Macromolecules 1994, *27,* 1509–1516

Layer Structure. 1. Poly(phenylene–terephthalamide)s Derived from Mono-, Di-, and Tetrakis(alkylthio)terephthalic Acids

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Received July 3, 1993; Revised Manuscript Received December 1, 1993•

ABSTRACT: Tetrakis(alkylthio)terephthalic acids were prepared by nucleophilic substitution of diethyl tetrachloroterephthalates. Three groups of substituted poly(phenylene–terephthalamide)s were prepared polycondensation of *N,N'*-bis(trimethylsilyl)-1,4-diaminobenzene with substituted terephthaloyl chlorides. Mono-, bis-, and tetrakis(alkylthio)terephthaloyl chlorides with octyl or hexadecyl side chains were used as reaction partners. These polyaramides form three different kinds of layer structures with H-bonded sheets of the main chains and partially ordered paraffin domains between these sheets. The reversible melting and crystallization of the paraffin domains can be monitored by ^{13}C NMR CP/MAS and DSC measurements. All polyaramides are infusible below 400 °C. Their solubilities were determined in 17 solvents. Extremely poor solubilities were found in all cases. It is discussed and demonstrated that polar aromatic side chains play the role of a "bound solvent" more efficiently than alkyl side chains.

Introduction

The present work is part of a broader systematic study of rigid rod polyaramides derived from substituted terephthalic acids.[1-4] The substituents have the purpose of improving the meltability, the solubility, and the compatibility with other (matrix) polymers with regard to molecular blends. Poly(*p*-phenylene–terephthalamide)s derived from 2,5-dialkoxyterephthalic acids have recently been studied by several groups.[5-11] A significant improvement of both meltability and solubility requires the combination of a 2,5-bis(dodecyloxy)terephthalic acid with a substituted *p*-phenylenediamine.[2,7,10,11] Better soluble and in special cases even meltable poly(*p*-phenylene–terephthalamides) may also be obtained on the basis of monosubstituted terephthalic acids, provided the substituent is a longer aromatic side chain with two or more benzene rings.[1,2,4,12] Some of the substituted rigid-rod polyaramides may even form lyotropic solutions,[2,12,13] but the correlation between substitution pattern and lyotropic solutions is not well understood. In order to improve the knowledge about structure–property relationships of substituted polyaramides, the present work was aimed at studying poly(*p*-phenylene–terephthalamide)s with one, two, or four alkyl side chains attached to the terephthalic acid.

Experimental Section

Materials. *n*-Octyl, *n*-dodecyl, and *n*-hexadecyl merecaptan were purchased from Aldrich Co. (Milwaukee, WI) and used without purification. Tetrachloroterephthalic acid was a gift of Bayer AG (Krefeld, FRG). It was converted to the diethyl ester (mp 60–61 °C)[14] by azeotropic esterification with ethanol/toluene. *N,N'*-Bis(trimethylsilyl)-1,4-diaminobenzene (mp 102–104 °C) was prepared according to the literature.[15] *N*-Methylpyrrolidone (NMP) was purified by one distillation over freshly dried K_2CO_3 and a subsequent distillation over P_4O_{10} (both in vacuum). γ-Picolin was refluxed and distilled over freshly powdered CaH_2.

Diethyl Tetrakis(alkylthio)terephthalates (Table 1). (A) Diethyl Tetrachloroterephthalate. Tetrachloroterephthalic acid (0.1 mol) was dissolved in hot xylene, distilled thionyl chloride (70 mL) was added, and the reaction mixture was refluxed for 24 h. The xylene solution was then concentrated in vacuum, and the residue was dissolved in dry toluene and concentrated again. Finally, the crude tetrachloroterephthaloyl chloride was refluxed in dry ethanol (200 mL) for 24 h, cooled to −20 °C, and the crystallized product was filtered off and recrystallized from ethanol. Yield: 80%. MP: 60–61 °C (mp 60–60.5 °C in ref 14).

(B) Nucleophilic Substitution. An *n*-alkyl mercaptan (50 mmol), potassium *tert*-butoxide (50 mmol), and benzyltriethylammonium chloride were refluxed for 1 h in 1,4-dioxane (250 mL) under nitrogen. After cooling, diethyl tetrachloroterephthalate (12 mmol) was added, and the reaction mixture was refluxed again for 30 h. Afterward the cold reaction mixture was poured into cold water and the product extracted with three 250-mL portions of CH_2Cl_2. The combined extracts were dried with sodium sulfate and concentrated. The octyl derivative was distilled in a high vacuum over a short-path apparatus. The hexadecyl derivative was recrystallized from ethanol.

Tetrakis(alkylthio)terephthalic Acids (Table 1). Diethyl tetrakis(alkylthio)terephthalate (12 mmol) and lithium iodide (14 mmol) were refluxed for 12 h in dry γ-picolin (250 mL). The reaction mixture was then concentrated in vacuo to ca. 50% of its original volume and poured into 2 N hydrochloric acid (600 mL). The product was extracted with two 400-mL portions of CH_2Cl_2, and the combined extracts were washed with 1 N hydrochloric acid and water and dried over sodium sulfate. The crude product isolated after concentration of the CH_2Cl_2 solution was recrystallized from acetonitrile.

Tetrakis(alkylthio)terephthaloyl Chlorides. Tetrakis(alkylthio)terephthalic acid (8 mmol) and hexamethyldisilazane (20 mmol) were refluxed in dry xylene for 12 h. The reaction mixture was concentrated in vacuo, and the residue was diluted with xylene (50 mL) and concentrated again. The crude bis(trimethylsilyl) ester and distilled thionyl chloride (10 mL) were dissolved and refluxed in dry chloroform (40 mL) for 12 h. After concentration in vacuum the crude terephthaloyl chloride was recrystallized from toluene/ligroin.

Polycondensations. *N,N'*-Bis(trimethylsilyl)-*p*-phenylenediamine (20 mmol) and dry lithium chloride (2.1 g) were dissolved in dry NMP (50 mL), and the solution was cooled to −15 °C under an atmosphere of dry nitrogen. The substituted terephthaloyl chloride (20 mmol) was added portionwise under intensive cooling and stirring. The cooling was maintained for 4 h after complete addition. The stirring was then continued for 48 h without cooling. Finally, the reaction mixture was diluted with NMP (30 mL) and precipitated into methanol. The isolated polyamide was several times washed with warm methanol and dried at 100 °C in vacuum.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C.

