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New Polymer Syntheses. 68. Kevlar-Type Polyaramides Derived from 2-Phenoxy-1,4-diaminobenzene

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ABSTRACT: 2-Phenoxy-1,4-diaminobenzene was prepared from phenoxyterephthaloyl chloride and trimethylsilyl azide. Its *N*,*N*′-bis(trimethylsilyl) derivative was polycondensed with terephthaloyl chloride and various substituted terephthaloyl chlorides. On the basis of WAXS and DSC measurements, all polyaramides are semicrystalline. Their thermostability in air is relatively low despite a fully aromatic character. When the side chain of the terephthaloyl units has a length of three aromatic rings, the melting points are reduced below 350 °C and reversible melting and crystallizing becomes possible. Surprisingly none of the meltable polyaramides formed an anisotropic melt. However, the polyaramides bearing one or two phenoxy groups formed a lyotropic solution in concentrated H_2SO_4. The solubilities of all polyaramides were determined in eight different solvents. Some polyaramides are soluble in aprotic organic solvents such as dimethyl sulfoxide or *N*-methyl-2-pyrrolidone.

Introduction

In the preceding paper[1] polyaramides derived from 1,4-diaminobenzene and various (aryloxy)- or (arylthio)terephthalic acids were described. Although the substituents of the terephthaloyl units improved significantly the solubility of these polyaramides, a meltable material was never obtained. The present work was aimed at synthesizing Kevlar-type polyaramides from phenoxy-1,4-diaminobenzene and various substituted terephthalic acids. Three aspects were of particular interest: (a) the solubility with regard to the preparation of blends from cosolvents, (b) the formation of lyotropic solutions, and (c) the meltability and the formation of anisotropic melts.

Kevlar-type polyaramides derived from substituted terephthalic acids have been described by several research groups.[2–7] Yet either these polyaramides were reversibly meltable (i.e., the melting and crystallizing cycle was more or less reproducible), but not fully aromatic,[2,3,5] or they were not reversibly meltable,[4,6,7] because of rapid thermal degradation.

Experimental Section

Materials. The substituted terephthalic acids and their acid chlorides were prepared as described previously.[8–11] 2,5-Bis(dodecyloxy)terephthaloyl chloride (mp 62–64 °C) was prepared according to the literature[12] (mp 60 °C). *N*,*N*′-Bis(trimethylsilyl)-1,4-diaminobenzene (mp 101–102 °C) was also prepared according to the literature[13] (mp 103–105 °C). *N*-Methyl-2-pyrrolidone (NMP) was distilled in vacuo, once over K_2CO_3 and twice over P_4O_{10}. Dry lithium chloride was purchased from Aldrich Co. It was stored over P_4O_{10} in vacuo, but used without further purification.

Phenoxy-1,4-diaminobenzene Dihydrochloride. Phenoxyterephthaloyl chloride (0.1 mol) and trimethylsilyl azide (0.24 mol) were stirred in dry dioxane (400 mL) at 80 °C for approximately 1 h until the evolution of N_2 had almost ceased. The reaction mixture was then refluxed for 1 h and concentrated in vacuo, the residue was diluted with toluene (300 mL), and the mixture was concentrated again. The crude residual diisocyanate was then diluted with dioxane (400 mL), concentrated HCl (25 mL) was added, and the mixture was refluxed until the evolution of CO_2 ceased (20–30 min). Afterward, the reaction mixture was concentrated in vacuo, and the crude product was recrystallized from ethanol/toluene: yield 44%. Anal. Calcd for $C_{12}H_{14}Cl_2N_2O$ (273.16): C, 52.77; H, 5.17; N, 10.26; Cl, 25.96. Found: C, 53.34; H, 5.09; N, 10.30; Cl, 25.49.

***N*,*N*′-Bis(trimethylsilyl)-2-phenoxy-1,4-diaminobenzene.** 2-Phenoxy-1,4-diaminobenzene dihydrochloride (0.1 mol) and chlorotrimethylsilane (0.25 mol) were suspended in toluene (600 mL), and triethylamine (0.45 mol) was added dropwise during the heating. Finally the complete reaction mixture was refluxed for 4 h, cooled with ice, and filtered under exclusion of moisture. The filtrate was concentrated in vacuo, and the product was isolated by distillation over a short-way apparatus (160–180 °C (0.005 mbar)): yield 96%; n^{20}_{D} 1.5571; ^1H NMR ($CDCl_3$) (TMS internal): 0.14 (s, 9 H) 0.18 (s, 9 H), 3.00 (s, 1 H), 3.41 (s, 1 H) 6.16–7.36 (8 H) ppm. Anal. Calcd for $C_{18}H_{28}N_2OSi_2$ (344.60): C, 62.74; H, 8.19; N, 8.13. Found: C, 62.59; H, 8.01; N, 8.37.

