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Layer structures: 10. Conformation and dynamics of long aliphatic spacers in smectic layers of poly(ester–imide)s based on 4-aminobenzoic acid trimellitimide

Nicolas Probst, Christoph Wutz and Hans R. Kricheldorf*
Institut für Technische und Makromolekulare Chemie der Universität, Bundesstr. 45, D-20146 Hamburg, FRG
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1,12-Dihydroxydodecane and 1,22-dihydroxydocosane were prepared from diacetylene precursors in such a way that the four central methylene groups were deuterated. These deuterated spacers were polycondensed with the acid chloride of *N*-(4′-carboxyphenyl)trimellitimide. Analogous poly(esterimide)s were prepared from fully protonated spacers. Furthermore, copolyesters were synthesized from a 1/1 mixture of 1,12-dihydroxydodecane and 1,22-dihydroxydocosane, one of which contained a deuterated dodecane spacer, whereas in the analogous polyester the docosane spacer is deuterated. All poly(ester–imide)s were subjected to a thermal treatment yielding a smectic-E phase in the solid state. ^{13}C nuclear magnetic resonance (n.m.r.) cross polarization magic angle spinning CP/MAS spectra revealed that spacers with ≥ 12 methylene groups contain *trans–trans* conformations even up to 100°C. ^{2}H n.m.r. spectroscopic measurement revealed that the spacers are nearly immobile at -180°C, but gain increasing mobility upon heating. Whereas the central segments of the docosane spacer can perform crank-shaft motions at ambient temperature, the motion of the dodecane spacer is restricted to kinks. At 100°C the middle segments of the spacers partly are capable of isotropic motion in the solid smectic-E phase. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ester-imide)s; smetic layers; spacers; ^{13}C n.m.r. CP/MAS)

INTRODUCTION

This work is part of a broader study dealing with polymers that form layer structures either in the solid and/or in the liquid crystalline (LC) state. An important class of polymers with a high tendency of forming smectic layer structures are polyimides containing aliphatic spacers[1–7]. Previous studies have shown[2,4,5] that the formation of layers is not directly correlated with the ‘‘crystallization’’ or any other kind of internal ordering of the mesogens. The formation of smectic layers is the exclusive result of a phase separation process on the molecular level. Polymer chains consisting of a regular sequence of non-polar groups (e.g. alkane spacers) and polar groups (e.g. imide rings) prefer a layer structure as energy minimum, even if the polar and non-polar building blocks do not adopt any additional ordering inside their layers.

Among the numerous polyimides forming smectic layer structures in the solid state[1–7], the poly(ester–imide)s (PEIs) of structure 1[2–5] are of particular interest for the following reasons. Firstly, the PEIs 1 do not form an enantiotropic LC phase, but they display a very short-living monotropic LC phase upon cooling below their melting point (T_m)[5]. Secondly, depending on the length of the spacer they can adopt three different kinds of smectic order in the solid state, namely: frozen smectic-A, smectic-B and smectic-E[2–5]. In this connection it should be emphasized that in the case of LC-main chain polymers (contrary to low molar mass mesogens) the only true LC phases are smectic-A and smectic-C. All higher ordered smectic phases consist of ‘‘two-dimensional crystals’’ of mesogens and are solid mesophases. Thirdly, whereas the PEIs with even spacers form layers quite rapidly upon cooling from the isotropic melt, those with short odd spacers can even form a normal amorphous phase. In other words variation of spacer and thermal history allows a broad variation of the molecular order in the solid state. This situation provides an interesting basis for studies of relationships between supermolecular order, local conformation and chain dynamics. The present study had the purpose of concentrating on PEIs containing long selectively deuterated spacers. In addition to the homopolyesters 2a and 2b the copolyestera 3a and 3b should be investigated. Thermotropic polyesters containing deuterated spacers were also studied by another group[8,9]. However, those authors exclusively concentrated on the properties of the nematic phase.

EXPERIMENTAL

Materials

Deuterium gas (D_2), 1,12-dihydroxydodecane and 1,16-dihydroxyhexadecane were purchased from Aldrich Co. (Milwaukee, WI) and used without further purification. 1,12-Dihydroxydodeca-5,7-diyne, 1-hydroxy-10-undecyne and platinum 5% on carbon were purchased from Lancaster (D-63165 Mülheim, FRG) and used without purification. Trimellitic anhydride, 4-aminobenzoic acid and thionylchloride were gifts of Bayer AG (Leverkusen, FRG).

