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New Polymer Syntheses. 69. Polyamides Derived from Deuterated Terephthalic Acid or Phenoxyterephthalic Acid

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ABSTRACT: Starting from deuterated phenol, phenoxyterephthalic acid with a deuterated side chain was synthesized. A broad variety of polyamides was prepared from this monomer and from tetradeuterated terephthalic acid. 1,6-Diaminohexane, 1,12-diaminododecane, 4,4′-trimethylenebis[piperidine], 1,4-diaminobenzene, 2-phenoxy-1,4-diaminobenzene, *N,N*′-diphenyl-1,4-diaminobenzene, and 4,4′-diaminodiphenyl ether were used as reaction partners. All polyamides were characterized by elemental analyses, inherent viscosities, ^{1}H-NMR spectra, DSC measurements, and WAXS powder patterns. Preliminary ^{2}H NMR measurements conducted at room temperature suggest that polyamides devoid of H bonds are less mobile than comparable polyamides with H-bonded pleeted sheets.

Introduction

The present work is part of a broader study of synthesis and characterization of selectively deuterated polycondensates. This study includes aromatic polyesters (mainly liquid-crystalline ones), poly(ester amide)s, and polyamides. ^{2}H NMR measurements at variable temperature should provide information on segmental mobility depending on chemical structure and thermal history. In all polycondensates two kinds of deuterated monomers were used to allow optimum comparability. Phenoxyterephthalic acid with a deuterated phenyl group was used as a source of information on the mobility of side chains, and deuterated terephthalic acid or deuterated hydroquinone should provide information on the mobility of the main chain. The present work describes synthesis and general characterization of selectively deuterated polyamides, whereas detailed ^{2}H NMR spectroscopic measurements will be discussed in future papers. With reference to this, it should be mentioned that ^{2}H NMR spectroscopic studies of deuterated Nylon-6,6 and poly(*p*-phenyleneterephthalamide) have recently been published by other authors.[1-4]

Experimental Section

Materials. Phenol-d_5 and terephthalic acid-d_4 were purchased from Alfred Hempel GmbH & Co (4000 Düsseldorf 30, FRG) and used without further purification. Dimethyl nitroterephthalate was purchased from Aldrich Co. (Milwaukee, WI) and used without additional purification. The aliphatic diamines were also purchased from Aldrich Co. and distilled in vacuo. *N,N*′-Bis(trimethylsilyl)-1,4-diaminobenzene[5] (mp 101–103 °C) and *N,N*′-bis(trimethylsilyl)-2-phenoxy-1,4-diaminobenzene[6] (n^{20}_D 1.5571) were prepared by means of chlorotrimethylsilane and triethylamine in refluxing toluene and isolated by distillation in vacuo. *N,N*′-Diphenyl-1,4-diaminobenzene was purchased from Aldrich Co. and used after drying over P_4O_{10} in vacuo. The silylation of *N,N*′-diphenyl-1,4-diaminobenzene was conducted by means of *n*-butyllithium and chlorotrimethylsilane according to literature[7] (mp 126–127 °C, mp 128–129 °C in ref 7). The dichloromethane used for interfacial polycondensations was distilled over P_4O_{10}. Sulfolane was distilled over powdered CaH_2 in vacuo.

Deuterated Terephthaloyl Chloride. Terephthalic acid-d_4 (0.2 mol) was refluxed with hexamethyldisilazane (0.15 mol) in xylylene (200 mL) until the evolution of NH_3 had ceased. The reaction mixture was then concentrated in vacuo, the residue diluted with xylylene (100 mL), and the mixture was concentrated again to remove residual hexamethyldisilazane. Finally, the residue was dissolved in chloroform (150 mL) and refluxed with thionyl chloride (50 mL) until the evolution of SO_2 ceased. Afterward the reaction mixture was concentrated in vacuo, the residue was dissolved in dry toluene (100 mL), and the mixture was concentrated again. The crystallization of the product was completed by portionwise addition of ligroin. Yield: 92%. Mp: 81–83 °C (mp 77–78 °C).[8]

(Phenoxy-d_5)terephthaloyl chloride was prepared analogously from (phenoxy-d_5) terephthalic acid;[9] yield: 90%. Mp: 51–53 °C. Anal. Calcd for $C_{14}H_3D_5Cl_2O_3$ (300.16): C, 56.02; Cl, 23.62. Found: C, 56.62; Cl, 23.40.

