calcd for $C_{20}H_{32}N_2O_2Si_2$ (388.66): C, 61.81; H, 8.30; N, 7.21. Found: C, 62.07; H, 8.15; N, 7.50. The ^1H NMR spectrum (in $CDCl_3$) showed a correct intensity ratio of $SiCH_3$ and OCH_3 protons.

3,5-Bis(azidosulfonyl)benzoyl Chloride. 3,5-Bis(azidosulfonyl)benzoic acid (0.1 mol) was refluxed in freshly distilled thionyl chloride until the evolution of HCl and SO_2 had almost ceased. The reaction mixture was then concentrated in vacuo, and the residue was recrystallized from chloroform/ligroin: yield 78%; mp 81–83 °C. Anal. Calcd for $C_7H_3ClN_6O_5S_2$ (350.71): C, 23.97; H, 0.86; Cl, 10.11; N, 23.96; S, 18.28. Found: C, 24.28; H, 0.93; Cl, 10.00; N, 23.74; S, 18.36. The IR spectrum (in KBr) displayed an "azide band" at 2142 cm^{-1} and a "carbonyl band" at 1770 cm^{-1}.

Polycondensations. (A) Free Diamine and Phenoxyterephthaloyl Chloride. 1,4-Diaminobenzene (20 mmol) was dissolved in NMP (40 mL, containing 2.1 g of LiCl) and cooled to 0 °C (or −18 °C, see Table I). Phenoxyterephthaloyl chloride (20 mmol) was added in portions with stirring, and cooling was continued for 6 h. The reaction mixture was stirred at ca. 20 °C for 48 h and then diluted with NMP containing 5 wt % LiCl. The diluted solution was poured into water, and the precipitated polyamide was washed with water and methanol and dried at 90 °C (15 mbar) and 220 °C (15 mbar). In some experiments a tertiary amine (40 mmol, see Table I) was added together with the 1,4-

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Table I
Yields and Inherent Viscosities of the Polyaramide 2a Prepared by Different Methods from 1,4-Diaminobenzene and Phenoxyterephthalic Acid

	reaction partners	temp (°C)	yield (%)	η_{inh}[a] (dL/g)
1	1,4-diaminobenzene, phenoxyterephthaloyl chloride	−15	99	3.13
2		0	99	3.20
3	1,4-diaminobenzene, phenoxyterephthaloyl chloride, pyridine	−15	99	2.34
4		0	99	2.30
5	1,4-diaminobenzene, phenoxyterephthaloyl chloride, *N,N*-dimethylaniline	−10	99	2.22
6	1.4-diaminobenzene, phenoxyterephthaloyl chloride, triethylamine	−15	98	0.65
7	*N,N'*-bis(trimethylsilyl)-1,4-diaminobenzene, phenoxyterephthaloyl chloride	−10	99	3.08
8		−15	99	5.13
9		−18	99	6.13
10	1,4-diaminobenzene, phenoxyterephthalic acid, triphenyl phosphite, pyridine	120	99	2.46

[a] Measured at 25 °C with c = 0.1 g/dL in concentrated H_2SO_4.

Table II
Yields and Properties of Polyaramides Prepared from *N,N'*-Bis(trimethylsilyl)-1,4-diaminobenzene and Various Substituted Terephthaloyl Chlorides in NMP at −18 °C

					elemental analyses			
polymer	yield (%)	η_{inh}[a] (dL/g)	elem formula (formula wt)		C	H	N	S
2a	99	6.13	$C_{20}H_{14}N_2O_3$ (330.3)	calcd	72.72	4.27	8.48	
				found	72.33	4.24	8.42	
2b	99	5.67	$C_{20}H_{14}N_2O_2S$ (346.4)	calcd	69.35	4.07	8.09	9.26
				found	69.23	4.06	7.99	9.21
2c	99	4.10	$C_{26}H_{18}N_2O_4$ (422.4)	calcd	73.92	4.30	6.63	
				found	72.31	4.31	6.68	
2d	99	3.55	$C_{29}H_{24}N_2O_3$ (448.5)	calcd	77.66	5.39	6.25	
				found	76.43	5.43	6.23	
2e	98	1.60	$C_{32}H_{22}N_2O_5S$ (578.7)	calcd	66.42	3.83	4.84	11.08
				found	66.12	3.72	4.89	10.68
2e'	99	0.95	$C_{32}H_{22}N_2O_5S$ (578.7)	calcd	66.42	3.83	4.84	11.08
				found	66.09	3.70	4.80	10.88
2f	99	2.50	$C_{36}H_{28}N_2O_5S$ (600.7)	calcd	71.98	4.70	4.66	5.34
				found	72.00	4.79	4.88	5.22