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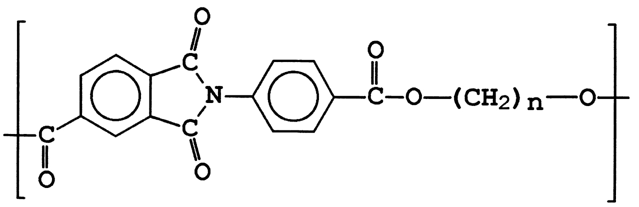
* To whom correspondence should be addressed



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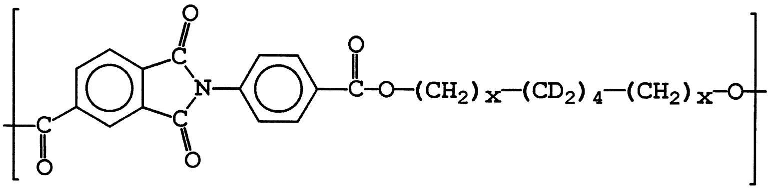

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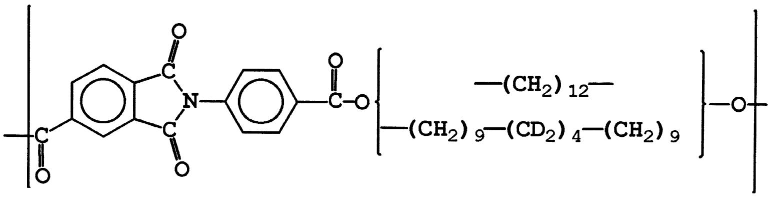
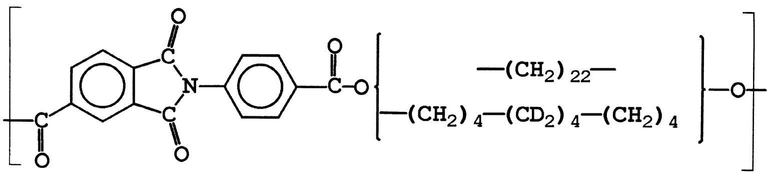
b: x = 9



3a



3b

The dichloride of 4-aminobenzoic trimellitimide was prepared as described previously[2,7].

Synthesis of 1,22-dihydroxydocosa-9-12-diyne

1-Hydroxy-10-undecyne (0.15 mol), Cu(II)acetate (0.15 mol) and CuCl (30 mg) were refluxed in a mixture of pyridine and methanol (500 ml volume ratio 1/1) for 7 h. Afterwards the reaction mixture was concentrated *in vacuo* to a volume of approx. 200 ml, and added dropwise to 6 N hydrochloric acid (1 l) with stirring. The product was extracted with five 400 ml portions of ethyl acetate, and the combined extracts were washed with a $NaHCO_3$ solution and dried over Na_2SO_4. The extract was concentrated *in vacuo* to a volume of approx. 100 ml, and the product was crystallized by portionwise addition of ligroin. The isolated product was then recrystallized from ethyl acetate/ligroin. Yield 64%; m.p. 81–82°C (m.p. 82°C in Ref. [10]); ^1H n.m.r. ($CDCl_3$/TMS) δ, 1.20–1.85 (m, 28 H), 2.25 (t, 4 H), 3.65 (t, 4 H) ppm.

1,22-Dihydroxy-docosane

1,22-Dihydroxydocosa-9,12-diyne (30 mmol) was dissolved in ethanol (500 ml) and 1 g of 5% Pt/carbon catalyst was added. The hydrogenation was conducted at 20°C and 1 atm. After completion of the H_2 uptake, the catalyst was filtered off, the filtrate was concentrated and the remaining product was recrystallized from an ethanol/water mixture (volume ratio 80/20). Yield 93%; m.p. 104–105°C (m.p. 105–106°C in Ref. [11]); ^1H n.m.r. ($CDCl_3$/TMS) δ, 1.26 (m, 36 H), 1.56 (m, 4 H), 3.63 (t, 4 H).

Deuteration of spacers

Platinum 5% on carbon (2 g) was added to a solution of 1,12-dihydroxy-5,7-diyne in dry 1,4-dioxane (1 l), and this mixture was shaken at 20°C in an atmosphere of D_2 until the required quantity of D_2 was consumed. The catalyst was filtered off, the filtrate was concentrated *in vacuo* and the 1,12-dihydroxydodecane-d_8 was distilled *in vacuo*. Yield 84%; m.p. 79–81°C; analysis calcd for $C_{12}H_{18}D_8O_2$ (210.38) C 68.50, found C 68.41. ^1H and ^{13}C n.m.r. spectra proved the absence of any double bond. 1,22-Dihydroxydocosane-d_8 was prepared analogously, but purified by recrystallization from ethanol/water (80/20 by volume). Yield 91%; m.p. 103–104°C; analysis calcd for $C_{22}H_{38}D_8O_2$ (350.6) C 75.35, found C 75.31.