The ^{1}H NMR spectra were recorded with a Bruker AC-100 FT-NMR spectrometer in 5-mm-o.d. sample tubes. A 9:1 (by volume) mixture of $CDCl_3$ and CH_3SO_3H served as solvent, and

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• Abstract published in *Advance ACS Abstracts,* February 1, 1994.

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Table 1. Yields and Properties of Tetrakis(alkylthio)terephthalic Acids and Their Diethyl Esters

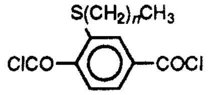
form. no.	yield (%)	mp (°C)	elem form. (fw)	elem anal. (calcd, found) C	H	S
3a	60	$[\alpha]^{20}_D = 1.535$	$C_{30}H_{68}Cl_2O_2S_4$ (780.0)	61.59, 61.78	8.79, 8.88	16.44, 16.41
3b	61	72–74	$C_{72}H_{132}Cl_2O_2S_4$ (1228.9)	70.37, 69.89	10.83, 10.54	10.44, 10.46
4a	92	$[\alpha]^{20}_D = 1.534$	$C_{44}H_{78}O_4S_4$ (799.3)	66.11, 66.12	9.84, 9.75	16.04, 16.02
4b	97	42–44	$C_{73}H_{172}O_4S_4$ (1238.2)	73.72, 72.86	11.56, 11.50	10.36, 9.80
5a	80	125–127	$C_{40}H_{70}O_4S_4$ (735.2)	65.34, 65.27	9.59, 9.80	17.44, 17.19
5b	75	107–108	$C_{72}H_{134}O_4S_4$ (1156.1)	72.54, 72.18	11.25, 11.05	10.76, 10.24

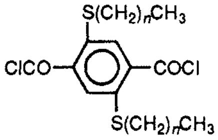
TMS, as internal standard. The IR spectra were obtained from KBr pellets on a Nicolet SXB-20 FT IR spectrometer.

The WAXS powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered Ca Kα radiation. The synchrotron radiation measurements were conducted at HASYLAB at DESY Hamburg using a wavelength of 1.50 Å. A position sensitive one-dimensional detector and a vacuum oven with a heating program of 20 °/min were used.

Results and Discussion

Syntheses. All polyamides of this work were prepared by polycondensation of *N,N*-bis(trimethylsilyl)-1,4-diaminobenzene with substituted terephthaloyl chlorides. The mono(alkylthio)terephthaloyl chlorides **1a** and **1b** as well as the bis(alkylthio)terephthaloyl chlorides **2a** and **2b** were described in previous papers.[16,17] In contrast the tetrakis(alkylthio)terephthaloyl chlorides **3a** and **b** were unknown. Diethyl tetrachloroterephthalates served as starting materials for their synthesis. A quantitative nucleophilic substitution of all four chloro atoms is feasible with *n*-alkyl mercaptide ions (eq 1) but not with alkoxide ions. For this reason, the present study was based on alkylthioterephthalic acids and not on alkoxyterephthalic acids.


1a: $n = 7$
1b: $n = 15$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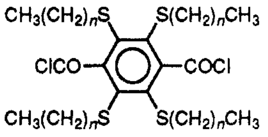
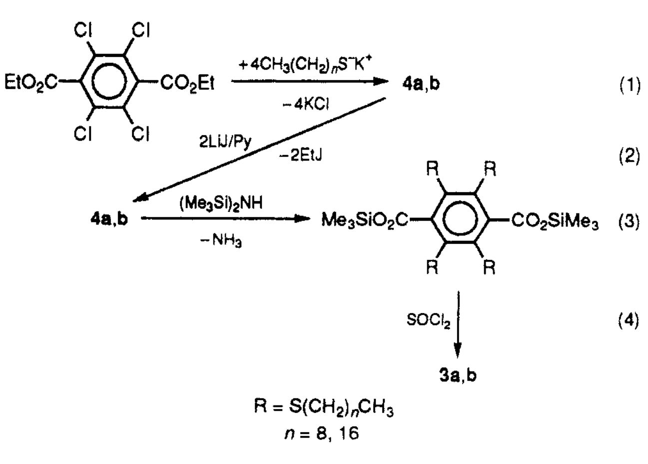
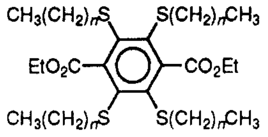
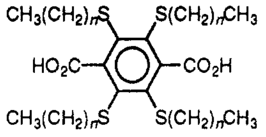

3a: $n = 7$
3b: $n = 15$

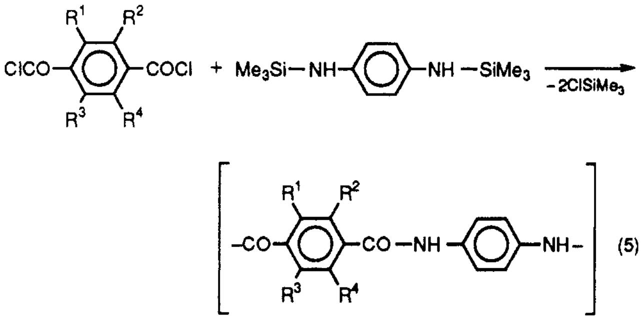


Due to the steric hindrance of the four alkylthio groups the saponification of the ethyl ester functions presented a serve problem. Even 4 N or 6 N sodium hydroxide in hot dimethyl sulfoxide (120 °C) was not reactive enough to effect a complete saponification. Therefore, the reaction mechanism was changed from a nucleophilic attack at the carbonyl group to an attack on the ethyl group, which is further removed from the steric hindrance. Lithium iodide in refluxing γ-picoline enabled a satisfactory saponification of **4a** and **b** (eq 3). The terephthalic acids **5a** and **b** were silylated (eq 3), and the crude trimethylsilyl esters were then chlorinated with thionyl chloride. This procedure is milder than the direct chlorination of **5a** and **b** and avoids the formation of HCl. The yields and some properties of **3a,b**, **4a,b**, and **5a,b** are summarized in Table 1. IR spectra of these monomers recorded from KBr pellets for **3a** and **b** a CO stretching vibration at 1780 cm^{-1}, for **4a** and **b** at 1730 cm^{-1}, and for **5a** and **b** at 1700 cm^{-1}. The ^1H NMR spectra measured in $CDCl_3$ (with internal TMS) show the typical signals of *n*-alkyl chains with a triplet of the $S–CH_2$ protons at 2.94–3.08 ppm.