[a] Measured at 25 °C with c = 1 g/L in concentrated H_2SO_4.

diaminobenzene.

(B) Silylated Diamine and Phenoxyterephthaloyl Chloride. *N,N'*-Bis(trimethylsilyl)-1,4-diaminobenzene (20 mmol) was dissolved in NMP (40 mL, containing 2.1 g of LiCl) and cooled to −18 °C. Phenoxyterephthaloyl chloride was then added in portions, and the reaction was conducted as described above. For the synthesis of polyamide **5**, silylated 3,3'-dimethoxybenzidine (20 mmol) dissolved in 100 mL of NMP (without LiCl) was used as the starting material. All polyaramides were at first dried at 120 °C and finally at 220 °C in vacuo to remove water and NMP as completely as possible (checked by ^{1}H NMR spectroscopy).

(C) Higashi Method. 1,4-Diaminobenzene (20 mmol), phenoxyterephthalic acid (20 mmol), and lithium chloride (2.1 g) were weighed into a three-neck reaction vessel (100 mL), and NMP (40 mL), pyridine (10 mL), and triphenyl phosphite (10.5 mL) were added from a pipet with stirring under a slow stream of nitrogen. The reaction mixture was heated to 120 °C for 2 h, afterward diluted with NMP (and LiCl), and precipitated into cold methanol. The isolated polyamide was intensively stirred, washed with methanol, and finally dried at 90 and 220 °C in vacuo.

(D) Modification of End Groups. *N,N'*-Bis(trimethylsilyl)-1,4-diaminobenzene (60 mmol) was dissolved in NMP (100 mL) and cooled to −15 °C. The terephthaloyl chloride (50 mmol) was then added in portions. After 2 h, 21 mmol of 4-methylbenzoyl chloride in THF or 21 mmol of 3,5-bis(azidosulfonyl)benzoyl chloride was added under cooling. After stirring for 12 h, the reaction mixture was worked up as described above.

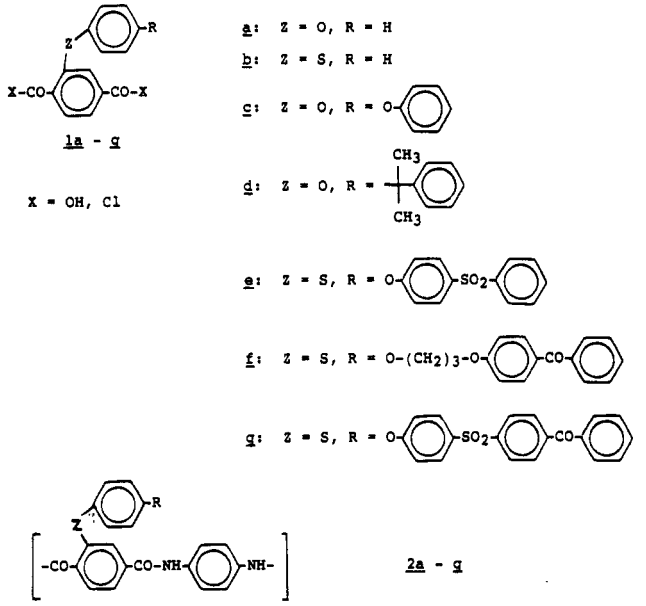
(E) Copolyamides. The copolyamides **8a** and **8b** were prepared according to procedure B. Mixtures of the different terephthaloyl chlorides (together 20 mmol) were reacted with silylated 1,4-diaminobenzene (20 mmol). In the case of polyamide **6** an equimolar mixture of the silylated diamines (together 20 mmol) was polycondensed according to procedure B.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25 °C. The DSC measurements were conducted with a Perkin-Elmer DSC-4 in aluminum pans at a heating rate of 20 °C/min. The WAXS powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered Cu Kα radiation. The thermogravimetric analyses were conducted with a Perkin-Elmer TGS-2 at a heating rate of 10 °C/min in N_2. The IR spectra were recorded from KBr pellets on a Nicolet SXB-20 FT-IR spectrometer. The ^{1}H NMR spectra were measured with a Bruker AC-100 or a MSL-300 FT-NMR spectrometer in 5-mm-o.d. sample tubes.

