New polymer syntheses:
74. Polybisoxazoles derived from bisalkoxy- or bisalkylthio-terephthalic acid

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Substituted poly(benzobisoxazole)s and poly(biphenylbisoxazole)s were synthesized by polycondensation of silylated diaminohydroquinone or 3,3′-dihydroxybenzidine with substituted terephthaloyl chlorides. Hexadecylthio-, 2,5-bis(hexadecylthio)- and 2,5-bis(hexadecyloxy)terephthaloyl chloride were used as reaction partners. A reaction temperature of 300°C was required for the final cyclization step of the reaction sequence. At this high temperature partial crosslinking occurred in most cases. The poly(biphenylbisoxazole)s melt in the temperature range of 310–350°C, but the characterization of the melt was affected by rapid thermal degradation. By means of wide-angle X-ray scattering powder patterns and ^{13}C nuclear magnetic resonance cross-polarization/magic-angle spinning spectroscopy, two kinds of sanidic layer structures were found for the solid state. The hexadecyl side chains form reversibly melting quasicrystalline paraffin domains between the layers of the main chain. The molar fraction of these ordered paraffin domains is significantly higher for bis(hexadecylthio)-substituted chains than for bis(hexadecyloxy)-substituted ones.

(Keywords: polybisoxazoles; synthesis; characterization)

INTRODUCTION

Unsubstituted poly(benzobisoxazole)s and poly(benzobisthiazole)s are of great interest as thermally stable materials for the production of high-modulus fibres or foils[1–3]. However, these polyheterocycles are infusible and only soluble in concentrated sulfuric acid. The present work is part of a broader study of substituted poly(benzobisoxazole)s and poly(bisthiazole)s. The influence of various substituents on the solubility, meltability and compatibility should be studied. Whereas the poly(benzobisoxazole)s described in previous parts of this series[4,5] bear aromatic side chains, the present work is concentrated on polymers derived from mono- or bishexadecyl-substituted terephthalic acids.

EXPERIMENTAL

Materials

2,5-Diaminohydroquinone and 3,3′-dihydroxybenzidine were gifts of Bayer AG (Krefeld, Germany) and used without purification. 2,5-Bis(hexadecyloxy)terephthaloyl chloride (m.p. 72–74°C)[6], 2,5-bis(hexadecylthio)terephthaloyl chloride (m.p. 85–87°C)[7] and hexadecylthioterephthaloyl chloride (m.p. 52–54°C)[8] were synthesized according to the literature. Marlotherm-S, a commercial product of Hüls AG (Marl, Germany), was used without drying or purification.

N,N′,O,O′-*Tetrakis(trimethylsilyl)-3,3′-dihydroxybenzidine*

3,3′-Dihydroxybenzidine (0.2 mol) was suspended in dry toluene (1 litre), chlorotrimethylsilane (0.9 mol) was added and this mixture was slowly heated with stirring. Triethylamine (0.9 mol) was added dropwise during the heating, and the reaction mixture was finally refluxed for 4 h. The cold reaction mixture was filtered with exclusion of moisture and the product was isolated from the filtrate by distillation over a short-way apparatus under exclusion of moisture. Yield 71%; m.p. 150–152°C (m.p. 157–159°C in ref. 9).

N,N′,O,O′-Tetrakis(trimethylsilyl)-2,5-diaminohydroquinone was prepared analogously. Yield 79%; m.p. 108–110°C (m.p. 93–96°C in ref. 10).

Polycondensations

A silylated dihydroxydiaminoaromatic (10 mmol) was dissolved in Marlotherm-S (20 ml) and a substituted terephthaloyl chloride (10 mmol) was added (in a glovebox under nitrogen). The reaction was gradually heated to 300°C over a period of 1.5 h. The reaction temperature was maintained for 3 h, and a small sample was removed for i.r. measurements every 30 min. The reaction mixture was mobile and homogeneous at 300°C, but almost solidified upon cooling. The cold reaction mixture was extracted twice with hot dioxane, and the remaining product was dried at 120°C *in vacuo*.