4a
4b


5a
5b

The polycondensation of silylated 1,4-diaminobenzene (eq 5) demonstrated again the severe steric hindrance caused by the four alkylthio groups. With mono- or disubstituted terephthaloyl chlorides all polycondensations proceeded as usual at initial reaction temperatures around −15 °C in NMP. With **3a** and **b** no reaction took place even at +80 °C. Finally, the polycondensation of a concentrated monomer solution in Marlotherm-S at 280 °C proved to be successful. Nonetheless, despite these extreme reaction conditions only relatively low inherent viscosities were obtained. The yields and several prop-



6a: $R^1 = S(CH_2)_7CH_3$; $R^2, R^3, R^4 = H$
6b: $R^1 = S(CH_2)_{15}CH_3$; $R^2, R^3, R^4 = H$
7a: $R^1, R^4 = S(CH_2)_7CH_3$; $R^2, R^3 = H$
7b: $R^1, R^4 = S(CH_2)_{15}CH_3$; $R^2, R^3 = H$
8a: $R^1, R^2, R^3, R^4 = S(CH_2)_7CH_3$
8b: $R^1, R^2, R^3, R^4 = S(CH_2)_{15}CH_3$

Table 2. Yields and Properties of Poly(*p*-phenylene–terephthalamide)s Prepared by Polycondensation of Silylated 1,4-Diaminobenzene and Alkylthioterephthaloyl Chlorides

polym form.	yield (%)	η_{inh}[a] (dL/g)	elem form. (fw)	elem anal. (calcd, found) C	H	S	N	T_{m_1}[b] (°C)	T_{m_2}[c] (°C)
6a	84	1.45	$C_{22}H_{26}O_2N_2S$ (382.5)	69.08, 68.84	6.85, 6.78	7.32, 7.56	8.38, 8.29		
6b	85	0.92	$C_{30}H_{42}O_2N_2S$ (494.7)	72.83, 72.87	8.55, 8.45	5.66, 5.68	6.48, 6.39	20	110
7a	76	1.78	$C_{30}H_{42}O_2N_2S_2$ (526.8)	68.39, 68.07	8.03, 7.92	5.32, 5.36	12.02, 12.02		
7b	84	0.52	$C_{46}H_{74}O_2N_2S_2$ (753.2)	73.35, 73.26	9.90, 9.52	3.72, 3.62	8.51, 8.54	51	195[c]
8a	86	0.40	$C_{46}H_{74}O_2N_2S_4$ (815.4)	67.76, 67.78	9.51, 8.63	3.44, 3.48	15.73, 15.63		
8b	78	0.26	$C_{78}H_{138}O_2N_2S_4$ (1364.42)	74.11, 73.72	11.00, 10.71	2.22, 2.37	10.44, 10.18	37	

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/CH_3SO_3H (volume ratio 4:1). [b] Endotherms in the second DSC heating curves (heating rate 20 °C/min). [c] DSC first heating curve.

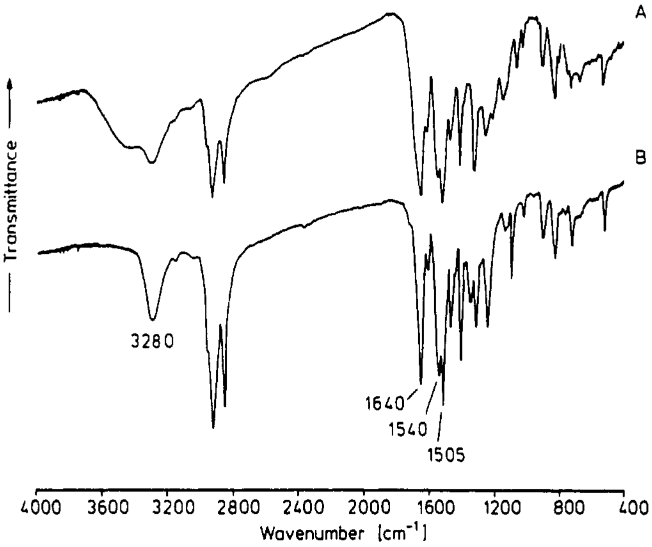


Figure 1. WAXS powder patterns of the polyamides (A) **7b** and (B) **7a**.

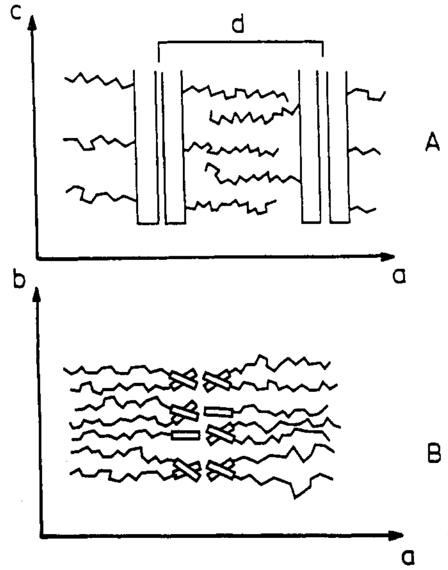


Figure 2. Schematic drawing of the chain packing of polyamides **6a** and **b** (A and B).

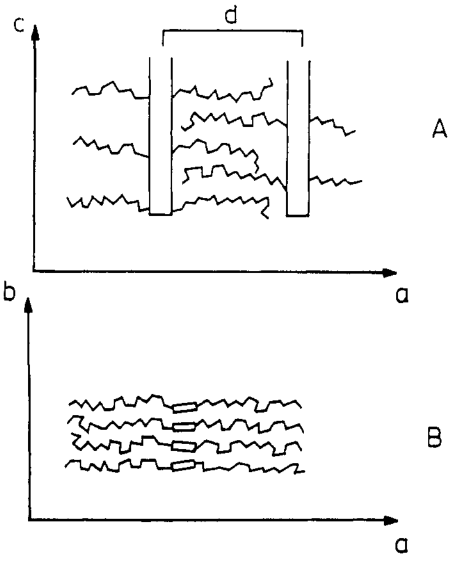


Figure 3. Schematic drawing of the chain packing of polyamides **7a** and **b** (A and B).

erties of the polyamides **6a,b**, **7a,b**, and **8a,b** are compiled in Table 2. All polyamides were characterized by ^{1}H NMR and IR spectra. The ^{1}H NMR spectra display the signals of aliphatic and aromatic protons with correct intensity ratios. The IR spectra also agree with the expected structure (see discussion below and Figure 7).