Results and Discussion

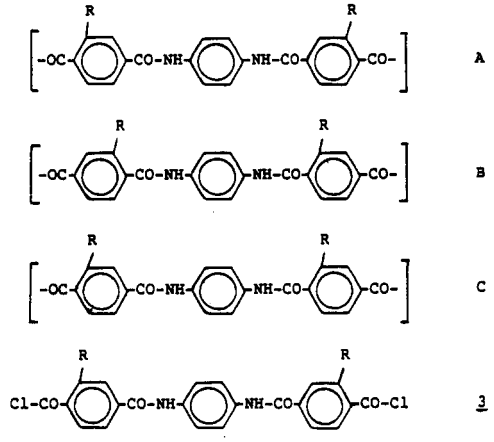
Syntheses. For the syntheses of monosubstituted Kevlar-type polyaramides the seven (aryloxy)- or (arylthio)terephthalic acids and -terephthaloyl chlorides **1a–g** were taken into consideration. In order to evaluate the optimum condensation procedure, syntheses of "phenoxy-Kevlar" (**2a**) were conducted under four different reaction conditions: (A) polycondensation of free 1,4-diaminobenzene with phenoxyterephthaloyl chloride, (B) polycondensation of free 1,4-diaminobenzene with phenoxyterephthaloyl chloride in the presence of a tertiary amine as HCl acceptor, (C) polycondensation of *N,N'*-bis(trimethylsilyl)-1,4-diaminobenzene with phenoxyterephthaloyl chloride (Imai's method[13]), and (D) polycondensation of 1,4-diaminobenzene with phenoxyterephthalic acid by means of triphenyl phosphite and pyridine (Higashi's method[14]).

The results summarized in Table I show that the highest viscosities were obtained by the "silyl method" (method C). One polycondensation with the free diamine (method A) gave a viscosity above 3.0 dL/g, but this condensation is a slow process, due to the partial protonation of the diamine, and requires long reaction times (≥5 days). Addition of a tertiary amine accelerates the polyconden-



sation, but favors side reactions. Thus, all further syntheses were conducted in such a way that *N,N'*-bis(trimethylsilyl)-1,4-diaminobenzene was condensed with the terephthaloyl chlorides **1a–q** (X = Cl). The yields and properties of the resulting polyaramides **2a–f** are listed in Table II. In the case of polyaramide **2q** a cross-linked material was obtained regardless of whether the "silyl method" (method C) or the "Higashi method" (method D) was used. Presumably the keto group, which is activated by the conjugated sulfonyl group, causes side reactions (e.g., formation of ketonimines). This assumption is supported by the fact that aromatic polyesters could be synthesized from **1q** (X = Cl). However, a detailed study of this problem was not intended.

Polyamides derived from 1,4-diaminobenzene and monosubstituted terephthalic acids may in principle contain sequences of the three "triads" A, B, and C. The synthetic



procedure used for **2a–g** is characterized by the addition of terephthaloyl chlorides to the silylated diamine and should result in random sequences. However, the inverse procedure, slow addition of diamine to the terephthaloyl chloride, should reduce or eliminate triad C, because initially trimers of structure **3** should preferentially be formed. The efficiency of this selectivity should depend on the steric and electronic influence of the substituent on the neighboring acid chloride group. In order to get a crude idea, if the inverse synthetic procedure yielded polyamides with different properties, the synthesis of **2e** was repeated by the inverse method (yielding **2e'**). However, both ^{1}H NMR spectra (Figure 1) and IR spectra