Polycondensations. In *N*-Methyl-2-pyrrolidone (NMP). Silylated 2-phenoxy-1,4-diaminobenzene (20 mmol) was dissolved in dry NMP (40 mL) containing 2.2 g of LiCl and cooled to −15 °C. The terephthaloyl chloride (20 mmol) was added at once with rapid stirring, and cooling was maintained for 4 h. After slow stirring for 16 h at 20 °C, the reaction mixture was diluted with NMP (200 mL, containing LiCl if necessary) and precipitated with stirring into 2 L of cold water. The polyamide was washed several times with water and methanol and dried at 120 °C for 20 h and 210 °C for 1 h in vacuo. In the case of **4** and **5** a clear solution was never obtained, because neither these polyamides nor bis(dodecyloxy)terephthaloyl chloride is soluble in NMP.

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 under nitrogen at a heating rate of 20 °C/min. The WAXS powder patterns were obtained on a Siemens D-500 powder diffractometer using Ni-filtered Cu Kα radiation. The thermogravimetric analyses were conducted with a Perkin-Elmer TSG-2 at a heating rate of 10 °C/min in N_2.

Results and Discussion

Syntheses. 2-Phenoxy-1,4-diaminobenzene, the basic starting material for all polyaramides of this work, was not known when this work was started. Meanwhile a multistep synthesis based on 4-nitroaniline has been published.[14] The synthetic strategy of this work was based on the Curtius degradation of 2-phenoxyterephthalic acid. However, several attempts to prepare the desired diamine from phenoxyterephthaloyl chloride and sodium azide never gave satisfactory results. An attempt starting from the bishydrazide of phenoxyterephthalic acid also failed. The only satisfactory approach was the reaction of phenoxyterephthaloyl chloride with trimethylsilyl azide[15] followed by acidic hydrolysis of the resulting diisocyanate in a "one-pot procedure" (eqs 1–3). The crystalline dihydrochloride **1** was transformed into the reactive bis(trimethylsilyl) derivative **2** which was isolated by distillation. The silylated diamine **2** was polycondensed with

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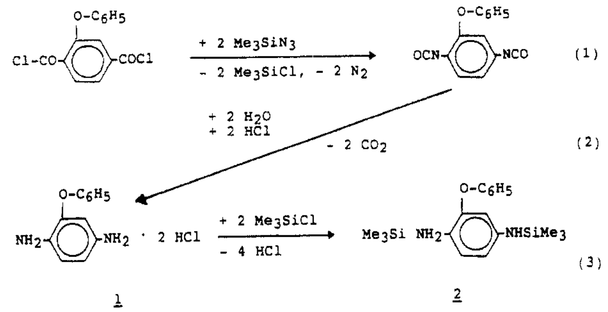
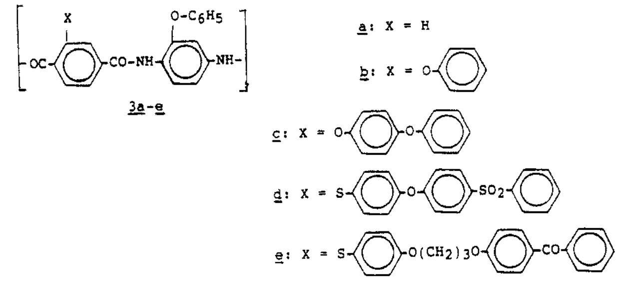
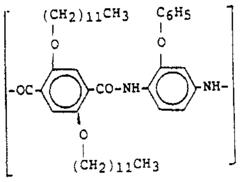


substituted terephthaloyl chlorides in *N*-methyl-2-pyrrolidone (NMP). The polyamides obtained in this way are derived from terephthalic acids (**3a**), from (aryloxy)- (**3b,c**) or (arylthio)terephthalic acids (**3d,e**), and from bis(dodecyloxy)terephthalic acid (**4**). For comparison with **4** the already known[4] polyaramide **5** was also synthesized. Yields and properties of these polyamides are summarized in Table I. Despite high yields, the inherent viscosities decrease with increasing steric demands of the side chain attached to the terephthalic acid (**3a–e**). This result may have two reasons. First, longer side chains cause increasing steric hindrance. Second, an increasing mass of the side chain reduces the number of main chains responsible for the viscosity when the viscosity measurements are conducted with a constant mass/volume ratio.