Polycondensation

The dimethyl ester of *N*-(4′-carboxyphenyl)trimellitimide (15 mmol), and α,ω-dihydroxyalkane (15 mmol) and dibutyltinoxide (20 mg) were weighed into a cylindrical glass reactor equipped with stirrer and gas-inlet and -outlet tubes. The reaction mixture was rapidly heated to 240°C (20 min) and slowly to 290°C (in steps of 10°C). The liberated methanol was removed with a slow stream of nitrogen. The cold product was dissolved in CH_2Cl_2/trifluoroacetic acid (volume ratio 9/1) and precipitated into methanol.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20°C. The differential scanning calorimetry (d.s.c.) measurements were conducted with a Perkin Elmer DSC7 in aluminum pans under nitrogen. The wide-angle X-ray difraction (WAXD) powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered CuK$_\alpha$-radiation.

The 100 MHz ^{1}H n.m.r. spectra were obtained on a Bruker AC-100 Fourier transform (*FT*)-n.m.r. spectrometer in 5 mm o.d. sample tubes using $CDCl_3$/TMS for the monomers and a 4/1 (by volume) mixture of $CDCl_3$ and trifluoroacetic acid for the polyesters. The solid-state n.m.r. spectra were recorded with a Bruker MSL 300 *FT*n.m.r. spectrometer (7.05 Tesla) at a ^{1}H frequency of 300.13 MHz. The ^{13}C n.m.r. CP/MAS was performed at 75.47 MHz using a double bearing variable temperature Bruker MAS probe, 7 mm zirconium oxide rotors, 4–5 kHz spinning rate, 1 ms contact time, and 4 s recycle delay.

The ^{2}H n.m.r. spectra were obtained with the same spectrometer at 46.07 MHz by using the solid-echo pulse technique with a puls delay τ_1 of 40 μs, a pulse length of 3.3 μs and quadrature phase detection. Due to a waiting time $\tau_w > 3 \cdot T_{1max}$ they are fully relaxed.

RESULTS AND DISCUSSION

Syntheses

For the ^{13}C n.m.r. and ^{2}H n.m.r. spectroscopic studies of this work five aliphatic spacers were required: three fully protonated and two selectively deuterated spacers. 1,12-Dihydroxydodecane and 1,16-dihydroxyhexadecane are commercial products and were purchased. 1,22-Dihydroxydocosane was prepared by hydrogenation of 1,22-dihydroxydocosa-10,12-diyne (4b, equation (2)), which was synthesized by ''Glaser-oxydation'' of commercial 1-hydroxy-10-undecyne (equation (1)). The deuterated spacers 6a and 6b were obtained by Pt-catalysed deuteration of the diacetylenes 5a and 5b (equation (3)). Finally, six poly(ester–imide)s were prepared by Bu_2SnO-catalysed transesterification of the alkane diols with the dimethyl ester of *N*-(4′-carboxyphenyl)trimellit-imide (equation (4)), quite analogous to the technical synthesis of polyethyleneterephthalate.

Three PEIs with fully protonated spacers were isolated (1, $n = 12$, $n = 16$, $n = 22$) and three deuterated PEIs (2a,b and 3a,b). Their yields and properties are summarized in *Table 1*.

Chain packing

Previous WAXD and d.s.c. measurements of PEI 1 ($n = 12$) have shown that this polymer can adopt three different solid phases depending on the thermal history. Partial deuteration of the spacer does not affect these properties, and *Figure 1* displays the WAXD powder patterns of the three different solid phases of 2a. Quenching from the isotropic melt yields a frozen smectic-A phase, in which the mesogens form a rather perfect layer structure without lateral order, indicated by the sharp layer reflection at $2\Theta = 3°$ and the amorphous halo in the wide-angle region. Heating above the glass transition temperature improves the two-dimensional order of the mesogens, so that a hexagonal order with a sharp reflection at $2\Theta = 20°$ is achieved, and thus a smectic-B phase is formed. Annealing above the melting point (T_m) of the smectic-B phase generates a higher melting smectic-E phase with a kind of orthorhombic order of the mesogenic groups giving rise to a number of wide-angle X-ray scattering (WAXS) reflections listed in *Table 2*.

In the case of 1 ($n = 16$) and 1 ($n = 22$), and for a random copolymer 1 ($n = 12/22$) slow heating of the precipitated PEIs or slow cooling of the isotropic melt exclusively produce one modification, namely the smectic-E phase, as

$$2\ HO\text{-}(CH_2)_9\text{-}C{\equiv}CH \xrightarrow{(CuAc_2)} HO\text{-}(CH_2)_9\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_9\text{-}OH$$

4

$$\downarrow {+4\ H_2}\ (Pt)$$

$$HO\text{-}(CH_2)_{22}\text{-}OH$$

$$HO\text{-}(CH_2)_x\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_x\text{-}OH$$