Measurements

The d.s.c. measurements were conducted on a Perkin–Elmer DSC-4 at a heating/cooling rate of 20°C min^{-1} in aluminium pans under nitrogen. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20°C.

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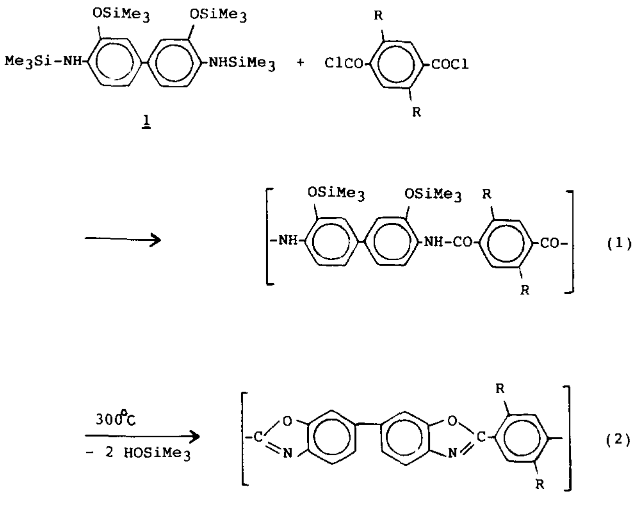
The WAXS powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered Cu Kα radiation.

The i.r. spectra were recorded from KBr pellets on a Nicolet SXB-20 *FT*i.r. spectrometer.

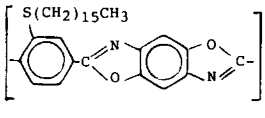
RESULTS AND DISCUSSION

Syntheses

Unsubstituted poly(benzobisoxazole)s are usually prepared in hot polyphosphoric acid. As reported previously, these harsh reaction conditions are not well suited for the synthesis of substituted poly(benzobisoxazole)s from substituted terephthalic acids because of side reaction of most substituents with the hot phosphoric acid. An alternative approach using milder conditions consists of the polycondensation of silylated diaminohydroquinone with substituted terephthaloyl chloride. Therefore this approach was also used in the present work. In addition to silylated 2,5-diaminohydroquinone, silylated 3,3'-dihydroxybenzidine (**1**) was used as nucleophilic monomer. The reaction sequence consists of two steps. The first one conducted at relatively low temperatures is the formation of a polyamide (equation (1)). Upon heating to temperatures $\geqslant$300°C, the cyclization takes place (equation (2)). Since the aliphatic side chains of the terephthaloyl chlorides used in this work are not stable enough at temperatures above 300°C, the reaction temperature was limited to this minimum value.



All polycondensations were conducted in Marlotherm-S, because this thermostable inert reaction medium allows one to conduct the entire reaction sequence in a 'one-pot procedure'. In order to optimize the reaction time at 300°C, small samples were taken from the reaction mixture every 30 min and analysed by i.r. spectroscopy. The disappearance of the NH and CO stretch vibrations at 3300 and 1655 cm^{-1} along with the appearance of two bands at 1675 and 1710 cm^{-1} allow the course of the cyclization to be monitored (*Figure 1*). It was found that the cyclization of the bishexadecylthio-substituted polyamides is more rapid than that of the bishexadecyloxy-substituted polyamides by a factor of 2. Obviously the greater steric demands of the sulfur atoms favour the cyclization for reasons of entropy. Yet, after 4 h even the cyclization of the bishexyloxy derivatives was complete. These long reaction times caused side reactions and most poly(bisoxazole)s were partially crosslinked. Nonetheless, satisfactory elemental analyses were obtained for most polymers. Using mono(hexadecylthio)terephthaloyl chloride, 2,5-bis(hexadecylthio)terephthaloyl chloride and 2,5-bis(dodecyloxy)terephthaloyl chloride, the poly(bisoxazole)s **2**, **3a**, **3b**, **4a**, **4b** and **5** were prepared. Their properties are summarized in *Table 1*.