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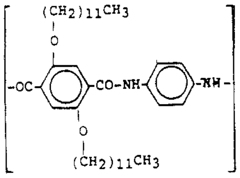

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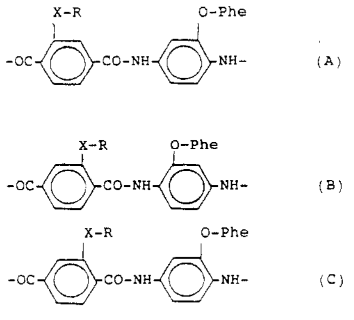
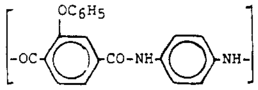
The chemical structure of polyamides built up by 2-phenoxy-1,4-diaminobenzene and monosubstituted terephthalic acids may in principle consist of the three different dyads A, B, and C. The synthesis of the polyaramides **3a–e** was conducted in such a way that the terephthaloyl chloride was added at once to a solution of the silylated diamine. Under these conditions a nearly random sequence is expected, which means the triads A, B, and C should be formed in an intensity ratio of 1/1/2. In order to prove this assumption, ^{13}C NMR spectra of polyamides **3d** and **3e** were recorded because these polyamides possess the most bulky substituents and a good solubility in solvents suited for NMR measurements. Unfortunately broad signals prevented the detection of triad effects even when 90.5-MHz spectra were measured. In order to obtain evidence for the influence of the reaction conditions on the sequence and properties of the double-substituted polyaramides **3b–e**, the synthesis of **3d** was repeated by the inverse procedure. A solution of the silylated diamine was slowly added to a cold (−15 °C) solution of the substituted terephthaloyl chloride. The characterization of the isolated polyaramide **3d′** revealed that IR and ^{1}H NMR spectra were identical with those of **3d**. However, the glass-transition temperature (T_g) and the melting temperature (T_m) of **3d′** were slightly higher than those of **3d** (Table I) despite a lower molecular weight. This slight difference might originate from a higher order of the chemical structure.



Solubilities and Lyotropic Systems. The solubilities of polyamides **3a–e**, **4**, and **5** were studied in eight different solvents or solvent mixtures in such a way that in the case of complete dissolution a final concentration of 6 g/L was obtained. The results compiled in Table II allow the following conclusions. First, one phenoxy group per repeating unit does not significantly change the solubility compared to normal Kevlar regardless of whether the phenoxy group is attached to the diamine (**3a**) or to the terephthalic acid (**6**).[1] Second, the solubility increases with the length of the substituent of the terephthaloyl unit. Third, compared to polyaramides of substituted terephthalic acids and unsubstituted 1,4-diaminobenzene, the additional phenoxy group of the diamine improves the solubility. Fourth, the polyaramides **4** and **5** show the lowest solubility of all polyaramides. This is clearly a consequence of the "paraffin phase" formed by the alkane side chains,[2-5] which cannot be dissolved by acidic solvents. The H-bonded network of the main chains cannot be broken up by aprotic solvents. Mixtures of methanesulfonic acid and chloroform (or CH_2Cl_2) are the only solvent systems found so far that dissolve polyamides of types **4** and **5**.



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The formation of lyotropic phases was checked in such a way that the finely powdered polyaramides were suspended in concentrated H_2SO_4, and these suspensions were allowed to stand at 20–25 °C for several days. It was found that the polyamides **3a** and **3b** form a lyotropic phase, and even in these cases a concentration above 15 wt % is required. The observed texture may be described as resembling "cirrus clouds" (Figure 1). In order to avoid confusion with stress-induced birefringence, the texture was observed over a period of 4 h, and no change was found. When a drop stretched out between two thin glass plates was slightly sheared, the texture of the mobile solution was deformed, but relaxed within 20–25 min. These results clearly confirm that the texture of Figure 1 indicates a lyotropic phase.