5a: x = 4

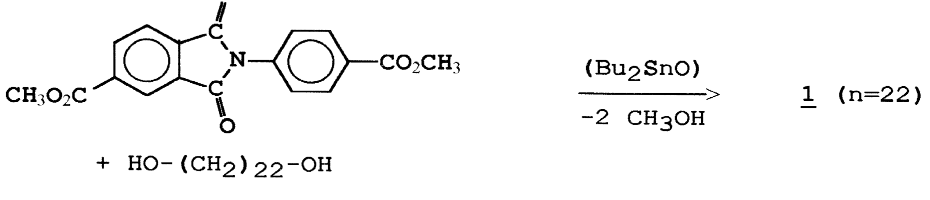
5b: x = 9

$$\downarrow {+4\ D_2}\ (Pt)$$

$$HO\text{-}(CH_2)_x\text{-}(CD_2)_4\text{-}(CH_2)_x\text{-}OH$$

6a: x = 4

6b: x = 9



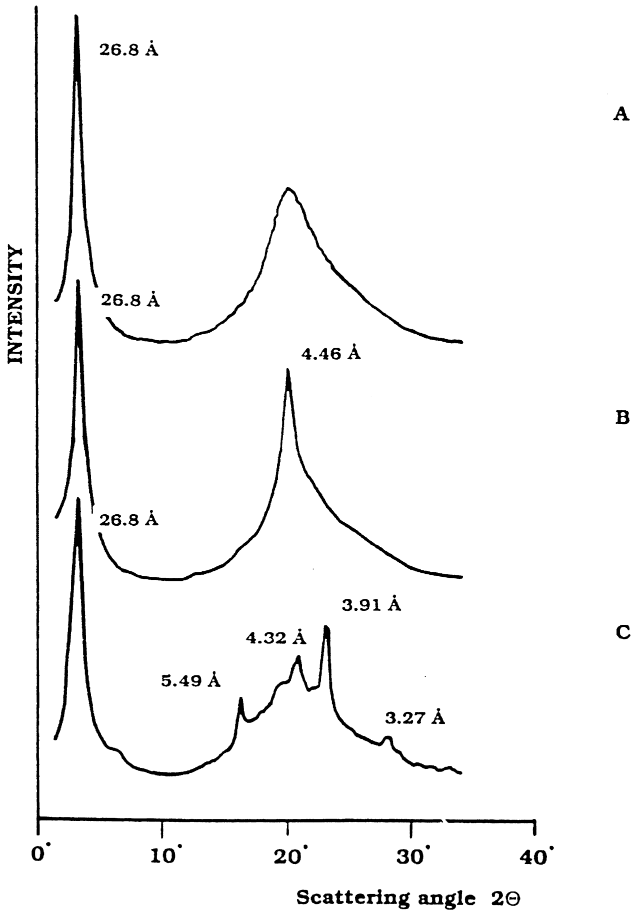


Figure 1 WAXD powder patterns of poly(ester–imide) 2a: (A) after quenching from the melt (180°C); (B) after heating of the quenched sample at 70°C for 1 h; (C) after annealing at 170°C for 24 h

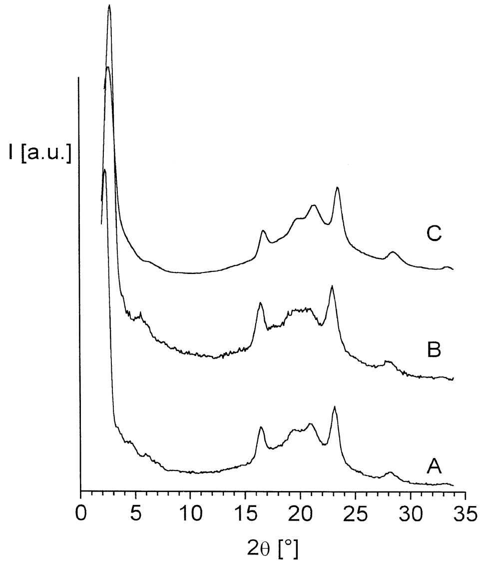


Figure 2 WAXD powder patterns of PEI 1, $n = 22$ (A), $n = 16$ (B), and *co*-PEI 1, $n = 12/22$ (C)

evidenced by the WAXD pattern of *Figure 2*. The position of the wide-angle reflections of the PEIs 1 are independent of the length of the spacer for $n \geq 12$. Obviously, these reflections exclusively result from the ‘‘two-dimensional crystals’’ within the smectic layers of the mesogenic aryl groups. The length of the spacer influences, of course, the position of the middle angle reflection (MAR, $2\Theta = 1–5°$) which indicates the layer distance (d-spacing). The measured d-spacings of the poly(ester–imide)s are evident from the WAXS pattern in *Figures 1* and *2* and are listed in *Table 2*.