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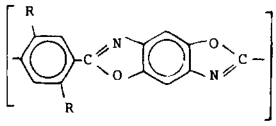
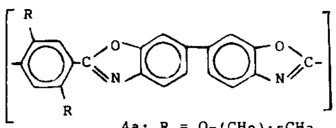
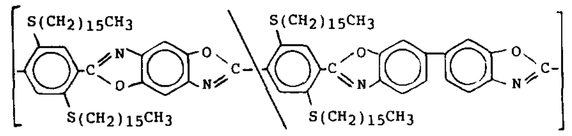


3a: R = O-(CH$_2$)$_{15}$-CH$_3$
3b: R = S-(CH$_2$)$_{15}$CH$_3$



4a: R = O-(CH$_2$)$_{15}$CH$_3$
4b: R = S-(CH$_2$)$_{15}$CH$_3$



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Chain packing and phase transitions

D.s.c. measurements of all poly(bisoxazole)s were conducted at a heating rate of 20°C min^{-1}. In all cases a weak endotherm was detectable in the temperature range of 55–65°C (*Figures 2* and *3*). The temperature of the peak maximum varied slightly upon repeated heating and cooling (*Table 1*). A reversible first-order transition in this temperature range is typical for the melting and crystallization of a paraffin phase formed by hexadecyl side chains. This interpretation was confirmed by ^{13}C n.m.r. c.p./m.a.s. measurements (*Figures 4* and *5*). The signal of the all-*trans* conformation (34–35 ppm), which is characteristic for the crystalline domains, is predominant in the n.m.r. spectra of **3b** and **4b**. Upon heating, the *trans* conformers gradually change to *gauche* conformers and reappear upon cooling. A surprising finding is the low fraction of *trans* conformation in the case of **3a** and **4a**. The absence of a separate '*trans* signal' in the ^{13}C n.m.r. spectra agrees with a barely detectable endotherm in the first heating trace (*Figure 2*) and the complete absence of an endotherm in the second heating curve. Such an enormous difference between polymers derived from 2,5-bis(hexadecylthio)- and 2,5-bis(hexadecyloxy)terephthalic acids is quite unexpected, and no satisfactory explanation can be forwarded at the current state of the research. Yet, as reported in a future paper, a similar difference was found for polyesters derived from 4,4'-dihydroxybiphenyl and 2,5-bis(hexadecyloxy)- or 2,5-bis(hexadecylthio)terephthalic acid. This means the results reported here are not a single case.