Furthermore, the following interesting observations were made. The polyamides **3a** and **3b** do not form lyotropic phases in NMP containing 5% (by weight) LiCl up to a concentration of 20 wt % polyamide. The absence of a lyotropic phase in NMP/LiCl may be due to insufficient solvation and association. Furthermore, the protonation

Table I
Yields and Properties of Polyamides Prepared by Polycondensations of *N,N'*-Bis(trimethylsilyl)-1,4-diaminobenzene and Various Substituted Terephthaloyl Chlorides

polymer	yield (%)	η_{inh}[a] (dL/g)	T_g[b] (°C)	T_m[c] (°C)	elem formula (formula wt)		elemental analyses C	H	N	S
3a	99	3.34		dec	$C_{20}H_{14}N_2O_3$ (330.3)	calcd	72.72	4.27	8.48	
						found	71.40	4.26	8.42	
3b	99	2.43		402 (dec)	$C_{26}H_{18}N_2O_4$ (422.4)	calcd	73.92	4.30	6.63	
						found	72.62	4.32	6.65	
3c	99	1.86		375 (dec)	$C_{32}H_{22}N_2O_5$ (514.5)	calcd	74.70	4.31	5.44	
						found	73.26	4.31	5.54	
3d	98	0.83	167	339	$C_{38}H_{26}N_2O_6S_2$ (670.7)	calcd	68.05	3.91	4.18	9.56
						found	68.04	3.89	4.32	9.61
3d'	98	0.58	171	343	$C_{38}H_{26}N_2O_6S_2$ (670.7)	calcd	68.05	3.91	4.18	9.56
						found	67.71	3.80	4.30	9.71
3e	98	0.74	128	322	$C_{42}H_{32}N_2O_6S$ (692.8)	calcd	72.82	4.66	4.04	4.63
						found	73.04	4.65	4.18	4.65
4	87	0.50[d]		402 dec	$C_{44}H_{62}N_2O_5$ (698.9)	calcd	75.61	8.94	4.01	
						found	75.51	8.85	4.27	
5	98	0.82[d]		dec	$C_{38}H_{58}N_2O_5$ (606.89)	calcd	75.21	9.63	4.62	
						found	74.98	9.52	4.86	

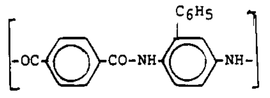
[a] Measured at 25 °C with c = 1 g/L in concentrated H_2SO_4. [b] From the second heating curve of DSC measurements conducted with a heating rate of 20 °C/min. [c] From the first heating curve after annealing at 230 °C for 4 h (heating rate 20 °C/min). [d] Measured at 25 °C with c = 2 g/L in CH_2Cl_2/methanesulfonic acid (volume ratio 4/1).

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

polymer	CH_2Cl_2	CH_2Cl_2 + TFA[b]	*m*-cresol	DMSO	DMF	NMP	NMP + 5% LiCl	H_2SO_4 (conc)
3a	–	–	–	–	–	–	++	++
3b	–	–	–	–	–	+	++	++
3c	–	–	–	+	–	++	++	++
3d	–	++	++	++	++	++	++	++
3e	–	++	++	++	++	++	++	++
4	–	–	–	–	–	–	–	–
5	–	–	–	–	–	–	–	–

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

of the amide groups in concentrated H_2SO_4 enhances the chain stiffness, and thus stabilizes the mesophase. More surprising is the finding that polyaramide **6**, the isomer of **3a**, does not form a lyotropic phase in H_2SO_4, when measured up to a concentration of 20 wt %, although its molecular weight (η_{inh} = 6.0 dL/g) is higher than that of **3a** (η_{inh} = 3.3 dL/g). In this connection it is of interest that a lyotropic phase was reported[6] for polyaramide **7** but not for **8**. This result and our observations confirm that the substitution pattern plays an important role for the formation of a lyotropic phase.



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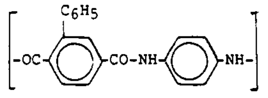

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Crystallinity and Thermal Properties. WAXS powder patterns of all polyaramides were measured at room temperature. They revealed that all members of series **3a–e** are semicrystalline (Figure 2). This result is a little surprising because the polyaramides **3b–e** should possess a more or less random sequence of the dyads A, B, and C as discussed above.