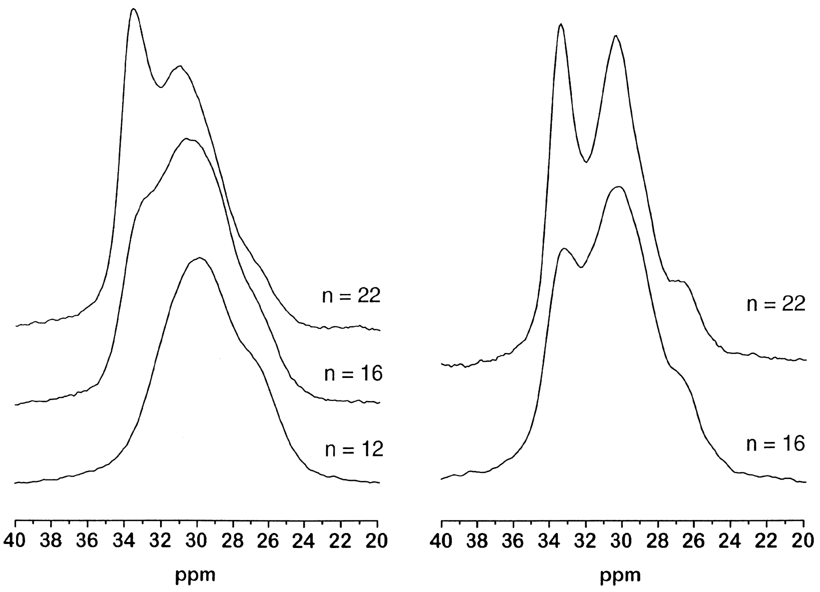
Although these X-ray data yield an indirect information on the effective length of the spacers, they do not give any direct information about their conformation. However, it is well known from semicrystalline polyethylene that ^{13}C n.m.r. CP/MAS spectra provide information on the conformation of an alkane chain in the solid state[12], assuming no rapid exchange on the n.m.r. time scale between the sites. The broad signal at 29–30 ppm covers tg- and gt-conformations, while the *trans–trans* triades give rise to a sharper signal at 33 ppm due to the γ-*gauche* effect[13]. In polyethylene the tt-conformations could be attributed to the crystalline regions. An interesting problem which, to the best of our knowledge, has never been studied before, is the question of whether alkane spacers in smectic phases can form ordered paraffin domains. Such a packing of alkane chain segments within a micro-crystal had been observed for the side-chains of hairy rod molecules forming a sanidic or biaxial-nematic layer structure[14]. However, in the smectic phase of main-chain molecules the spacers are fixed at both sides to the rigid mesogen layer. Nevertheless, the formation of stable ordered *trans–trans* sequences in the methylene spacers of the PEI should be detectable by ^{13}C n.m.r. CP/MAS spectroscopy.

Figure 3 depicts the aliphatic region of the ^{13}C n.m.r. CP/MAS spectra of 1 ($n = 12$, 16 and 22) recorded at 20°C (a)

Table 1 Yields and properties of the poly(ester–imide)s 1, 2a,b and 3a,b

Polymer formula	Yield (%)	η^a_{inh} (dl g^{-1})	T^b_g (°C)	T^b_m (°C)	T^b_c (°C)	Elemental formula (formula weight)	Elemental analyses			
								C	H	N
1, $n = 12$	95	0.72	44	183	113	$C_{28}H_{31}NO_6$	Calcd	70.03	6.5	2.93
						(477.5)	Found	70.13	4	2.99
1, $n = 16$	98	0.62	55	160	116	$C_{32}H_{39}NO_6$	Calcd	72.02	7.3	2.63
						(533.6)	Found	71.38	7	2.60
1, $n = 22$	96	0.43	41	156	124	$C_{38}H_{51}NO_6$	Calcd	73.87	8.3	2.27
						(617.8)	Found	73.24	2	2.24
2a	87	0.36	45	162	108	$C_{28}H_{23}D_8NO_6$	Calcd	69.25	–	2.89
						(485.6)	Found	69.48	–	2.81
2b	62	1.30	–	145	107	$C_{38}H_{43}D_8NO_6$	Calcd	72.92	–	2.24
						(625.8)	Found	73.21	–	2.27
3a	96	0.65	50	140	88/97	$C_{66}H_{74}D_8N_2O_{12}$	Calcd	71.84	–	2.54
						(1103.9)	Found	71.66	–	2.19
3b	97	0.54	47	136	84/100	$C_{66}H_{74}D_8N_2O_{12}$	Calcd	71.84	–	2.54
						(1103.9)	Found	71.53	–	2.49

[a] measured at 20°C with $c = 2\ g\ l^{-1}$ in CH_2Cl_2/trifluoroacetic acid (volume ratio 9/1)
[b] from d.s.c. measurements with a heating/cooling rate of 20°C min^{-1}



(a) (b)

Figure 3 Spectra, 75.4 MHz ^{13}C n.m.r. CP/MAS, of PEI 1 with $n = 12$, 16 and 22 at 20°C (a) and at 100°C (b)

and 100°C (*b*). An intensive broad peak at 29–30 ppm indicates that the *gauche* conformations are predominant in all three cases and at both temperatures. However, the spectrum of 1 ($n = 16$) also exhibits a weak shoulder at 33 ppm, indicating the presence of *trans–trans* conformations in the spacer[13]. In the case of PEIs 1 $n = 22$, a separate peak is observable at 33 ppm. Surprisingly, its intensity does not decrease at 100°C and due to motional narrowing it is more clearly detectable at this temperature (*Figure 3b*). On the one hand, the tt-signal at 33 ppm, which increases with the spacer length, indicates that particularly the long spacers exhibit a high degree of conformational order. On the other hand, it should be emphasized that these ^{13}C n.m.r. spectra cannot prove the existence of ordered paraffin domains.