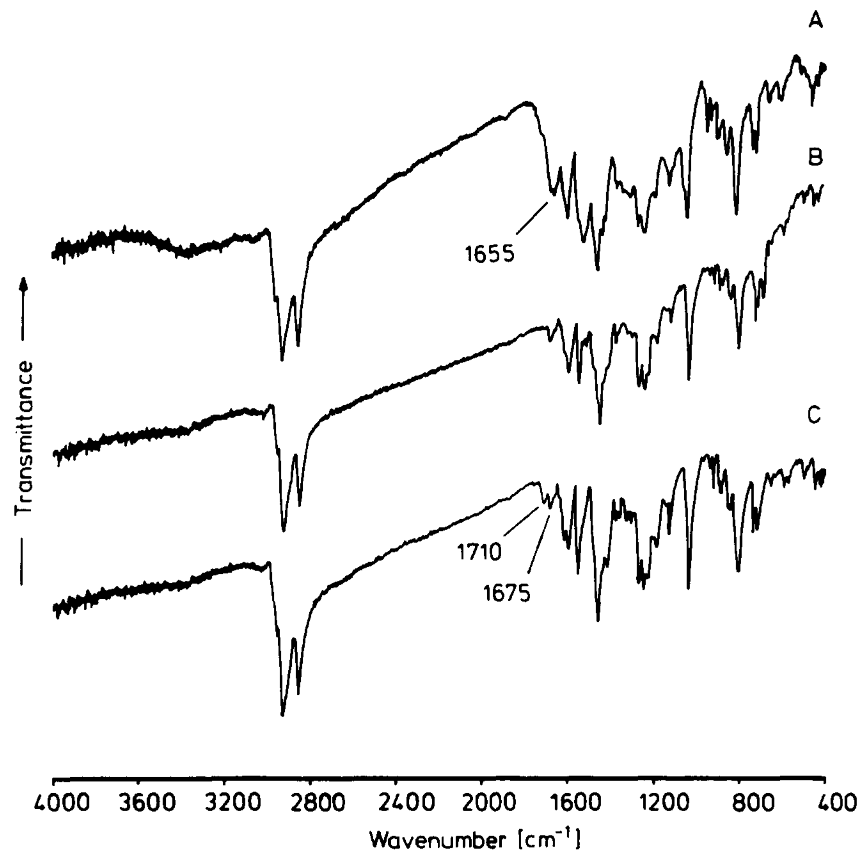

Figure 1 I.r. spectra (KBr pellets) of polymer **4b** after reaction times of 60 min (A), 120 min (B) and 160 min (C) at 300°C in Marlotherm-S

Table 1 Cyclization time and properties of the poly(bisoxazole)s

Polymer	Cyclization time^a (h)	η_{inh}^{b} (dl g^{-1})	Empirical formula (mol. wt)	Elemental analyses	C	H	N	S	T_{m1}^{c}	T_{m2}^{c}
2	3.0	insol.	$C_{30}H_{38}N_2O_2S$	Calcd	73.43	7.81	5.71	6.53	55(–)	–
			(490.7)	Found	73.23	7.68	5.49	6.15		
3a	3.0	1.24	$C_{46}H_{70}N_2O_4$	Calcd	77.26	9.87	3.92	–	66(60)	–
			(715.1)	Found	76.48	9.64	4.05	–		
3b	2.5	≫0.20	$C_{46}H_{70}N_2O_2S_2$	Calcd	73.94	9.44	3.75	8.58	65(69)	–
			(747.2)	Found	73.55	9.43	3.65	8.60		
4a	4.0	1.14	$C_{52}H_{74}N_2O_4$	Calcd	78.94	9.43	3.54	–	57(–)	353
			(791.2)	Found	77.61	9.87	3.51	–		
4b	2.5	>0.20	$C_{52}H_{74}N_2O_4S_2$	Calcd	75.86	9.06	3.40	7.79	65(43)	315
			(823.3)	Found	75.89	8.88	3.57	7.40		
5	3.0	1.15	$C_{98}H_{144}N_4O_4S_4$	Calcd	74.95	9.24	3.57	8.17	60(65)	350^d
			(1570.5)	Found	74.12	9.25	3.62	8.11		

[a] Duration of the cyclization at 300°C
[b] Measured at 20°C with $c = 2\,g\,l^{-1}$ in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1)
[c] From d.s.c. measurements with a heating rate of 20°C min^{-1}, second heating in parentheses
[d] From optical microscopy with a heating rate of 10°C min^{-1}

The WAXS powder patterns of the poly(bisoxazole)s **3**–**5** display a similar structure. A sharp intensive reflection appears at $2\theta = 3.3$–$3.9°$. The second and third orders of this reflection are also detectable (*Figure 6*). These reflections indicate the existence of a sanidic layer structure, which is typical for rigid-rod main chains with long aliphatic side chains[6–8,11–14]. A broad reflection shows up around $2\theta = 20°$ (4–5 Å). This reflection represents, for instance, the direct distance between directly neighbouring alkyl chains. Its diffuse character indicates that the ordered paraffin domains are not really crystalline, and may be better described as columnar mesophases. A more detailed description of such paraffin domains was recently presented for polyesters by Biswas *et al.*[14]. The sharper reflection around $2\theta = 25.5°$ (3.5 Å) may originate from the packing of the main chains along the *b* axis as defined in *Figures 7* and *8*.