The DSC measurements confirm the existence of crystallites in the case of **3b–e**. The heating trace of **3a** does not exhibit any glass-transition step or endotherm, but indicates thermal degradation above 420 °C. A melting endotherm is detectable in the case of **3b**, illustrating a strong influence of the second substituent on the properties of this polyaramide. However, rapid thermal degradation above T_m prevents the reproducibility of the melting and crystallization process. The same results were obtained for polyamide **3c** despite a slightly lower melting temperature (Figure 3A). Interestingly, both materials **3b** and **3c** have in common that the first heating curve displays a weak endotherm at 262–263 °C (Figure 3A). After annealing at 250 °C (2 h), this endotherm is even more pronounced and appears at 280–282 °C (Figure 3B). Presumably, this endotherm indicates a reversible phase transition in the solid state. Its interpretation requires detailed X-ray studies at high temperatures and is beyond the scope of this work.

In contrast to the DSC measurements of **3a–c**, the DSC curves of **3d** exhibit a distinct glass-transition step (Figure 4). Regardless of whether the samples were dried at 120 or 210 °C, the heating curves display a melting endotherm at 339 °C. The corresponding crystallization exotherm is observable in the cooling trace, and the second heating proves the reproducibility of the melting process (Figure 4), provided the sample was not heated above 360 °C. Optical microscopy confirms the formation of a mobile melt above 340 °C and solidification below 280 °C. When heated to 410 °C, neither recrystallization upon cooling nor melting upon reheating is detectable. This observation demonstrates that the thermal stability of **3d** is not higher than that of **3a–c**. When a sample of **3d** is annealed at 320 °C for 16 h, the heating trace is almost a bar of a glass-transition step and a sharp endotherm appears at 373 °C (Figure 4D). Surprisingly, inspection of the DSC pan and examination by optical microscopy agree in that the annealed sample does not melt above 373 °C. WAXS powder patterns reveal an additional weak reflection (Figure 5B), but the degree of crystallinity is not significantly enhanced. Annealing of polyamides **3c–e** at 320 °C for 16 h finally proves that under these conditions intensive cross-linking occurs, so that all samples turn completely insoluble in all common solvents. Thus, the