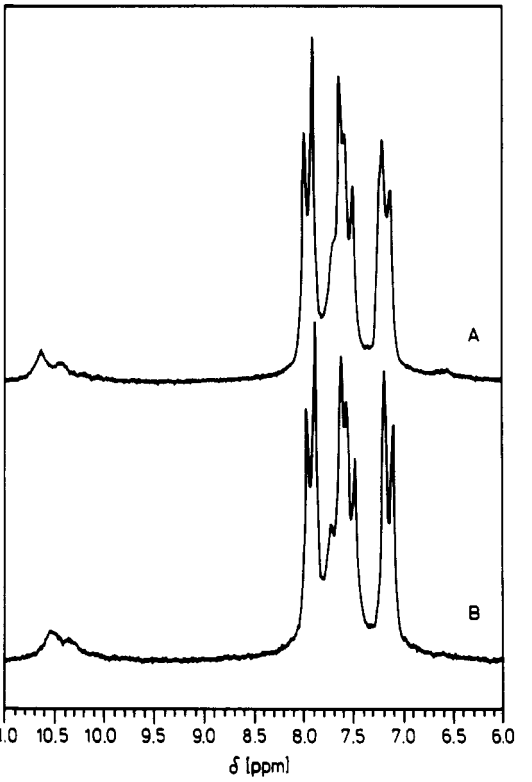
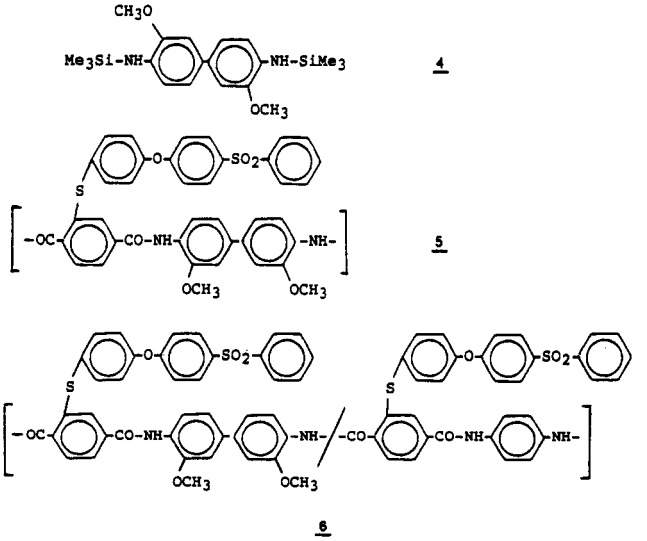


Figure 1. ^{1}H NMR spectra (100 MHz) of polyamides **2e** (A) and **2e'** (B) measured in dimethyl sulfoxide-d_6.

were identical and neither WAXS powder diffraction nor DSC measurements nor solubilities gave any indication of a significant difference.

Structural Variations. As discussed below the polyaramides **2e** and **2f** are of particular interest due to their good solubility in organic solvents. In order to study the structure/property relationships of the chemically and thermally more stable polymer **2e** in more detail, its structure was varied in three directions. A first modification was achieved by the homo- and cocondensation of the *N,N'*-bis(trimethylsilyl) derivative of 3,3'-dimethoxybenzidine (**4**). Yields and properties of polyaramides **5** and **6** and all further polyaramides are listed in Table III.