An interesting aspect of the formation of paraffin domains between the layers of aryl groups is the difference of their sterical demands. The cross-section of the mesogens is almost twice as high as the cross-section of an alkane chain in *trans* conformation. Therefore, the formation of ordered paraffin domains creates more free volume in its direct neighbourhood and causes a slight contraction of the *d*-spacing when compared to fully extented repeating unit (see figure 13 of Ref. 15). More detailed n.m.r. measurements are in progress and will be presented in a future publication.

^{2}*H n.m.r. line shape analysis*

In order to study the molecular motion of the spacers in the smectic phase the poly(ester imide)s which had been deuterated selectively in the four central methylene groups were subjected to ^{2}H n.m.r. measurements. For an alkane chain in the solid state two types of molecular motions are considered. One is the kink-3-bond motion[16], corresponding to *trans–gauche* isomerization of adjacent methylene groups. The other mechanism is the crankshaft-5-bond motion[17]. In the rapid exchange limit the corresponding line shapes can be calculated from the averaged field gradient tensor[18,19]. In the crankshaft motion the C–D-bonds move on a cone with an opening angle of 70.5°. Potential calculations indicate 120°-3-site jumps[20] but a free rotation gives the same line shape[21], which is a narrowed Pake-spectrum with a splitting of $3/d$, where d is the splitting of the rigid pattern. In the kink motion the C–D-bonds perform two-site jumps on a 54.7° cone. In this case the line shape depends on the population of the sites and is thus a measure for the amount of *trans*-conformation. For an equal population the spectrum has a width of 120 kHz with a central peak, which is split more and more with increasing *trans* amount. Isotropic motion leads to a central lorentzian line in the ^{2}H n.m.r. spectrum.

Figure 4 shows the fully relaxed ^{2}H n.m.r. spectra of PEI 2a at different temperatures. At − 100°C the line shape essentially corresponds to the rigid powder pattern (Pake-diagram) with a splitting of 120 kHz. With increasing temperature the spectrum is narrowed due to molecular

Table 2 Measured and calculated atomic distances d (Å) of the poly(ester–imide)s 1, 2a, 2b, and 3

PEI formula	*d*-spacing measured (Å)	*d*-spacing calculated^a (Å)			WAXS reflections (Å)				
		tt	tg	gg					
1, $n = 12$	28	30.1	28.0	26.4	5.49	4.32	3.91	3.27	
1, $n = 16$	31.5	35.2	32.4	30.0	5.4	4.7	4.3	3.9	
1, $n = 22$	38	42.8	39.2	35.7	5.4	4.7	4.3	3.9	
2a	28	30.1	28.0	26.4	5.5	4.3	4.0	3.3	
2b	37.5	42.8	39.2	35.7	5.4	4.7	4.3	3.9	
3a	30.5	30.1	28	26.4	7.75	5.24	4.35	3.85	3.17
3b	30.0	30.1	28	26.4					

^{a}calculated by a force field program

motion, while the rigid components disappear. The line shape at 20°C is commonly observed in amorphous polymers or glassy liquid crystals and referred to as a ‘‘kink spectrum’’. It results from conformational exchanges between two non-equally-populated sites[22]. Above 60°C, that is about 100°C below the melting point, the middle segments of the dodecane spacer is capapble of quasi-isotropic motions indicated by the central Lorentzian line.

The motional behavior of PEI 2b is different, obviously due to the larger number of conformational isomers in the docosane spacer. At low temperatures the line (*Figure 5*) shape is more or less the same when compared to 2a, but at 40°C a splitting of 20 kHz is observed which can be attributed to a crank-shaft motion at intermediate frequency. However, the splitting and the broadness of the spectrum of 120 kHz indicates a superposition of crank-shaft motion and kink-motion. A pure crank-shaft motion in the rapid exchange limit which had been found in the nematic LC phase[23] was not observed for the spacers in these smectic systems. At 80°C the central Lorentzian line occurs and