Chain Packing of 6a,b and 7a,b. This study did not intend to elucidate all details of the chain packing of the polyamides **6**–**8**, but the basic aspects should be discussed. The basis of this discussion is the fact that all polyamides and also most polypeptides with a regular sequence of amide groups form sheet structures. The sheets consist of a parallel or antiparallel array of main chains interconnected by H bonds.[18-21] Such sheet structures were also postulated for polyaramides derived from 2,5-dialkoxyterephthalic acids (**9** and **10**).[5-11] The side chains form a "paraffin layer" between the sheets (or stacks) of the main chains. The existence of similar layer structures is now assumed in the present work for the polyamides **6**–**8**.

The existence of H-bonded sheets of main chains is evidenced by the IR spectra of **6**–**8** (Figure 1). The shape of the "NH band" (stretching vibrations) in the range 3000–3500 cm^{-1} is almost identical with that of unsubstituted poly(*p*-phenylene–terephthalamide) (Figure 1A). In addition to an intensive band around 3280 cm^{-1} a shoulder up to 3500 cm^{-1} is detectable, indicating that not all NH bonds are in optimum positions. In the case of poly(*p*-phenylene–terephthalamide) the N–H vibration at different frequencies may be attributed to the crystalline and noncrystalline regions. Remarkably, the IR spectra of **7a,b** and **8a,b** exhibit one almost symmetrical NH band around 3280 cm^{-1} without a significant shoulder (Figure 1B). This band indicates an almost perfect sheet structure with little disorder. The H bonds of polyamides **6**–**8** are as strong or slightly stronger than those of unsubstituted poly(*p*-phenylene–terephthalamide), which shows the maximum of the NH band at 3310 cm^{-1}.

On the basis of H-bonded sheet structures the following questions need discussion: (1) Do **6a** and **b** form double-sheet structures (Figure 2) or single-sheet structures (Figure 3) analogous to **7a,b** or **8a,b**? (2) Are the alkyl chains interdigitated, as illustrated in Figures 2–4, or not? (3) Are the alkyl chains tilted relative to the sheets of the main chains (Figure 4A,C)? (4) Do the side chains form ordered paraffin domains?

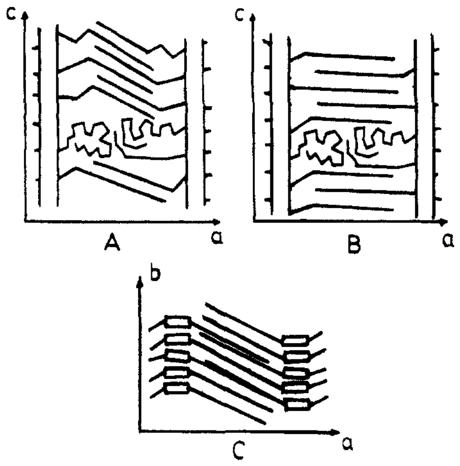


Figure 4. Schematic drawing of the coexistence of ordered paraffin domains and coiled side chains in a tilted (A) or (C) and in a perpendicular (B) array relative to the main chains.

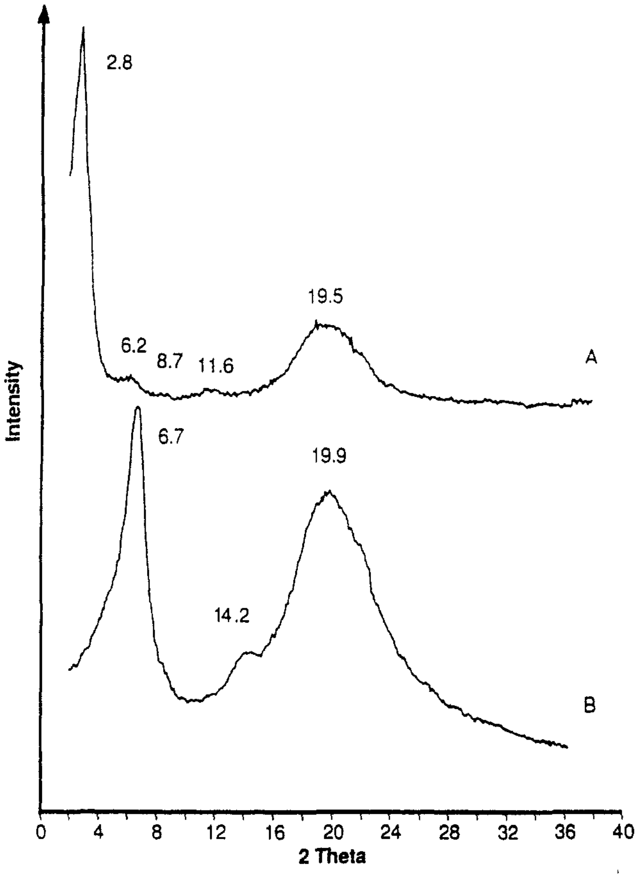


Figure 5. IR spectra (KBr pellets) of (A) polyamide **6b** and (B) polyamide **7b**.

In order to answer these questions at least partially, WAXD patterns (Figure 5) and ^{13}C NMR CP/MAS (Figure 6) spectra were recorded at 20 °C and higher temperatures. Unfortunately, the WAXD patterns yield little information. The layer distances (*d* spacings) calculated from the intensive middle angle reflection which is present in all WAXD patterns are listed in Table 3. Also listed are the theoretical *d* spacings for completely interdigitated (Figures 2–4) or noninterdigitated layers, calculated on the basis of fully extended side chains (all-trans conformation) perpendicular to the stacks of the main chains. The comparison of experimental and theoretical values suggests that all polyaramides of this work form interdigitated layer structures. These data also suggest that **6a,b** form a double-sheet structure, as illustrated in Figure 2. In the case of a single-sheet structure, such as that of Figure 3, the *d* spacings should be considerably shorter than those of **7a,b**. In fact they are greater by a value of 4.5 Å, which corresponds to the breadth of benzene ring. This interpretation is based on the assumption that the side chains of **6a,b** and **7a,b** are arranged in a similar fashion, an assumption which is confirmed by data discussed below. In this connection it should be emphasized that the layer structures discussed here for **6**–**8** and in the literature[5–10] for **9** and **10** represent a phase separation on the molecular level. In the case of **6a,b** the double-layer structure of Figure 2 represents the thermodynamical optimum of such a phase separation, taking into account the formation of H-bonded sheets of main chains. Furthermore, similar double layers were reported for 3-alkyl substituted poly(4-hydroxybenzoate)s.[22]