Another type of copolyamide was prepared by the cocondensation of the terephthaloyl chloride **1e** with the terephthaloyl chloride **7**. The hitherto not yet described terephthaloyl chloride **7** was prepared by acetylation and chlorination of [(4-hydroxyphenyl)thio]terephthalic acid

Table III
Yields and Properties of Polyaramides Prepared by Copolycondensation of Terephthaloyl Chloride 1e with Various Comonomers or Chain Stoppers

polymer	yield (%)	η_{inh}[a] (dL/g)	T_g[b] (°C)	elem formula (formula wt)	elemental analyses	C	H	N	S
5	99	0.96	175	$C_{40}H_{30}N_2O_7S_2$ (714.81)	calcd	67.21	4.23	3.92	8.97
					found	66.68	4.05	4.07	8.61
6	99	1.22	184	$C_{72}H_{52}N_4O_{12}S_4$ (1293.46)	calcd	66.86	4.05	4.33	9.92
					found	66.26	4.18	4.33	9.72
8a	99	2.20		$C_{86}H_{60}N_6O_{14}S_5$ (15.61.75)	calcd	66.14	3.87	5.38	10.26
					found	65.78	3.82	5.41	10.24
8b	99	1.10		$C_{150}H_{104}N_{10}O_{24}S_9$ (2.719.06)	calcd	66.26	3.86	5.15	10.61
					found	65.75	4.44	6.14	10.54
9a	99	1.90		$C_{84}H_{58}N_6O_{13}S_5$ (1.519.71)	calcd	66.39	3.85	5.53	10.55
					found	66.16	4.47	5.43	9.78
9b	98	0.95		$C_{148}H_{102}N_{10}O_{23}S_9$ (2.677.03)	calcd	66.40	3.84	5.23	10.78
					found	65.82	3.99	5.22	10.11
10a	97	0.55		$C_{342}H_{240}N_{22}O_{52}S_{20}$ (6130.98)	calcd	67.00	3.95	5.03	10.46
					found	64.65	3.92	4.71	10.42
10b	95	0.88		$C_{340}H_{232}N_{34}O_{60}S_{24}$ (6523.21)	calcd	62.60	3.59	7.30	11.80
					found	61.99	3.67	7.15	11.66

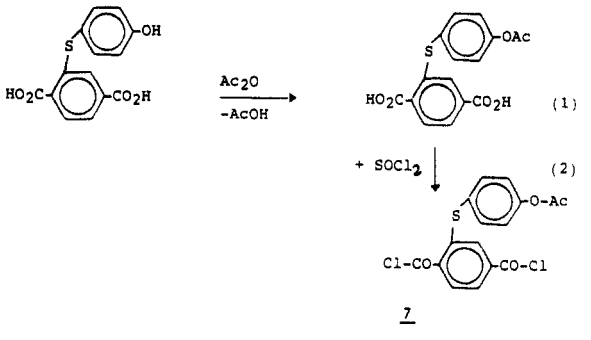
[a] Measured at 25 °C with c = 1 g/L in concentrated H_2SO_4. [b] From DSC measurements with a heating rate of 20 °C/min.

Table IV
Solubilities[a] of Polyaramides Measured at a Potential Concentration of 6 g/L

polymer	CH_2Cl_2	CH_2Cl_2 + TFA[b]	*m*-cresol	DMSO	DMF	NMP	DMF + 5% LiCl	NMP + 5% LiCl	H_2SO_4(conc)
2a	–	–	–	–	–	–	–	++	++
2b	–	–	–	–	–	–	–	++	++
2c	–	–	–	–	–	–	–	++	++
2d	–	–	–	–	–	–	–	++	++
2e	–	–	–	+[c]	–	++	++	++	++
2f	–	++	–	++	–	++	++	++	++
5	–	++	++	++	++	++	++	++	++
6	–	++	–	++	++	++	++	++	++
8a	–	–	–	–	–	–	–	–	++
8b	–	–	–	–	–	+	++	++	++
9a,b	–	–	–	++	–	++	++	++	++
10b	–	–	–	–	–	+	+	+	+

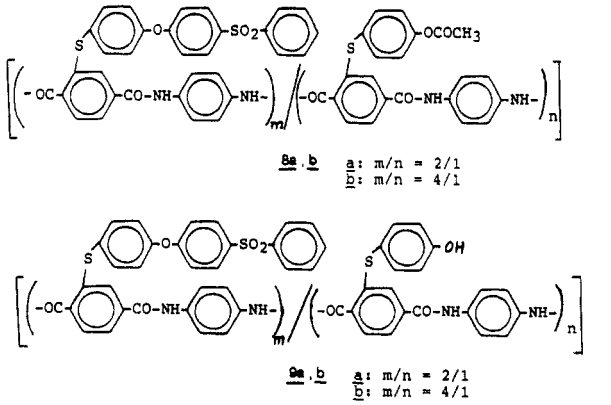
[a] Key: ++, soluble at 25 °C; +, soluble upon heating; –; insoluble. [b] Trifluoroacetic acid (volume ratio 4/1). [c] Partially soluble upon heating.