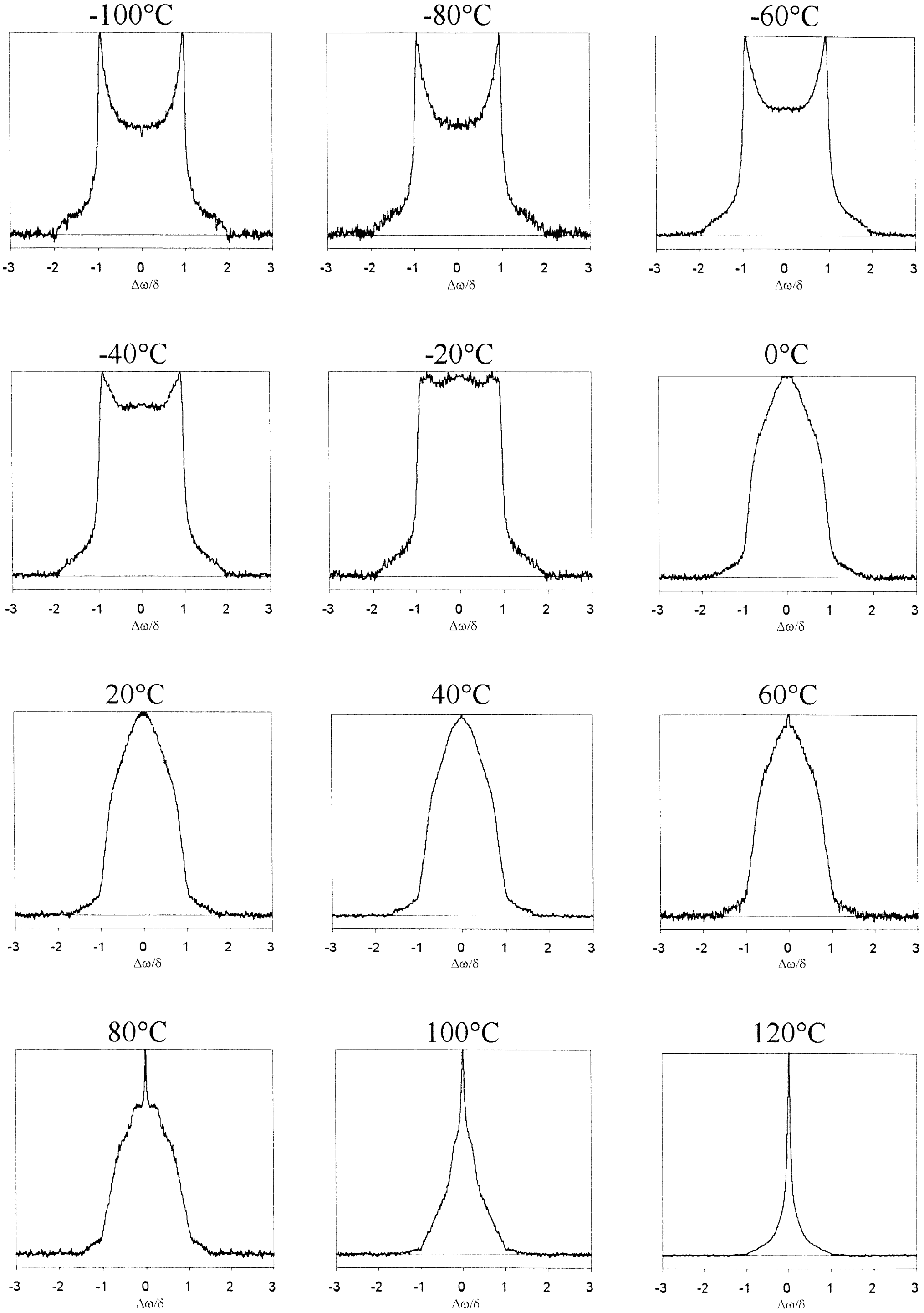


Figure 4 Fully relaxed ^2H n.m.r. spectra of PEI 2a with variation of the temperature