Interfacial Polycondensations. A deuterated terephthaloyl chloride (**1** or **2**, 20 mmol) was dissolved in dry dichloromethane (100 mL) and cooled to 0 °C. An aliphatic diamine (20 mmol) was dissolved or suspended in a mixture of water (55 mL) and 1 N sodium hydroxide (45 mL) cooled to 0 °C. Both solutions were combined and mixed with a high-speed stirrer for 30 min. When the polyamide was soluble (e.g. **6**), the organic phase was diluted with dichloromethane (100 mL), washed several times with water, concentrated in vacuo, and precipitated into diethyl ether. When the polyamide was insoluble, it was isolated by filtration washed several times with water and methanol and dried at 80 °C in vacuo.

Polycondensations in *N*-Methylpyrrolidone-2 (NMP). A silylated aromatic diamine (20 mmol) was dissolved in dry NMP (40 mL containing 2 g of LiCl) and cooled with stirring under nitrogen to ca. −15 °C. The deuterated terephthaloyl chloride (20 mmol) was then added at once, and the reaction mixture was rapidly stirred for next 10 min until the acid chloride had dissolved. Slow stirring was continued for the next 20 h. The resulting gel was then diluted with NMP (200 mL + 4 g of LiCl) and slowly precipitated with stirring into water (2 L). In the case of polyamide **7a** 100 mL of dry NMP containing 5.2 g of $CaCl_2$ was used.

Thermal Polycondensations. Deuterated terephthaloyl chloride (20 mmol), silylated *N,N*′-diphenyl-1,4-diaminobenzene (20 mmol), and 30 mL of dry sulfolane were weighed into a cylindrical reactor equipped with stirrer and gas inlet and outlet tubes. The reaction mixture was stirred at 180 °C under nitrogen for 16 h, afterward diluted with sulfolane (75 mL) and precipitated with stirring into methanol. The precipitated polyamides (**9**, **10**) were washed several times with methanol and dried at 120 °C in vacuo.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 or 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 100-MHz ^{1}NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5-mm-o.d. sample tubes.

The ^{2}H NMR spectra were measured with a Bruker MSL-300 FT NMR spectrometer at 25 °C. A saturation recovery pulse sequence with ten 90° x-pulses were used (pulse length for 90°

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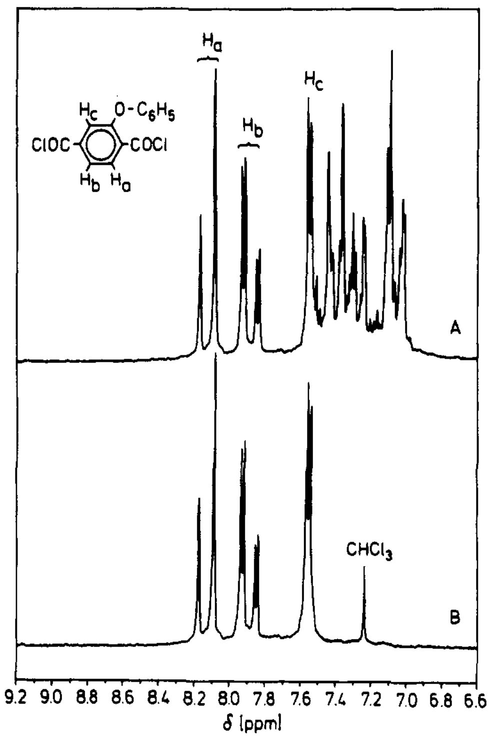


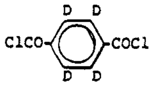
Figure 1. 100-MHz ^{1}H NMR spectra of (A) phenoxyterephthaloyl chloride and (B) phenoxyterephthaloyl chloride with a deuterated phenoxy group in $CDCl_3$.

$= 4.3$ μs, used pulse length $= 3.3$ μs). The waiting time was 3 times the longest relaxation time of each sample. For the spin echo pulse sequence a spacing of 20 μs between x- and y-pulses was used.

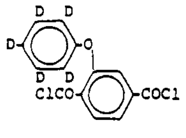
The WAXS powder patterns were obtained on a Siemens D 500 diffractometer using Ni-filtered Cu Kα radiation.