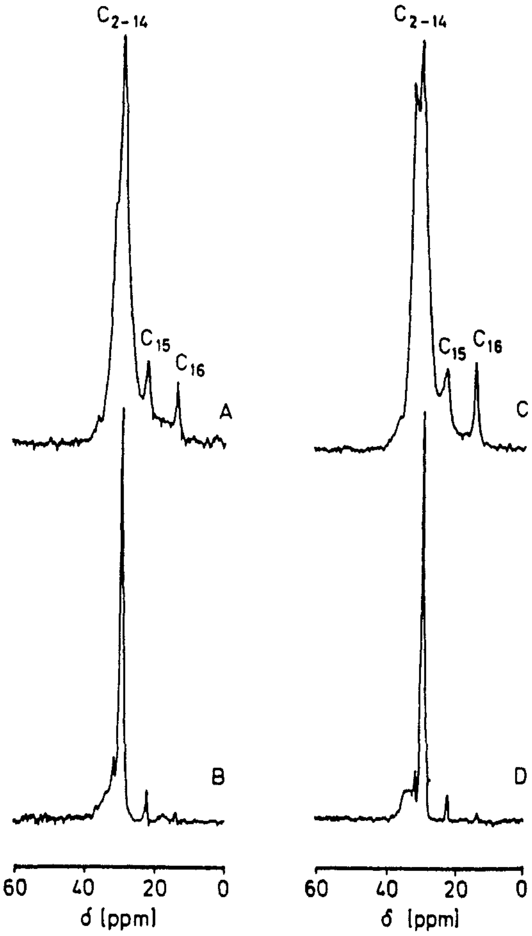
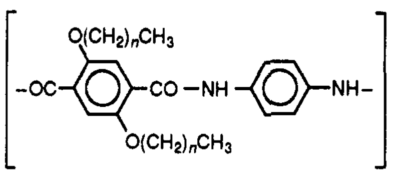


Figure 6. ^{13}C NMR CP/MAS spectra of (A) polyamide **6b** at 25 °C, (B) **6b** at 60 °C, (C) polyamide **7b** at 25 °C, and (D) **7b** at 60 °C.

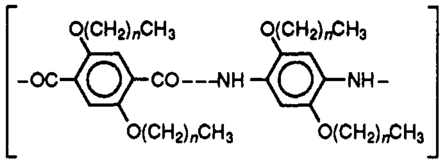
Table 3. Experimental Layer Distances As Determined from WAXS Powder Patterns and Theoretical Distances Calculated for Sanidic Layer Structures with Fully Extended Alkyl Side Chains

		theor *d* spacing				theor *d* spacing	
polym form.	exp *d* spacing	with interdig[a]	without interdig[b]	polym form.	exp *d* spacing	with interdig[a]	without interdig[b]
6a	17.7	21.8[c]	32.0	**6b**	26.0	32.0	52.4
7a	13.2	17.7	26.2	**7b**	21.5	27.4	47.8
8a	19.8	17.2	27.4	**8b**	31.1	27.4	47.8

[a] A value of 2.52 Å was used for the pitch of an ethylene unit in an all-trans alkyl chain and a value of 4.6 Å for the breadth of a benzene ring, 5.8 Å for a benzene ring with one sulfur, and 7.0 Å for a benzene ring with two sulfur atoms attached. [b] *d* spacings calculated as for footnote a but without interdigitating. [c] *d* spacings calculated for double stacks of main chains according to Figure 2.



9a–d
(n = 7, 11, 13, 15)



10a–f
(n = 1, 9, 10, 11, 13, 15)

The comparison of *d* spacings (Table 3) also indicates that the alkyl chains of **6a,b** and **7a,b** are tilted relative to the main chains, because the experimental *d* spacings are shorter than those calculated for the perpendicular side chains. This conclusion is supported by the CH_2 increments of the "pitch" of the alkyl chains. For both **6a,b** and **7a,b** an indentical CH_2 increment of 1.04 Å is found, which contrasts with an increment of 1.27 Å for a perpendicular array of the main and side chains. However, neither the X-ray data nor the ^{13}C NMR measurements (discussed below) say anything about the direction of the tilting, as illustrated by Figure 4A,C. For the polyamides **9** a completely different type of chain packing ("model A") was reported[5–10] with the side chains in a perpendicular array (CH_2 increment: 1.25 Å). Furthermore model A assumes a zigzag array of main chains in the *a–b* plane (as defined in Figures 2–4) with a narrower sequence of layers in the *b* direction.[8] This model A is based on an X-ray reflection of $2\vartheta = 25°$ interpreted as a layer distance of 3.6 Å in the *n* direction. This reflection is lacking in the WAXD patterns of **6a,b** and **7a,b**, which indicates together with the tilting of the alkyl chains that the chain packing of polyamides **9a–d** is largely different from that of **7a,b** (and **6a,b**).

Finally, the question (no. 4 above) of ordered paraffin domains needs discussion. ^{13}C NMR CP/MAS spectroscopy (Figure 6) and DSC measurements (Figure 8) agree in that part of the side chains of **6b** and **7b** form ordered paraffin domains. The signal at 33–34 ppm in the ^{13}C NMR spectra represents the trans conformation of C_3–C_{14} of the hexadecyl groups.[9–23] Upon heating to 60 °C these trans conformations disappear (Figure 6B,D) because the ordered domains melt away. This interpretation is confirmed by DSC measurements which display the corresponding endo- and exotherms (Figure 7). These ordered paraffin domains may be labeled a "columnar mesophase" because the WAXD reflections of true crystallites are lacking.[24] A high mobility of the alkyl chains is also indicated by the singlet signal of the CH_3 "end groups". In an immobile anisotropic environment the CH_3 signal displays a doublet splitting.[9] Analogous NMR results were reported for **9a–d**.[8,9,25] The recent NMR results of Spiess and co-workers[25] also indicate that the lateral extension of the ordered paraffin domains is relatively small for **9a–d**. They are separated by less ordered domains with predominance of gauch conformations. This information was taken into account for the schemes of Figure 4.