(eqs 1 and 2). This monomer is of particular interest

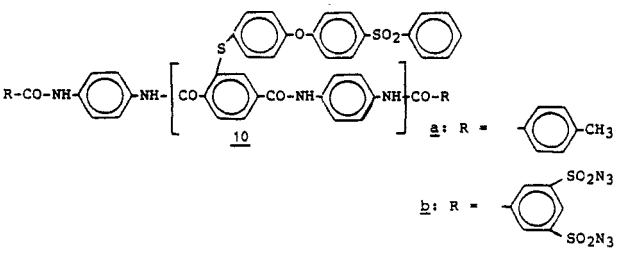


because it allows the introduction of functional groups into the polyaramides. Saponification of the acetate group in the copolyaramides **8a,b** yielded the copolyaramides **9a,b**. Copolyaramides with such functional groups might be useful for transesterification reactions in the preparation of polymer blends by a so-called reactive blending process.

Finally, the molecular weight and the end groups were modified. 4-Methylbenzoyl chloride was added as a chain stopper to the polycondensation of **1e** and silylated 1,4-diaminobenzene. The stoichiometry of **1e** and 4-methylbenzoyl chloride was designed such that an average degree of polymerization of 10 was obtained. The incorporation of 4-methylbenzoyl chloride was confirmed by ^{1}H NMR measurements. The signal of the CH_3 end group showed up at δ = 2.46 ppm (in DMSO-d_6 with internal TMS). Also the inherent viscosities of **2e** and **10a** indicate



that the desired termination steps occurred. In a similar polycondensation 3,5-bis(azidosulfonyl)benzoyl chloride was used as a chain stopper. The IR spectrum of polyaramide **10b** (Figure 2B) exhibits the typical stretching vibrations of the azidosulfonyl groups. As discussed below the end groups influence the solubility of **2e**.



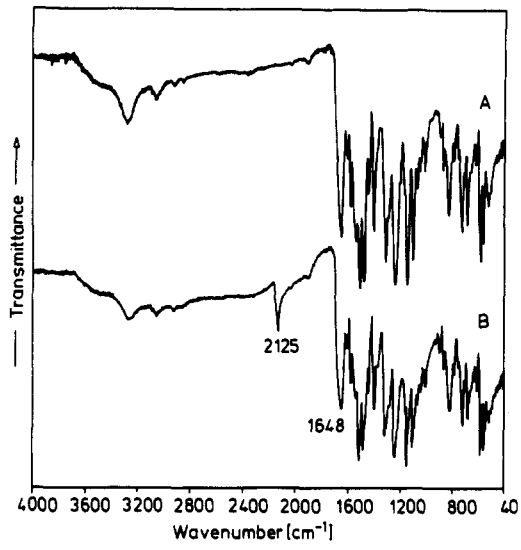
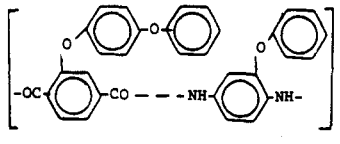


Figure 2. IR spectra (KBr pellet) of polyaramides **2e** (A) and **10b** (B).