Results and Discussion

Syntheses of Deuterated Monomers. The deuterated monomers used in this work are terephthaloyl chloride (**1**) and 2-phenoxyterephthaloyl chloride (**2**). In order to avoid H/D exchange monomer **1** was prepared from commercial terephthalic acid-d_4 in such a way that the acid was silylated with hexamethyldisilazane and the bis(trimethylsilyl) ester was reacted with thionyl chloride (eqs 1 and 2). The synthesis of (phenoxy-d_5)terephthalic acid from deuterated phenol and dimethyl nitroterephthalate has recently been described.[9] Again, the free dicarboxylic acid was silylated and then treated with thionyl chloride in refluxing chloroform. The success of this synthetic strategy is illustrated by the ^{1}H NMR spectra of Figure 1 which provide a comparison of deuterated and protonated phenoxyterephthaloyl chloride.



1



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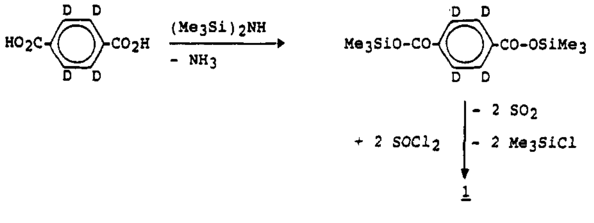
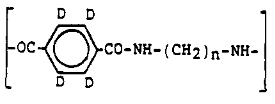


(1)

(2)

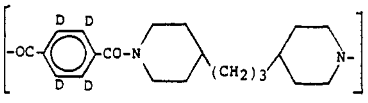
Syntheses of Polyamides. The three deuterated polyamides **3a**, **3b**, and **4** were prepared from monomer **1** and 1,6-diaminohexane, 1,12-diaminododecane, or 4,4'-trimethylenebis[piperidine] by interfacial polycondensation. Their yields and properties are listed in Table I. The protonated analogs of polyamides **3a** and **4** have been described by other authors.[10,11] The protonated polyamide **3b** has been reported in a patent of ICI.[12] The three polyamides **5a**, **5b**, and **6** were prepared from monomer **2** again by interfacial polycondensation (for yields and properties see Table I). The protonated analogs of these polyamides have been described quite recently.[13] The aromatic polyamides **7a–c** and **8a–c** were prepared from monomer **1** or **2** by polycondensation with N,N'-bissilylated 1,4-diaminobenzene, bissilylated 2-phenoxy-1,4-diaminobenzene, or N,N'-bis(trimethylsilyl)-4,4'-diaminodiphenyl ether. All polycondensations were conducted in dry N-methylpyrrolidone containing LiCl (5 wt %) at -15 °C as recommended by Imai and co-workers.[14,15] Yields and properties are compiled in Table II.



a: n = 6

b: n = 12

3a, b



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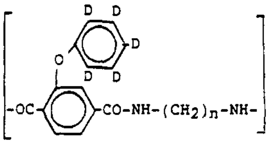
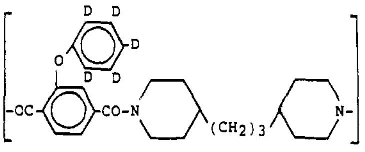


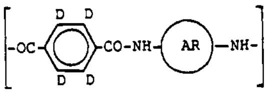
a: n = 6

b: n = 12

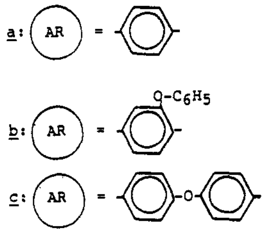
5a, b

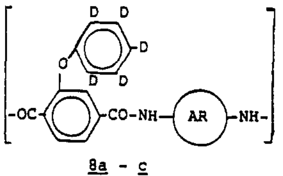


6

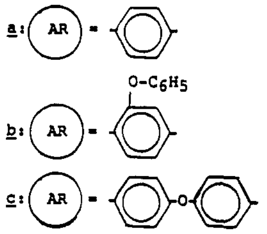


7a - c





8a - c



The protonated polyaramide **7a** is a commercial product. The protonated analogs of **7b**, **8a**, and **8b** were recently described in previous parts of this series.[6,16] The protonated analog of **7c** has been described in ref 15 and the protonated analog of **8c** in a patent of Hüls AG.[17] The polyaramides **9** and **10** were obtained by polycondensation

Table I
Yields and Properties of Deuterated Polyamides Derived from Aliphatic α,ω-Diamines