The atomic distances calculated from the 'small-angle

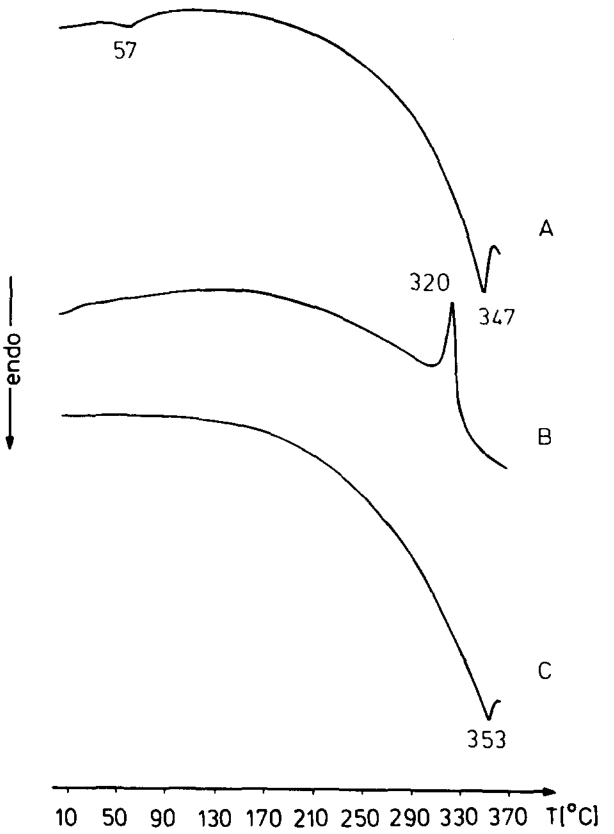

Figure 2 D.s.c. measurements (heating/cooling rate 20°C $\min^{-1}$) of poly(biphenylbisoxazole) **4a**: (A) first heating, (B) first cooling and (C) second heating

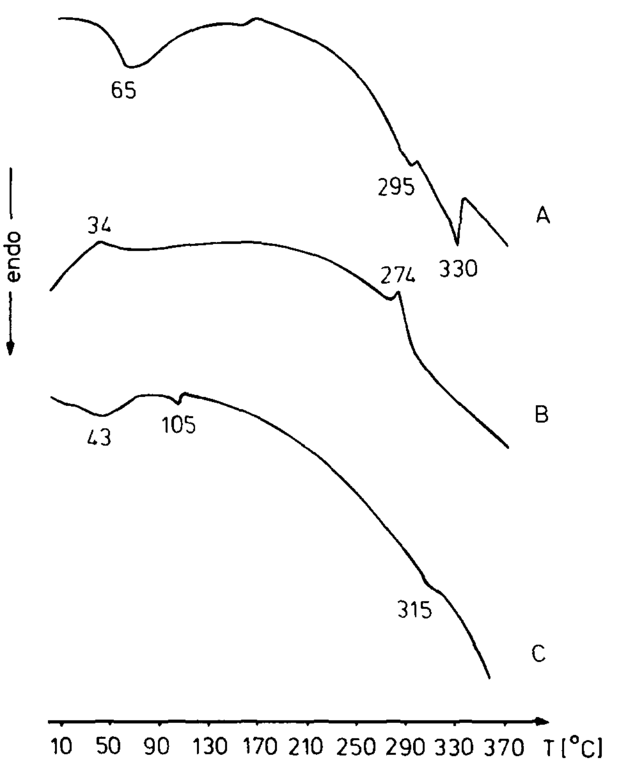

Figure 3 D.s.c. measurements (heating/cooling rate 20°C $\min^{-1}$) of poly(biphenylbisoxazole) **4b**: (A) first heating, (B) first cooling and (C) second heating