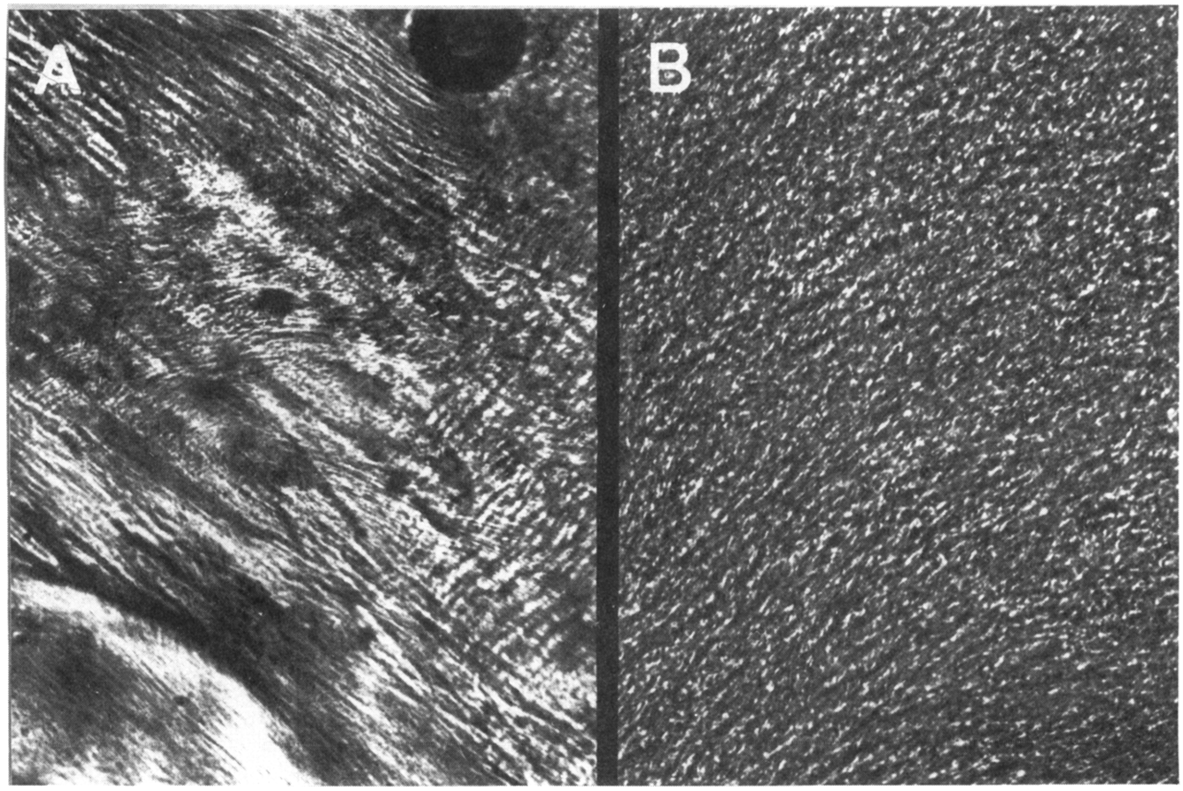

Figure 1. Texture of the lyotropic phase of **3b** in concentrated H_2SO_4 (20% by weight): (A) after slight shearing and (B) after relaxation (30 min) from shearing.

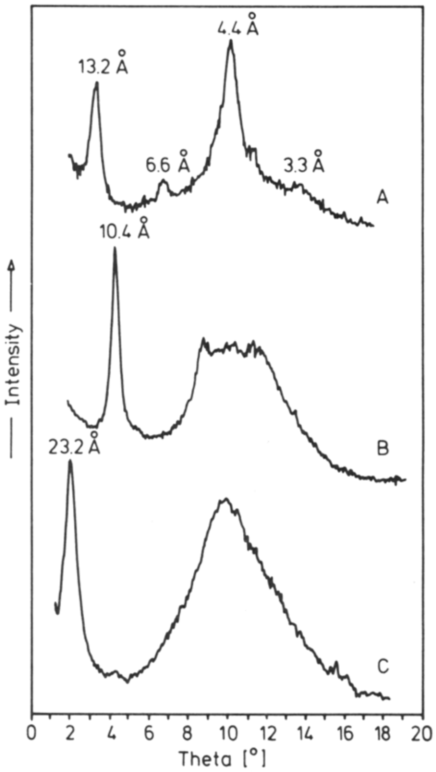

Figure 2. WAXS powder patterns of (A) polyamide **3a**, (B) polyamide **3b**, and (C) polyamide **3c** (all samples annealed at 320 °C for 4 h).

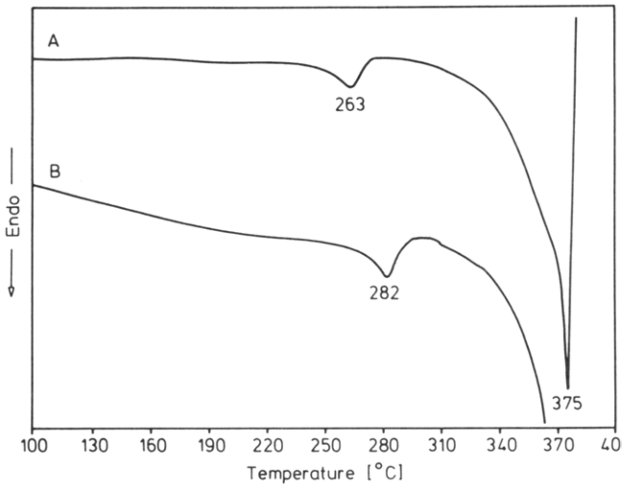

Figure 3. DSC measurements (heating rate 20 °C/min) of polyamide **3c** (A) annealed at 230 °C for 4 h and (B) annealed at 250 °C for 2 h.

lack of meltability of the annealed sample **3d** is clearly the consequence of heavy cross-linking and not of a change of modification or extent of crystallinity.

In contrast to **3d**, the melting process of **3e** at 322 °C (with formation of a mobile melt) was not reversible even when the first heating was limited to 360 °C. Apparently the partially aliphatic side chain reduces the thermal stability further. Nonetheless, an important result of this investigation is the finding that the melt of both polyaramides **3d** and **3e** was isotropic. This unexpected result may have two explanations.

First, rotation around the CO–NH bond eliminates the stiffness of the main chain. ^{1}H NMR spectroscopic studies of two research groups[16,17] agree in that the rotational barrier of polyamides derived from terephthalic acid[16] or 4-aminobenzoic acid[17] are so low that frequent rotation around the CO–N bond occurs above 100 °C and slow rotation even above 50 °C. The "rigid-rod" character of Kevlar in lyotropic solutions is, thus, mainly a consequence of a thermodynamically favored linear conformation. However, the properties of normal Kevlar in H_2SO_4 solution do not allow any conclusion on the conformational situation of substituted polyaramides in the molten state.