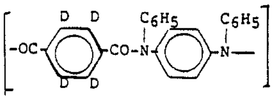
polymer	yield (%)	η_{inh}[a] (dL/g)	T_g[c] (°C)	T_m[c] (°C)	elem formula (fw)	elem anal.	C	N
3a	88	1.10[b]	144	377	$C_{14}D_4H_{14}N_2O_2$ (250.34)	calcd	67.17	11.19
						found	65.41	10.86
3b	87	0.50	116	302	$C_{20}D_4H_{26}N_2O_2$ (334.50)	calcd	71.81	8.38
						found	70.97	8.18
4	86	1.43	149	278	$C_{21}D_4H_{24}N_2O_2$ (344.50)	calcd	73.22	8.13
						found	72.69	8.02
5a	68	0.83	108	201	$C_{20}D_5H_{17}N_2O_3$ (343.45)	calcd	69.94	8.16
						found	69.32	7.88
5b	70	0.81	75	145	$C_{26}D_5H_{29}N_2O_3$ (427.61)	calcd	73.03	6.55
						found	72.56	6.51
6	83	0.51	134	amorphous	$C_{27}D_5H_{27}N_2O_3$ (437.52)	calcd	74.12	6.40
						found	73.55	6.33

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1). [b] Measured at 25 °C with $c = 1$ g/L in concentrated H_2SO_4. [c] From DSC measurements with heating and cooling rates of 20 °C/min.

Table II
Yields and Properties of Deuterated Polyamides Derived from Aromatic Diamines

formula no.	yield (%)	η_{inh}[a] (dL/g)	T_g[b] (°C)	elem formula (fw)	elem anal.	C	N
7a	99	2.28 4.44		$C_{14}D_4H_6N_2O_2$ (242.28)	calcd	69.41	11.56
					found	68.48	11.51
7b	99	2.70		$C_{20}D_4H_{10}N_2O_3$ (334.37)	calcd	71.84	8.38
					found	71.81	8.36
7c	99	3.90		$C_{20}D_4H_{10}N_2O_3$ (334.37)	calcd	71.84	8.38
					found	71.39	8.40
8a	99	2.10 3.30		$C_{20}D_5H_9N_2O_3$ (335.38)	calcd	71.63	8.35
					found	70.97	8.41
8b	97	1.40		$C_{26}D_5H_{13}N_2O_4$ (427.48)	calcd	73.05	6.55
					found	72.66	6.62
8c	98	1.54	218	$C_{26}D_5H_{13}N_2O_4$ (427.48)	calcd	73.05	6.55
					found	72.11	6.44
9	93	1.96	232[c]	$C_{26}D_4H_{14}N_2O_2$ (394.47)	calcd	79.17	7.10
					found	78.76	7.12
10	91	0.90	202	$C_{32}D_5H_{17}N_2O_3$ (487.58)	calcd	78.83	5.75
					found	77.92	5.70

[a] Measured at 25 °C with $c = 1$ g/L in concentrated H_2SO_4. [b] From DSC measurements with heating and cooling rates of 20 °C/min. [c] T_m = 409 °C (DSC measurements with heating rate of 20 °C/min after annealing at 400 °C).



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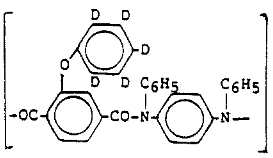

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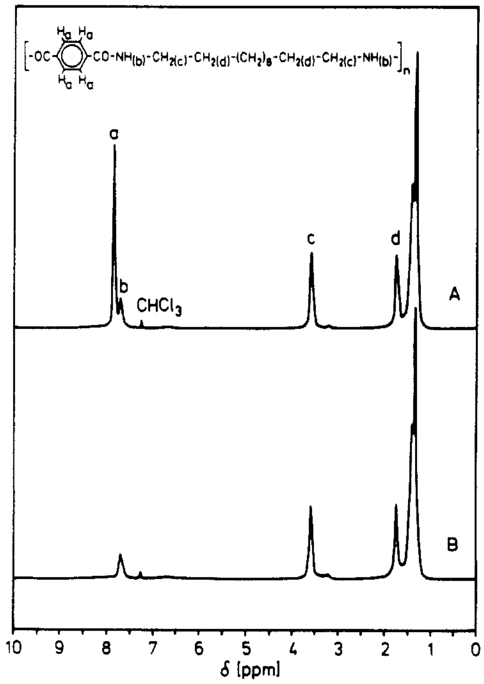