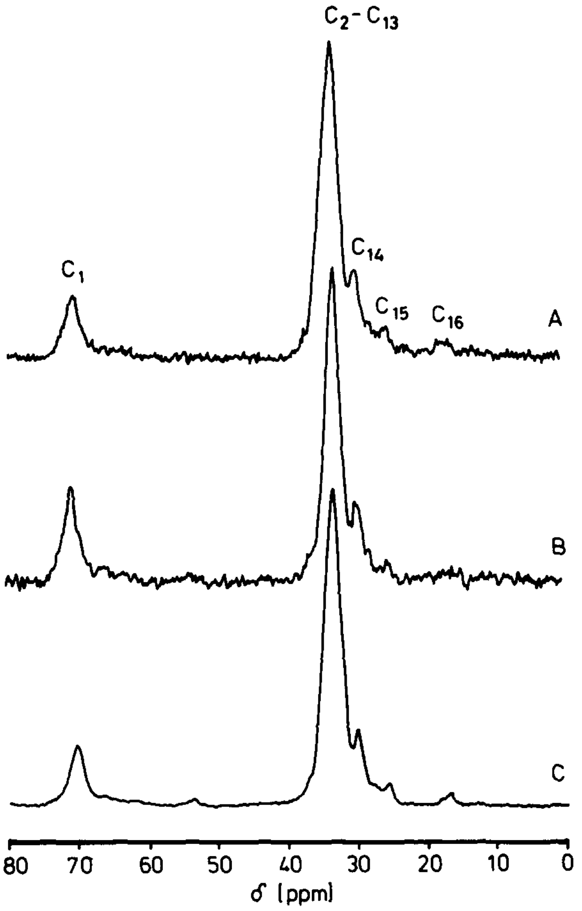

Figure 4 The 75.4 MHz ^{13}C n.m.r. c.p./m.a.s. spectra of poly(biphenylbisoxazole) **4a**: (A) 25°C, (B) 60°C and (C) after cooling to 25°C

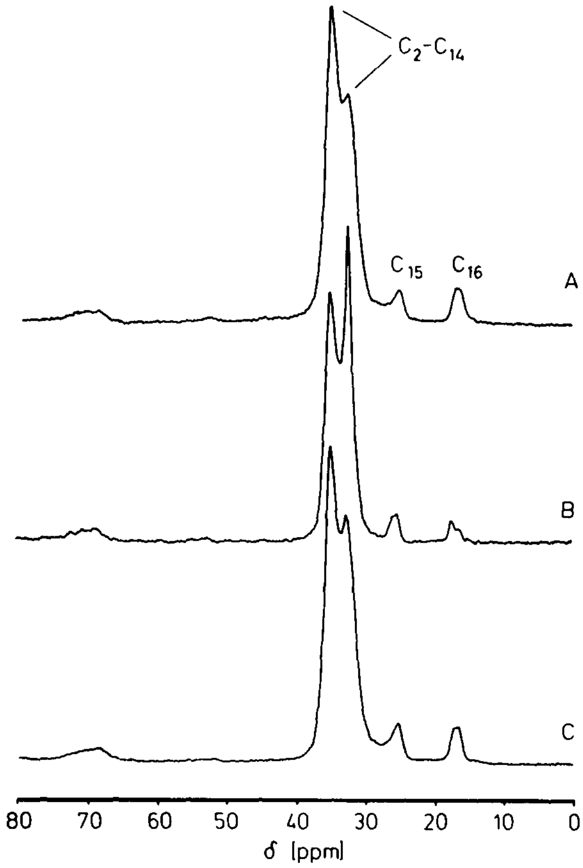

Figure 5 The 75.4 MHz ^{13}C n.m.r. c.p./m.a.s. spectra of poly(biphenylbisoxazole) **4b**: (A) 25°C, (B) 60°C and (C) after cooling to 25°C