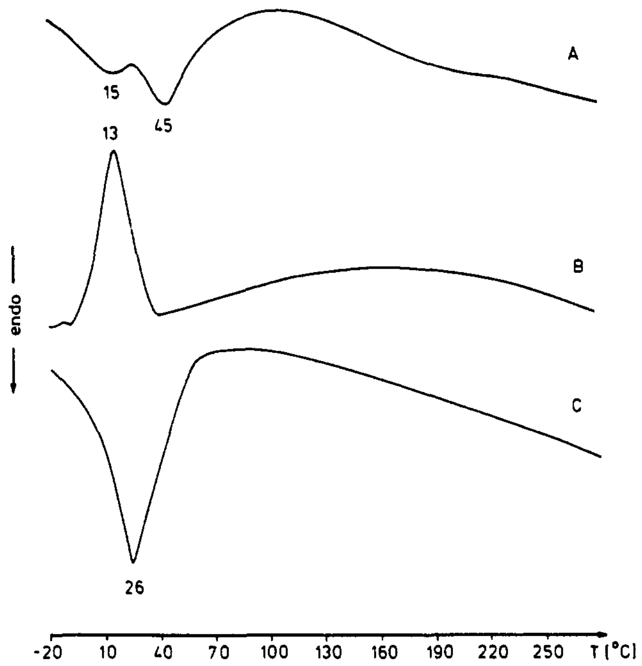


Figure 7. DSC curves (heating/cooling rate 20 °C/min) of polyamide **8b**.

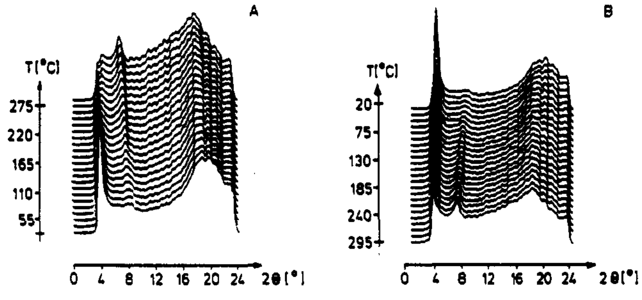


Figure 8. WAXS synchrotron radiation measurements of **7b** at a heating and cooling rate of 20 °C/min.

Chain Packing of 8a,b. The IR spectra of **8a,b** suggest that the packing of the main chains, i.e. the structures of the H-bonded sheets, is almost identical with that of **7a,b**. In contrast, all measurements and observations prove that the chain packing of **8a,b** is completely different from that of **10b–f**.[7,23] For **10b–f** a zigzag array of the main chains in the *a–b* plane was postulated on the basis of a 3.5-Å Bragg reflection and attributed to strong H bonds. However, any reliable evidence for strong H bonds is lacking and the low melting temperatures and the solubility in chloroform do not agree with the existence of stable H-bonded sheet structures. Furthermore, the seemingly tilted side chains do not interdigitate at room temperature but start to do it above the melting point.

In the case of **8b,b** the *d* spacings are 16–17 Å shorter than those calculated for a noninterdigitating layer structure with perpendicular side chains. Furthermore, they are 10 Å shorter than those of the noninterdigitated polyamides **10a–f** with tilted side chains[7] and suggest the existence of interdigitated layers in the case of **8a,b**. The fact that the experimental *d* spacings of **8a,b** are 3–4 Å greater than the theoretical values may be attributed to a spacing effect of the four sulfur atoms per repeating units. The diameter of sulfur (2.08 Å) is more than 50% greater than that of oxygen and may prevent the same close contact between side chains and the opposite main chain which has been assumed for the theoretical values (17.2 and 27.4 Å). The CH_2 increment of 1.4 Å derived from **8a** and **b** is higher than the theoretical value (1.27 Å) of the fully extended alkane chains. This difference may be explained by the assumption that the percentage of trans conformations on the octyl chains is lower than that in the hexadecyl chains. This assumption is rea-

Table 4. Solubilities[a] of the Polyaramides 6a,b–8a,b in Various Solvents

	conc H_2SO_4	MSA[b]	CH_2Cl_2/MSA[b]	CH_2Cl_2/TFA[c]	*m*-cresol	NMP[d]/5% LiCl	NMP[d]	DMAc[e]	DMSO[f]
6a	+	++	++	–	–	++	(+)	–	–
6b	(+)	(+)	+	–	–	+	–	–	–
7a	–	–	++	–	–	++	(+)	–	–
7b	–	–	+	–	–	–	–	–	–
8a	–	–	++	++	–	–	–	–	–
8b	–	–	++	–	–	(+)	–	–	–

[a] For 20 mg of polymer/4 mL of solvent: ++ soluble at 25 °C, + soluble at 80 °C, (+) partially soluble, – insoluble. [b] Methanesulfonic acid (volume ratio 4/1 for CH_2Cl_2). [c] Trifluoroacetic acid (volume ratio 4/1 for CH_2Cl_2). [d] *N*-Methylpyrrolidone-2. [e] *N*,*N*-Dimethylacetamide. [f] Dimethyl sulfoxide.

sonable, because the alkylene segments bound to the terephthaloyl units are for steric and electronic reasons (sulfide groups) in a situation which is unfavorable for trans conformations. In contrast, the main part of the hexadecyl groups may easily form ordered paraffin domains with all-trans conformations.

The assumption of interdigitated perpendicular alkyl chains raises the question if the basal plane of the main chains in the *b*–*c* frame (as defined in Figures 2 and 3 and ref 21) can accommodate such a high number of densely packed side chains. From crystalline paraffins it is known that four extended alkane chains occupy a cross section or basal plane of approximately 72 Å^2. In this connection it is important to note that the WAXD patterns of **8a,b** do not show a 3.5 ± 1 Å Bragg reflection. Therefore, a sheet structure similar to that of poly(*p*-phenylene–terephthalamide) may be assumed with a direct distance of 5.4–5.6 Å between main chains in the *b* direction. For Kevlar a value of 5.2 Å was reported[21] but the steric demands of the substituents may cause a widening of the "*b* spacing" to a value of 5.5–5.6 Å typical for monolayers of dialkoxy substituted polyesters and polyimides.[6,8,9]

With a value of 13 Å for the length of the repeating unit a basal plane of 72–73 Å^2 results per repeating unit in the *b*–*c* frame. Hence, the assumed interdigitating of four alkyl chains per repeating unit might be possible.