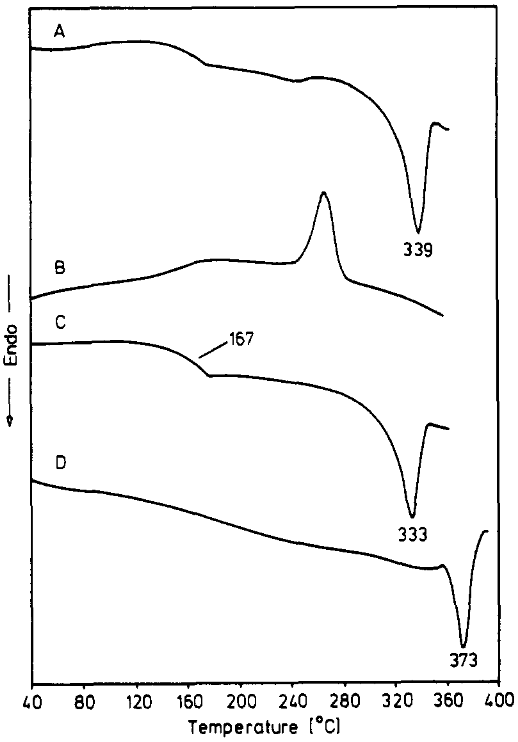

Figure 4. DSC measurements (heating and cooling rate 20 °C/min) of polyaramide **3d**: (A) first heating, (B) first cooling, (C) second heating, and (D) first heating after annealing at 320 °C for 16 h.

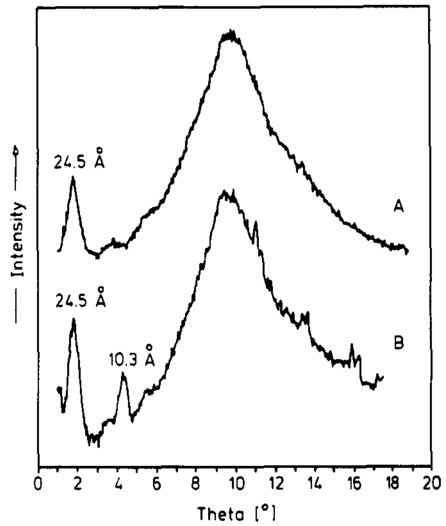

Figure 5. WAXS powder patterns of polyamide **3d**: (A) annealed at 230 °C for 4 h and (B) annealed at 320 °C for 16 h.

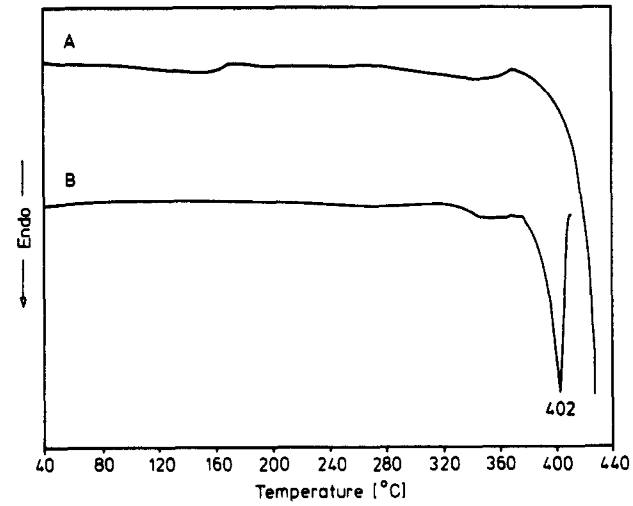

Figure 6. DSC heating traces (heating rate 20 °C/min) of (A) polyamide **5** and (B) polyamide **4**.

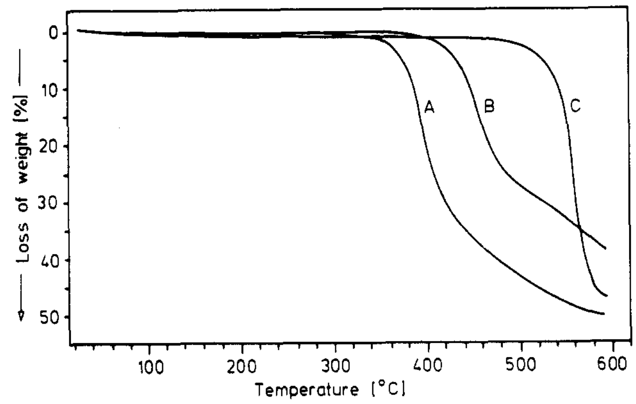

Figure 7. Thermogravimetric measurements conducted at a heating rate of 10 °C/min in N_2: (A) polyamide **3b**, (B) polyamide **3a**, and (C) Kevlar.