Figure 2. 100-MHz ^{1}H NMR spectra of (A) the fully protonated polyamide **3b** and (B) polyamide **3b** in TFA/$CDCl_3$ (1:1).

of monomer **1** or **2** with the *N,N'*-bis(trimethylsilyl) derivative of *N,N'*-diphenyl-1,4-diaminobenzene in sulfolane at 180 °C. The protonated analog of **9** was prepared in this way by Imai et al.[7] The protonated version of polyamide **10** has not been described to date. The properties of **9** and **10** are discussed below. Since the syntheses of all these polyamides were conducted under mild conditions no H/D exchange is expected. The elemental analyses and ^{1}H NMR spectra (e.g. Figure 2) indeed agreed with the formulas depicted above.

Properties of Polyamides 9 and 10. For the protonated version of polyaramide **9** a melting temperature (T_m) of 395 °C was reported,[18] but neither a WAXS pattern nor detailed DSC measurements were published. The WAXS pattern of **9** confirms that this polyamide is indeed a highly crystalline material (Figure 3B). The DSC curves of the sample dried at 120 °C exhibit two endotherms at 392 and 408 °C (Figure 4A). Quenching from the melt at 415 °C yields an amorphous material which displays a

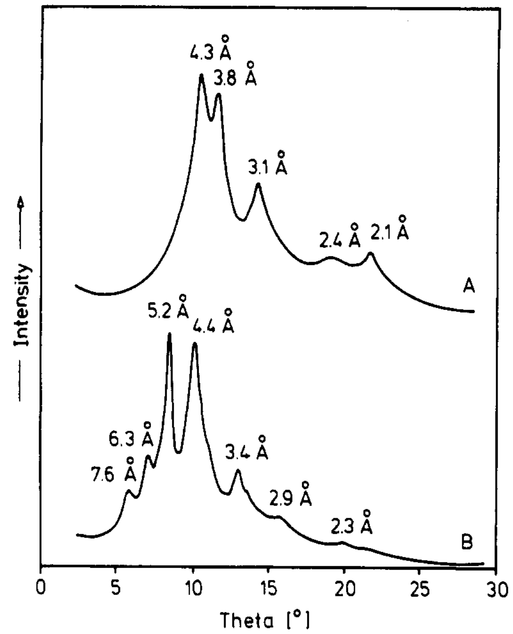

Figure 3. WAXS powder patterns measured at 25 °C: (A) polyamide **7a** (Kevlar); (B) polyamide **9**.

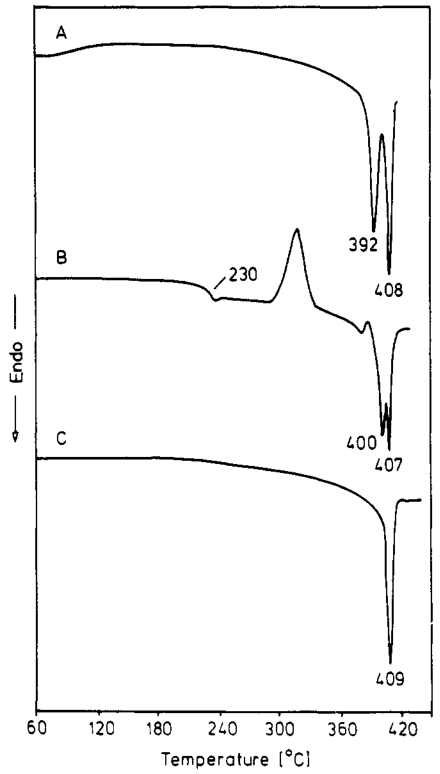

Figure 4. DSC measurements (heating/cooling rates 20 °C/min) of polyamide **9**: (A) first heating; (B) second heating after quenching from the melt at 415 °C; (C) third heating after annealing at 400 °C (2 min).

crystallization exotherm and again two melting endotherms (Figure 4B). However, after annealing at 400 °C (2 min), the first endotherm has disappeared (Figure 4C). These observations indicate that polyamide **9** is a highly crystalline, reversibly melting material which does not form a mesophase (confirmed by optical microscopy). It is soluble in concentrated H_2SO_4, *m*-cresol, and mixtures of trifluoroacetic acid with chloroform or dichloromethane, but not in aprotic solvents.