For such a dense packing of alkyl chains a high percentage of trans conformation is expected. Surprisingly, the ^{13}C CP/MAS spectra only yield for **8b** a value around 40–50%, similar to that of **7b** (Figure 5). A significant degree of mobility is again indicated by the singlet signal of the CH_3 groups. Taken together, the results presented in this work fit in with the hypothesis that **8a,b** form a largely interdigitated layer structure with a perpendicular array of main and side chains, but they certainly do not prove it yet. However, the results discussed above along with the physical properties discussed below demonstrate that (a) the chain packing of **8a,b** is completely different from that of **10a–f** and (b) the main chains of **8a,b** form almost planar sheet structures based on strong H bonds.

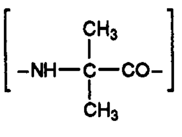
Solubility. Para-linked aromatic polyesters, polyamides, and polyimides containing two alkoxy groups per repeating unit were characterized by Ballauff and Wegner as rigid-rod polymers with bound solvent.[7,26–28] Therefore it was expected that the solubilities of the alkylthio substituted polyamides studied in this work will be significantly better than that of poly(*p*-phenylene–terephthalamide) (Kevlar, Twaron) and that the solubilities will increase with the increasing number and length of the alkyl groups.

The solubilities of the polyamides 6–8 were systematically studied in 17 common solvents at 20 °C and 80%. All polyaramides proved to be insoluble in liquids such as chloroform, trichloroethylene, tetrahydrofuran, 1,4-dioxane, ethyl acetate, chlorobenzene, trifluoroacetic acid, or formic acid. The results obtained with nine additional solvents are listed in Table 4. The three most important conclusions can be summarized as follows: (A) The solubilities do not increase with the number of alkyl groups. (B) The solubilities do not increase with the length of the side chains. In all pairs of polyaramides the hexadecyl substituted species show the lower solubilities. (C) **7b** possesses the lowest solubility of all polyamides. It is insoluble in all simple solvents and is, from this point of view, even less soluble than the unsubstituted poly(*p*-phenylene–terephthalamide) which dissolves at least in concentrated sulfuric acid.

These somewhat unexpected results do not depend on the presence of sulfur atoms. When the solubilities of the dialkoxy substituted polyamide **9** were analyzed, they showed a perfect agreement with those of **7b**. The reason for these extremely low solubilities is obviously the existence of the layer structures schematically illustrated in Figures 2–4. Strong acids such as sulfuric or methanesulfonic acid and highly polar nonacidic solvents such as NMP, can break H bonds but cannot penetrate and dissolve the paraffin phases between the sheets of the main chains. Nonacidic solvents of low polarity such as chloroform, trichloroethylene, ethyl acetate, or toluene dissolve paraffin, but they cannot interrupt the H-bonded network of the main chains. In good agreement with this interpretation, the only solvent system that dissolves all polyamides of this work is a combination of dichloromethane (or chloroform) and methanesulfonic acid.

In this connection, it is interesting to note that the solubilities of poly(α-amino acids) obey similar structure–property relationships as do the polyaramides **6–8**. As illustrated by poly(α-aminoisobutyric acid) (**11**), poly(L-norleucine) (**12**), or poly(L-phenylalanine) (**13**), nonpolar side chains reduce the solubility. None of these three poly(α-amino acids) is soluble in formic acid, dichloroacetic acid, or trifluoroacetic acid, in contrast to the soluble polyglycine.[29–31] Chloroform and other nonacidic solvents dissolve neither substituted nor unsubstituted poly(α-amino acids). The only solvent combination which dissolves all poly(α-amino acids) without serious degradation (in contrast to H_2SO_4) is again the combination of methanesulfonic acid and chloroform or dichloromethane.

The results discussed above clearly demonstrate that the concept of "aliphatic side chains as bound solvent" is not applicable to polyaramides and polypeptides. This concept is one-sided, because it exclusively relies on entropic effects. It is consistent with experimental data only, when solvents and polymers of low or moderate polarity (e.g. polyphenylenes or polyesters) are studied. However, it must fail for highly polar solvents and polymers, because the gain in entropy does not overcome the strong enthalpic effects resulting from H bonds, ion–dipole, and dipole–dipole interactions. This interpretation is underlined by the fact that alkanes are immiscible with all low molar mass protic solvents, such as alcohols, phenols, amines, carboxylic acids, or amides (e.g. formamide, *N*-methylacetamide, etc.). Alkanes are also im-



$$\left[-NH-C(CH_3)_2-CO- \right]$$

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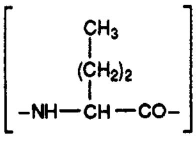

$$\left[-NH-CH((CH_2)_2CH_3)-CO- \right]$$

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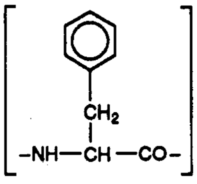

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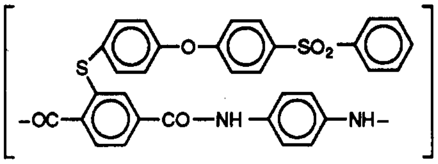

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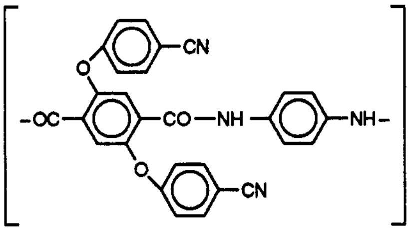

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miscible with numerous highly polar nonprotic solvents, such as nitromethane, nitrobenzene, acetonitrile, benzonitrile, dimethylsulfoxide, sulfolane, dimethylformamide, or *N*-methylpyrrolidone. Hence, it is obvious that long alkyl side chains cannot act as bound solvent for dissolution in such polar solvents. Two polyamides, a monosubstituted one (**14**) and a disubstituted one (**15**), may suffice to confirm this conclusion. Both polyaramides are soluble not only in H_2SO_4 and MSA but also in NMP and hot DMSO with or without addition of LiCl. It is obvious that polar aromatic side chains are significantly more efficient as "bound solvent" than alkyl groups, because of favorable enthalpic interactions with any kind of polar solvents. The broad validity of this concept is illustrated by the good solubilities of rigid-rod polyesters,[32-34] poly(benzobis(oxazole)s,[35] poly(benzobis(thiazole))s[36] and polyphenylenes[37,38] bearing aromatic substituents.