A second hypothetical explanation for the lack of an anisotropic melt is the steric demands of the aromatic substituents which may prevent any intermolecular interaction required for the stabilization of an anisotropic phase. Both phenomena, the substituent effect and the formation of *cis*-amide groups, may act in a synergistic way to prevent the formation of a nematic melt. In this connection, it is of interest that aromatic polyesters derived from monosubstituted hydroquinones and monosubstituted terephthalic acids possess unusually low isotropization temperatures.[18]

In order to obtain an amorphous Kevlar-type polyaramide, or a material with a T_m below that of **3e** and **3d**, polyamide **4** was synthesized. Surprisingly, both DSC measurements and optical microscopy agree in that the T_m of **4** is as high as 402 °C (Figure 6B). At this temperature rapid degradation prevents any characterization of the melt with regard to textures. This result was unexpected because WAXS powder patterns of polyamide **5** suggested that this polymer forms a mobile mesophase above 200 °C.[4] Unfortunately, no detailed characterization of polyamide **5** has been published so far. Therefore, its synthesis was repeated under the reaction conditions used for **3a–e** and **4**. Although, the WAXS pattern recorded at 200 °C was identical with that reported in the literature (Figure 1b in ref 4), no melting was detectable by optical microscopy. A powder of solid particles could be observed up to temperatures where darkening of the material prevents any further characterization. A dark powder was also detected when the DSC pans were opened after heating to 400 °C. Furthermore, no melting endotherm was detectable in the DSC curve above 40 °C (Figure 6A). Above 400 °C the thermal degradation was rapid and intensive. In contrast, the formation of a melt was clearly observable under the microscope and in the DSC pans, when polyamide **4** was heated to 410 °C. Thus, these results clearly demonstrate that two dodecyloxy side chains attached to terephthalic acid improve neither the solubility nor the meltability of Kevlar-type polyaramides. In both regards one aromatic side chain, such as that of polyamide **3d** or **3e**, is by far more effective.

The conspicuous difference between **5** (or **4**) and **3d** or **3e** is obviously the consequence of more or less stable sheet structures formed by the main chains via H bonds in perpendicular directions. H bonds may vary in length and direction and are compatible with a lower or higher degree of order of the array of main chains. In the case of 5 the WAXS pattern displays one sharp small-angle reflection, indicating a rather perfect layer structure. A slight disorder of the sheet structures may exist which prevents the appearance of further sharp X-ray reflections without signficant destabilization of the solid state. The stiffer and longer side chains of **3d** and **3c** apparently cause a stronge distortion of the sheet structure and favor the "solvation" of the main chains in the solid state.

Finally the thermostabilities of the polyaramides **3a–e** need a short comment. As illustrated by Figure 7 aryloxy or arylthio substituents considerably reduce the thermal stability of Kevlar-type polyamides. Therefore, any kind of measurements above 350 °C and in particular above 400 °C will be affected by thermal degradation. Thus, these substituted polyaramides are even less thermostable than aromatic polyesters derived from the same substituted terephthalic acids.[9,10,18]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for financial support.

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Registry No. 1, 129307-98-8; 2, 142802-69-5; **3a** (copolymer), 142802-78-6; **3a** (SRU), 142865-66-5; **3b** (copolymer), 142802-77-5; **3b** (SRU), 142865-68-7; **3c** (copolymer), 142802-74-2; **3c** (SRU), 142865-71-2; **3d** (copolymer), 142802-73-1; **3d** (SRU), 142865-74-5; **3e** (copolymer), 142802-71-9; **3e** (SRU), 142865-76-7; **4** (copolymer), 142802-76-4; **4** (SRU), 142865-77-8; **5** (copolymer), 142802-75-3; **5** (SRU), 107530-16-5; phenoxyterephthaloyl dichloride, 115673-75-1; trimethylsilyl azide, 4648-54-8; chlorotrimethylsilane, 75-77-4.