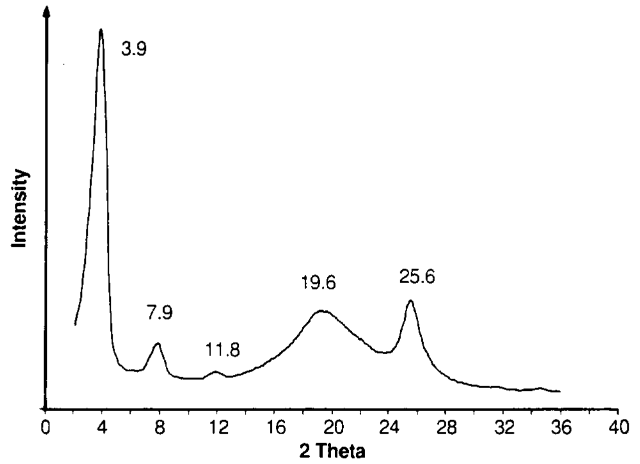

Figure 6 WAXS powder pattern of poly(biphenylbisoxazole) **4a**

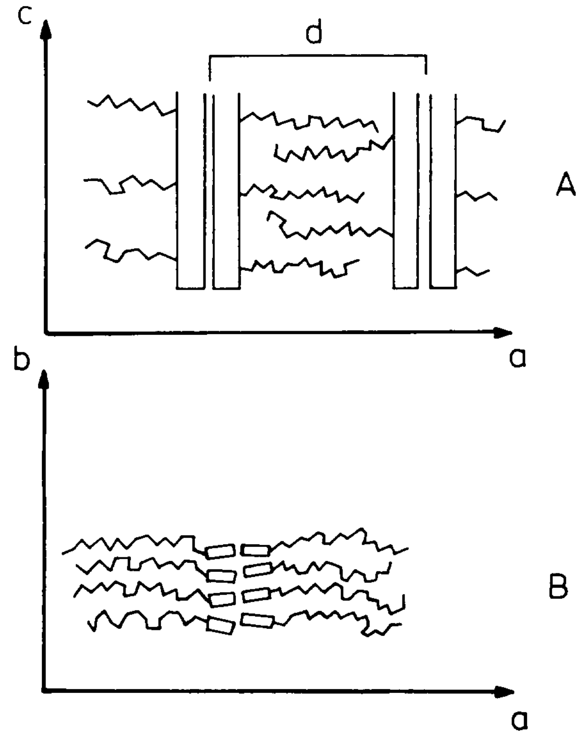

Figure 7 Schematic drawing of the sanidic chain packing typical for the poly(bisoxazole)s **3a**, **3b**, **4a**, **4b** and **5**

reflections' are summarized in *Table 2* and compared with theoretical values calculated for fully extended side chains adopting the all-*trans* conformation. This comparison suggests that the poly(bisoxazole)s form a sanidic order with almost perfect interdigitating of the side chains (*Figures 7* and *8*). Because of the great distance between side chains along the main chain, only part of the chain segments of neighbouring chains can form an ordered domain. Its formation leads to partial distortion of the chain segments attached to the main chain. Furthermore, free volume is created, which may be more or less filled by coiled side chains with a predominance of *gauche* conformations. A schematic illustration of this scenario is given in *Figure 9*. It also explains why the experimental *d*-spacings are somewhat shorter than the theoretical values based on fully extended alkyl chains.

The layer distance of the monosubstituted poly(benzobisoxazole) **2** is significantly greater than that of all