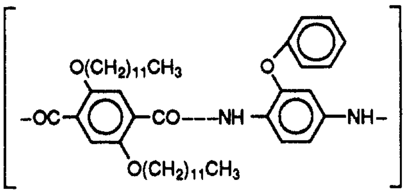
Meltability. The concept of alkyl side chains as "bound solvent" not only concerns the solubility of rigid-rod polymers but also their melting temperatures (T_m). When the polyaramides **6a,b**, **7a,b**, and **8a,b** were examined by DSC measurements, no melting endotherm was detectable up to 400 °C. Above this temperature rapid degradation prevents any reliable characterization. Optical microscopy revealed in the case of **8b** a melting process around 400 °C, but rapid thermal degradation did not allow a clear cut characterization of the melt with regard to an anisotropic phase.

In the case of **7b** the DSC measurements revealed a second phase transition at higher temperatures (around 200 °C). This phase transition extends over a broad temperature range (approximately 40 deg) and is reversible. WAXS measurements with synchrotron radiation at a heating rate of 20 °C/min revealed that the small angle reflection at 21.5 Å slowly dissappears whereas reflections at 10.4 and 17.6 Å gain in intensity (Figure 8). Furthermore, the broad reflection around $2\vartheta = 20°$ shifts to a somewhat smaller scattering angle. These changes may tentatively be interpreted as narrowing of the layer distances and lateral expansion of the mobile alkyl side chains due to a more pronounced coiling. The relatively high temperature of this phase transition suggests that a conformational change of the main chains is involved. These suggestions are supported by the absence of this transition in the case of **6b** and **8b**. In the case of **6b** the interaction between pairs of main chains in the back-to-back array might hinder such a conformational change. In the case of **8b** the dense packing of alkyl chains might prevent the transition. Whatever are the details of this transition, it is clearly not a melting process.

The absence of a melting process below 400 °C in the case of **6–8** agrees with the properties of polyamides **9b**. Steuer et al.[7] reported a kind of softening process, when pressure was applied to a sample of **9b** heated to 300 °C. However, Kricheldorf and Schmidt[1] did not find any melting process below 400 °C, when three samples of **9b** (prepared by three different polycondensation methods) were studied. Surprising and particularly interesting are the thermal data reported by Steuer, Hörth, and Ballauff[7] for the polyaramides **10a–f**. Regardless of the lengths of the alkyl groups, all members of this series seemingly melt between 190 and 200 °C, and most of them possess isotropization temperatures in the range 250–270 °C. This result is a contradiction to the entropy expected for the alkyl substituents in their role as bound solvent. Furthermore, a comparison between **10f** and **8b** is of interest, because both polyaramides possess the same number of alkyl substituents with identical lengths. Hence, their entropic influence on T_m and T_i should be almost identical. However, the T_m of **10f** is apparently 200 °C and the T_i is at least 150 deg below those of **8b**. If this difference is correct, it demonstrates again that the entropic effects of the alkyl side chains do not dominate the thermal transitions of poly(*p*-phenylene–terephthalamide)s. Obviously, enthalpic effects, such as the stability of the H-bonded sheets, play an important role, and the substitution pattern influences the structure and stability of the sheets. Solubility and meltability of **10a–f** suggest that a stable, planar sheet structure does not exist.

Finally, alkyl side chains and polar aromatic substituents should be compared with regard to their influence on the T_m of polyaramides. Since the T_m depends on the melting enthalpy and not only on entropy changes (ΔS_m), the influence of the side chains on the melting enthalpy (ΔH_m) needs to be considered. The layer structures in the solid state represent a phase separation between the side chains and main chain, and thus, the compatibility between both types of chains in the nematic or isotropic melt will influence ΔH_m. In this connection the properties of low molar mass compounds are again illustrative. Benzanilide, acetanilide, or terephthalanilide (as models of the main chain) are insoluble in alkanes even above 200 °C. Yet all three amides are soluble in hot diphenyl ether, diphenyl sulfone, and benzophenone which may serve as models of aromatic substituents. Clearly, the miscibility of amides with polar aromatic compounds is considerably higher than with alkanes due to more favorable enthalpic interactions. A better compatibility between the side chain and main chain in the molten state reduces ΔH_m and, thus, T_m.

The meltability of substituted polyaramides agrees with these considerations. The polyamide **16** shows a well defined melting process,at 405–410 °C, with formation of a mobile isotropic melt. This high T_m of **16** confirms that the less substituted **9b** does not melt below 400 °C. When both dodecyl groups of **16** are replaced by one polar aromatic substituent, the melting decreases to 340 °C in the case of **17** or 320 °C in the case of **18**. Taken together, these results confirm that polar aromatic side chains play



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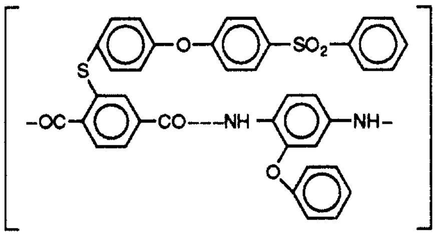

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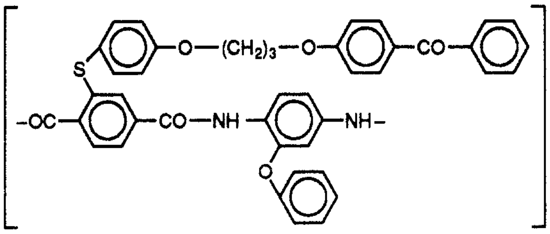

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the role of a bound solvent more effectively than alkyl groups, due to favorable enthalpic interactions.

Conclusion

The present work complements previous studies of poly(*p*-phenylene–terephthalamides) based on terephthalic acids with one[1,2] or two[4] longer aromatic substituents. The aliphatic side chains of the polyaramides studied in the present work neither significantly lower the melting temperatures nor improve the solubilities. These findings, the WAXS powder patterns, and IR and NMR spectroscopic results are consistent with the formation of sanidic layer structures, built up by H-bonded sheets of main chains and more or less ordered paraffin domains between these sheets. The details of these layer structures differ largely from those of polyaramides based on 2,5-dialkoxyterephthalic acids. Despite a lower flexibility, polar aromatic substituents are more effective in reducing the melting temperatures and improving the solubilities and compatibilities of poly(*p*-phenylene–terephthalamides). Obviously, enthalpic effects dominate over entropic effects. In other words, polar aromatic side chains play the role of a bound solvent more effectively than alkyl side chains.

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