Solubilities and Lyotropic Systems. The solubilities of all polyaramides were determined in nine different solvents or solvent mixtures at a (potential) concentration of 6 g/L. The results compiled in Table IV allow some interesting conclusions. First, the four polyamides **2a–d** have nearly identical solubilities, and their solubilities also resemble those of normal Kevlar. From Kevlar and similar quasi linear polyaramides it is known that the main chains form a two-dimensional network with intermolecular H bonds perpendicular to the main chain. The substituents are then accommodated in layers between these H-bonded "sheets". The low solubilities of **2a–d** suggest that these "sheet structures" are nearly as perfect and stable as those of Kevlar itself. A significant improvement of the solubilities occurs when the length of the substituents increases beyond two aromatic rings (**2e, 2f**). Obviously two effects are cooperating. First, the solvation of the longer and more polar side chains makes a greater contribution to the total solvation. Second, the side chains of **2e** and **2f** are longer than the repeating unit. Hence, their accommodation in the interlayer requires a widening of the distance between the sheets. This looser packing of sheets reduces the thermodynamical stability of the crystal lattice and eases the penetration of solvent molecules. The quasi amorphous WAXS patterns of **2e** and **2f** (Figure 3B) also suggest that the sheets themselves are distorted. The significance of these arguments is supported by the finding that the solubilities of polyamide 11[15] are very similar to



11

those of **2e**. In the case of 11 the sum of the pendant aromatic rings is the same as for **2e**, and thus, the problem of their accommodation between the H-bonded sheets is nearly the same despite a different chemical structure. Surprisingly, the modification of both end groups has a measurable influence on the solubilities of **2e**, whereas the solubilities of **10a** are almost identical with those of **2e**; the dissolution of **10b** requires heating in all solvents (Table IV). The solubilities of the copolyamides **8b** and **9a,b** are similar to those of **2e**, but the incorporation of the short side chain reduces the solubility in pure NMP as demonstrated by the properties of **8a** (Table IV).

Another surprising result is the good solubilities of the homopolyamide **5** and, although to a lesser extent, of the copolyamide **6**. Despite the greater stiffness imparted by these benzidine units, **5** is soluble in dimethyl sulfoxide, *m*-cresol, and CH_2Cl_2/TFA mixtures. The solubility of **2e, 2f, 5, 6, 10a,** and **10b** in pure NMP is of particular interest, because it was found that these polyaramides are also compatible at low concentrations (≤10 wt %) with poly(vinylpyrrolidone). These "molecular blends" allow one to investigate the hypothesis of "molecular reinforcement". The characterization of such blends and their mechanical properties will be described in a future paper. In order to elucidate whether the polyamide **2a–f** can form lyotropic phases, the finely powdered materials were dissolved in concentrated H_2SO_4 at 25 °C, so that concentrations of 5, 10, 15, or 20 wt % were obtained. However, in no case was a lyotropic phase observed.

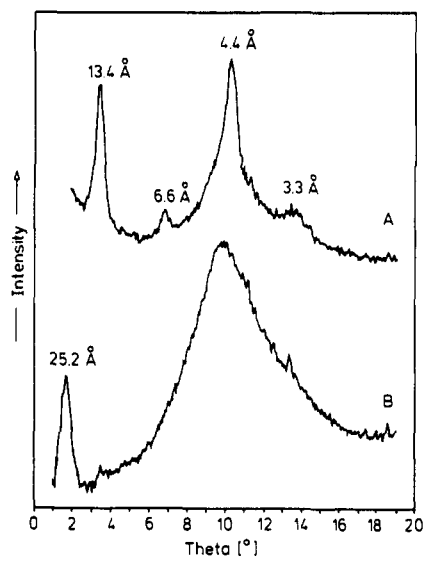


Figure 3. WAXS powder patterns of (A) polyamide **2a** annealed at 320 °C for 4 h and (B) polyamide **2f** annealed at 320 °C for 4 h.

Crystallinity and Thermal Properties. The WAXS powder patterns indicate that the degree of crystallinity of all polyaramides is relatively low despite annealing. Even in the optimum case, i.e., **2a** and **2b**, the crystallinity is only on the order of 35–45% (Figure 3A). The WAXS patterns of **2a** and **2b** are nearly identical; four reflections are detectable (ϑ = 3.3, 6.8, 10.2, and 13.3°). The reflection around ϑ = 10° obviously represents the direct distance between neighboring chains in a H-bonded sheet. This reflection shows up in the WAXS patterns of all polyaramides, but is broader in the case of other polyaramides and looks like an amorphous halo in the case of **2e,f** (Figure 3B) and **6**. This broad reflection suggests that the sheet structures are disturbed, an interpretation which fits in with the improved solubilities. The WAXS patterns of all polyaramides also display a sharp reflection between ϑ = 1.5° and ϑ = 3.5°. This reflection "migrates" to smaller angles with increasing length of the substituent. Presumably, this reflection represents the distance between the H-bonded sheets.