In conjunction with this, it may be of interest to compare **7a** and **9** also with regard to the formation of lyotropic phases. When 5 or 10% (w/v) solutions of **9** in concentrated sulfuric acid were examined by optical microscopy with crossed polarizers, only isotropic phases were found. At higher concentrations of **9** (15 or 20% w/v) heterogeneous suspensions were obtained. Upon heating to temperatures above 100 °C, the crystallites of **9** gradually dissolved, yielding an isotropic solution. Upon cooling, part of polyamides **9** crystallized again. In other words **7a** and **9** are quite different with regard to lyotropic solutions.

When a phenoxy group is attached to the terephthaloyl unit of **9** the properties change dramatically. Polyaramide **10** is completely amorphous with a T_g around 202 °C. It is soluble not only in numerous protic solvents, such as concentrated H_2SO_4, trifluoroacetic acid, or *m*-cresol, but also in nonprotic solvents, such as *N*-methylpyrrolidone-2, chloroform, and dichloromethane. This conspicuous change of properties stands in sharp contrast to those of normal poly(*p*-phenyleneterephthalamide) (Kevlar), where introduction of one phenoxy group does not cause a significant change of crystallinity or solubility. A hypothetical explanation results from the assumption that the crowding of substituents in the case of **10** favors the formation of cis-amide groups. It is well-known from ^{1}H NMR studies of monomers and polyamides[19,20] that the rotational barrier of aromatic amide groups is so low that frequent rotation around the CO–N bond occurs at temperatures above 100 °C. Therefore, the rigid-rod character of poly(*p*-phenyleneterephthalamide) and related polyaramides is a result not of a high rotational barrier but of a thermodynamically favored quasi linear conformation.

^{2}H NMR Spectroscopy. Detailed ^{2}H NMR spectroscopic studies of individual polyamides will be published in future papers. Those studies will comprise both T_1 measurements and line form analyses at temperatures up to 300 °C. In the present work a series of ^{2}H NMR spectra should be presented with two aims. First, it should demonstrate the successful incorporation of deuterated monomers into the polyamides under investigation. Second, it should allow a comparison of polyamides forming intermolecular H bonds with polyamides devoid of H bonds. Thus, the spectra of Figures 5 and 6 were arranged in such a way that they combine H-bonded and H-bond-free polyamides of similar structure.

A qualitative evaluation of these spectra can easily be made by comparing the intensities of pairs of signals at high frequencies (±55 to 60 kHz) with the pairs of signals at low frequencies (±10 to 15 kHz). The "outer pair" of signals represents ^{2}H nuclei in immobile monomeric units, whereas the "inner pair" represents the mobile nuclei. Inspection of Figures 5 and 6 reveals that the H-bond-free polyamides are almost bare of mobile monomeric units in contrast to the H-bonded counterparts. Even in the case of Figure 5E,F it is clear that the H-bonded polyamide **8a** contains a higher molar fraction of mobile phenoxy groups than polyamide **10**. This qualitative difference is clearly not the result of different crystallinities. It is obvious that the monomeric units may be less mobile in the crystalline phase and a higher degree of crystallinity will reduce the total fraction of mobile groups. This relationship is illustrated by the influence of annealing on the ^{2}H NMR spectrum of polyamide **5a** (Figure 6A,B). However, the H-bond-free polyamides **6** and **10** are completely amorphous in contrast to their H-bonded counterparts which are semicrystalline. Polyamide **4** is mainly amorphous when precipitated from cold methanol and dried below 120 °C or when quenched from the melt. The spectrum of Figure 5B was measured from such an amorphous sample. However, polyamide **4** crystallizes upon annealing above T_g.