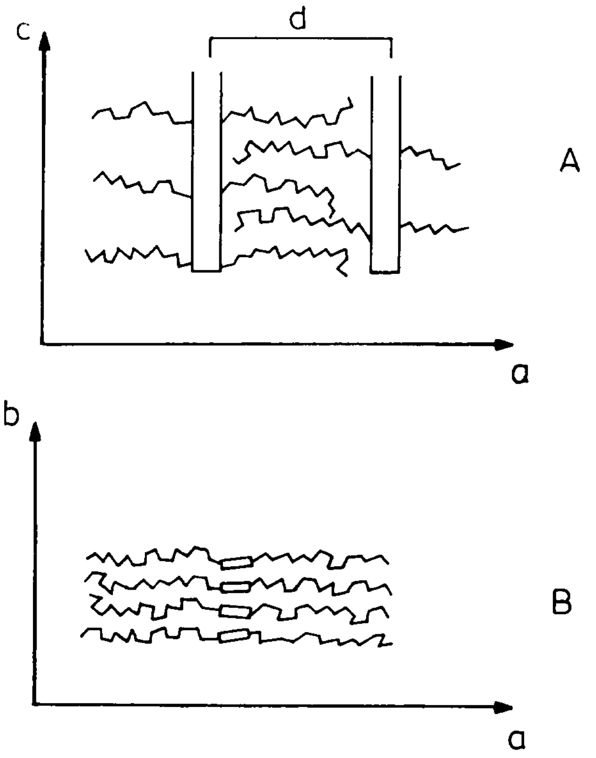

Figure 8 Schematic drawing of the sanidic chain packing typical for **2**

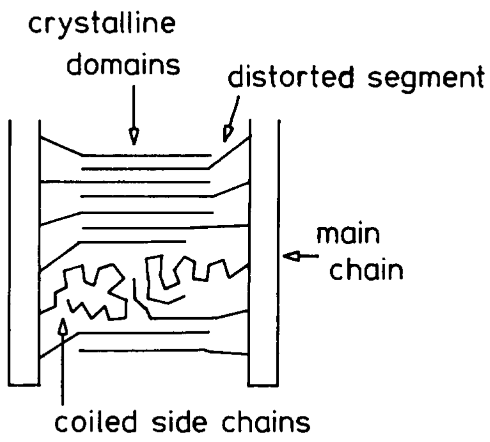

Figure 9 Schematic illustration of the three-dimensional arrangement of the hexadecylthio side chains in polymers **3b**, **4b** and **5**

Table 2 Experimental layer distances and calculated distances

	Experimental atomic distances (Å)		Calculated layer distances (Å)
Polymer	A^a	B^b	C^c
2	32.7	3.5	34.5
3a	27.6	3.4	28.5
3b	28.5	3.4	29.5
4a	22.6	3.5	28.5
4b	24.5	3.5	29.5
5	26.0	3.5	29.5

[a] Direct layer distances
[b] Distances between neighbouring main chains
[c] Layer distances calculated for fully extended hexadecyl side chains (length 22.5 Å) and a value of 6.0 Å for the width of monothio- or bisoxo-substituted benzene rings and a value of 7.0 Å for a bisthio-substituted benzene ring

disubstituted poly(bisoxazole)s. The comparison of **2** with **3b** reveals a difference of 4.2 Å (*Table 2*). This is slightly more than the width of a benzene ring and suggests that chain packing involves a back-to-back array of the main chain (*Figure 7*) including a distortion of the main chains. A similar chain packing was found for monoalkyl-substituted poly(4-oxybenzoate)s[15] and for several polyesters, poly(ester anhydride)s and polyamides of monoalkylthioterephthalic acids[8,16]. In contrast to **2** the disubstituted poly(bisoxazole)s form a sanidic type of chain packing with a 'monolayer' of main chains (*Figure 8*). This type of sanidic chain packing is in principle known from several poly(esters)[6,11] and polyamides[12] based on 2,5-bis(alkyloxy)terephthalic acids.

In addition to the endotherms around 50–60°C, the d.s.c. curves of **4a**, **4b** and **5** also display an endotherm in the temperature range of 300–350°C (*Figures 2* and *3*). Optical microscopy with crossed polarizers revealed that these endotherms represent true melting processes. Unfortunately, the melting process is followed by rapid thermal degradation, which prevented a detailed characterization of the melt. A birefringence was observable during the first minute of the melting and rapidly vanished with prolonged heating. Despite different heating and cooling procedures, we were not able to reach a clear-cut discrimination between the following alternatives:

(i) stress-induced birefringence in combination with an isotropic character of the relaxed melt, or

(ii) liquid-crystalline melt combined with an isotropization caused by thermal degradation.

Although a straightforward characterization of the melt was not feasible, the existence of a well defined melting process is interesting for itself. As illustrated by *Figure 6* the WAXS powder patterns indicate a disordered packing of the main chains. In principle, the WAXS patterns are compatible with the assumption of a highly viscous liquid state. Since the d.s.c. curves along with optical microscopy clearly indicate a first-order melting process, the chain packing at room temperature (and below 300°C) needs to be described as a solid state, and, more precisely, as a conformational disordered crystalline state.

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