The DSC measurements of most polyaramides do not show any phase transition above 30 °C. Only in the case of polyamides **5** and **6** was a glass transition clearly detectable (Table III). In agreement with these DSC results no melting or sintering process was detectable by optical microscopy up to temperatures around 400 °C, where thermal degradation prevents any reasonable characterization. However, it will be shown in the subsequent paper that DSC endotherms and mobile melts are observable if the substituents bring the T_m down to temperatures ≤410 °C.

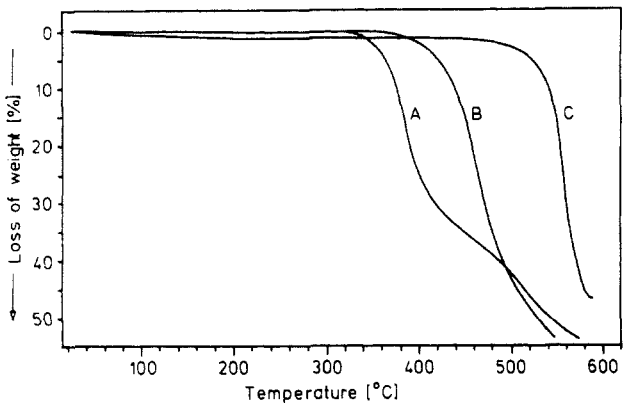


Figure 4. Thermogravimetric analyses conducted under nitrogen at a heating rate of 10 °C/min: (A) polyamide **2c**, (B) polyamide **2e**, and (C) Kevlar.

Finally, the thermostability of several polyamides was examined. Thermogravimetric analyses of normal Kevlar and **2a–f** were conducted under nitrogen at a heating rate of 10 °C/min. As demonstrated in Figure 4 the aryloxy and arylthio groups attached to the terephthaloyl units significantly reduce the thermostability compared to that of normal Kevlar. These TGA curves demonstrate that any kind of measurements above 350 °C will be affected by thermal degradation. This result means that these substituted polyaramides are thermally less stable than aromatic polyesters derived from the same substituted terephthalic acids.[8,9,16]

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Registry No. 2a (copolymer), 142802-86-6; **2a** (SRU), 142865-67-6; **2b** (copolymer), 142802-87-7; **2b** (SRU), 142865-65-4; **2c** (copolymer), 142802-88-8; **2c** (SRU), 142865-69-8; **2d** (copolymer), 142802-84-4; **2d** (SRU), 142865-70-1; **2e** (copolymer), 142802-83-3; **2e** (SRU), 142865-72-3; **2f** (copolymer), 142802-89-9; **2f** (SRU), 142865-73-4; **5** (copolymer), 142802-90-2; **5** (SRU), 142865-75-6; **6** (copolymer), 142802-91-3; **8** (copolymer), 142802-92-4; **9** (copolymer), 142802-94-6; 2-[(4-acetoxyphenyl)thio]terephthaloyl chloride, 142802-80-0; 2-[(4-hydroxyphenyl)thio]terephthalic acid, 142802-79-7; *N,N'*-bis(trimethylsilyl)-3,3'-dimethoxybenzidine, 142802-81-1; 3,3'-dimethoxybenzidine, 119-90-4; chlorotrimethylsilane, 75-77-4; 3,5-bis(azidosulfonyl)benzoyl chloride, 142802-82-2; 3,5-bis(azidosulfonyl)benzoic acid, 58585-69-6; pyridine, 110-86-1; *N,N*-dimethylaniline, 121-69-7; triethylamine, 121-44-8; triphenyl phosphite, 101-02-0; poly(vinylpyrrolidone), 79563-75-0; (1,4-diaminobenzene)(phenoxyterephthaloyl chloride) (copolymer), 142802-85-5.