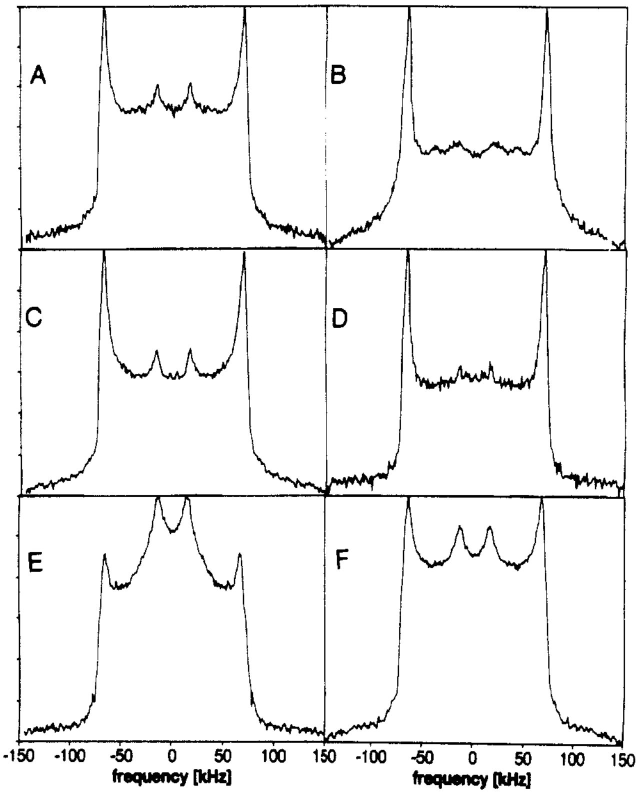

Figure 5. ^{2}H NMR spectra (fully relaxed) measured at 25 °C: (A) polyamide **3a** dried at 80 °C after precipitation; (B) polyamide **4** dried at 80 °C after precipitation; (C) polyamide **7a** dried at 120 °C after precipitation; (D) polyamide **9** dried at 120 °C after precipitation; (E) polyamide **8a** dried at 120 °C after precipitation; (F) polyamide **10** dried at 120 °C after precipitation.

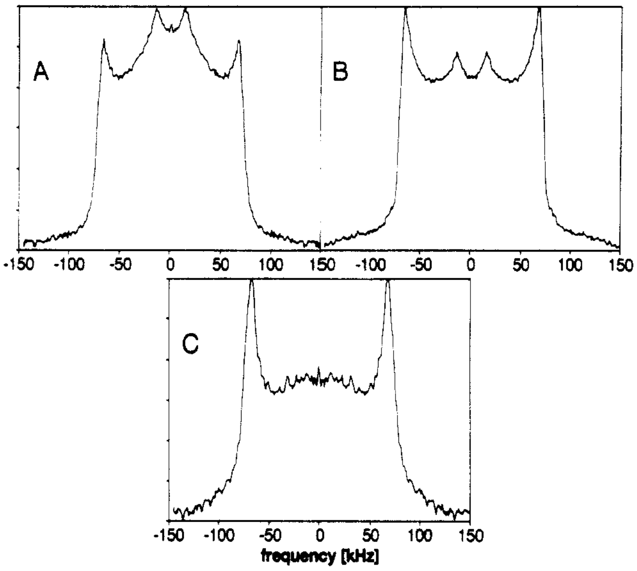

Figure 6. ^{2}H NMR spectra (fully relaxed) measured at 25 °C: (A) polyamide **5a** dried at 80 °C after precipitation; (B) polyamide **5a** annealed 4 h at 180 °C; (C) polyamide **6** dried at 80 °C after precipitation.

Surprising also is the observation of mobile benzene rings in the stiff and highly crystalline polyaramide **7a** (Kevlar). However, this observation has already been published by another research group[3,4] and is, thus, now confirmed for two samples of different origin (Figure 5C,D). The H-bond-free polyamide **9** is also crystalline, and the WAXS powder patterns (Figure 3) surprisingly indicate that its crystallinity may be as high as that of **7a** Kevlar. Upon annealing at 400 °C, the crystallinity even increases and may reach a level >80% (also true for **7a**). The qualitative interpretation of the line form discussed here is fully supported by line shape measurements and analyses conducted at shorter relaxation times. The above interpretation is also confirmed by detailed relaxation time (T_1) measurements which will be published separately.

Thus, the results of this study clearly demonstrate that the amorphous phase of H-bonded polyamides is more mobile than the amorphous phase of H-bond-free polyamides. Since the H bonds are an attractive force between neighboring amide groups, the higher mobility in H-bonded polyamides cannot be explained by a greater distance of the aromatic building blocks in general. The only speculative explanation that can be offered at the current stage of research is the assumption that the H bonds form a three-dimensional irregular network in the amorphous phase which leaves more space for a small fraction of individual phenyl and phenylene rings than the more homogeneously packed H-bond-free polyamides. It is well-known from IR spectroscopy that amorphous polyamides can form more than 90 or even 95% of all possible H bonds in their amorphous phase but a small part cannot be formed. Since the H bonds are stronger than van der Vaals or dipole–dipole interactions, an irregular network of H bonds my well involve sites where the neighboring chain segments have some space for a limited mobility. The well-known uptake of water by H-bond-forming polyamides may be considered as a clue in this direction.

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