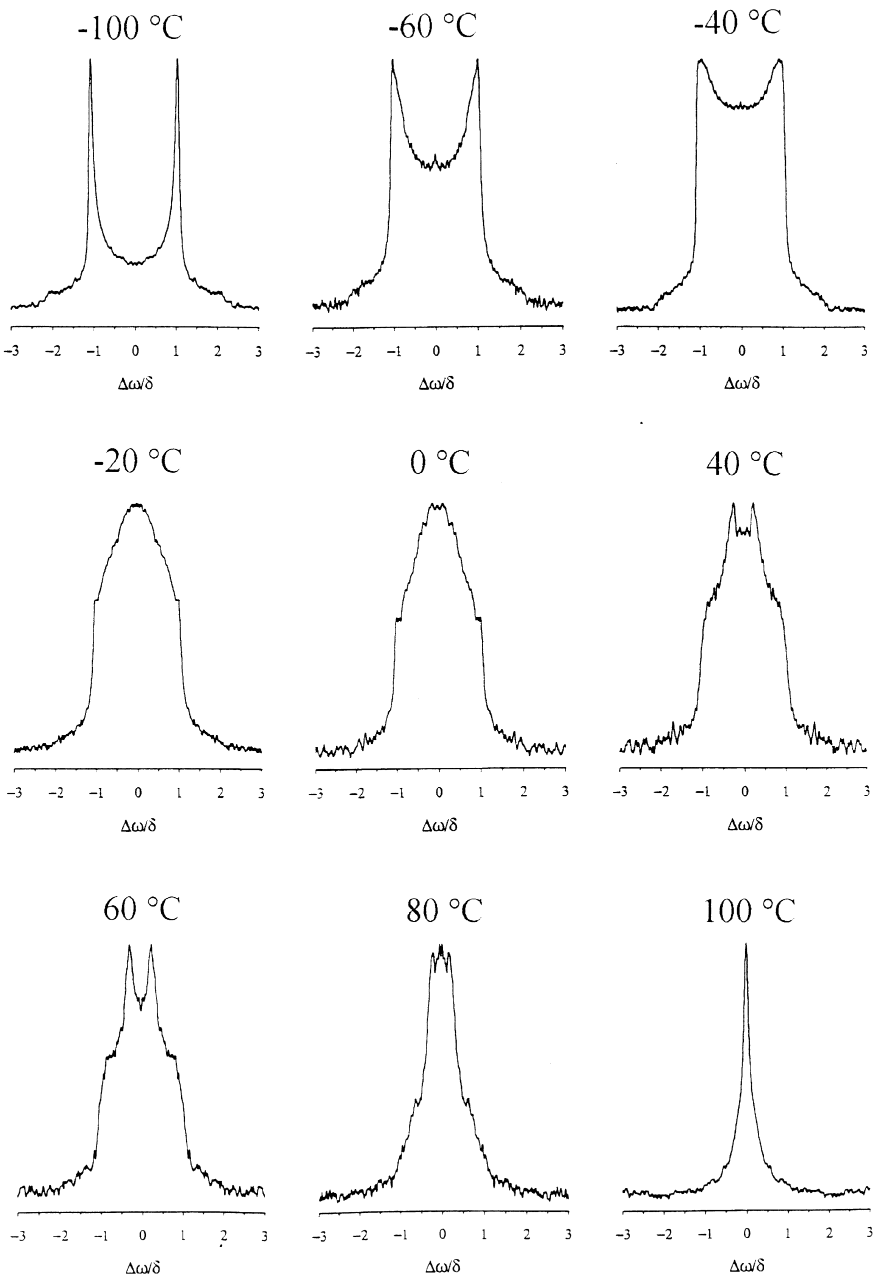
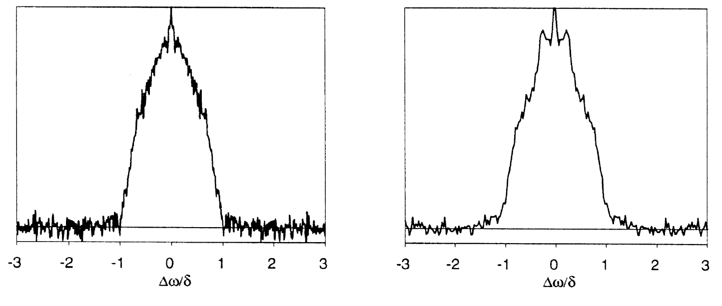


Figure 5 Fully relaxed ^2H n.m.r. spectra of PEI 2b at different temperatures

dominates the line shape above 100°C. Obviously, the central spacer segments can partly perform quasi-isotropic motions, although the mesogenic groups are still embedded into the crystal lattice. Since the tt-conformations are still stable at this temperature, this finding is a contradiction to the hypothesis of an ordered paraffin domain. Moreover, the tt-sequences must be localized rather in the outer parts of the spacers.



(a)

(b)

Figure 6 Comparison of ^2H n.m.r. spectra of the copoly(ester−imide)s 3a (a) and 3b (b) at 60°C

The main difference in the motional behavior of the $n = 12$ and the $n = 22$ spacer becomes obvious by comparison of the line shapes at 60°C. While the middle segments of the long docosane spacer can perform crank-shaft motions which involve five bonds, their motion in the shorter dodecane spacer is restricted to kinks due to the fixing towards to rigid mesogen layer.

Essentially, the same dynamics of the spacers were found in the random copolymer containing $n = 12$ and $n = 22$ spacers. In *Figure 6* the ^{2}H n.m.r. spectra of the deuterated docosane spacer 3a is compared to the line shape of the deuterated dodecane spacer 3b at 60°C. Once more the long spacer can perform crank-shaft motions while the shorter spacer cannot. The frequencies of the motions correspond essentially to the dynamics of the homopolymers. Obviously, the molecular motion of the central spacer segments are determined rather by the fixing of the spacer ends and the temperature than by lateral interactions with other spacers.

However, a detailed line-shape analysis by comparison of measured and calculated spectra will be presented in a future paper.

CONCLUSION

1,12-Dihydroxydodecane and 1,22-dihydroxydocosane having four deuterated methylene groups were synthesized from diacetylene precursors. Poly(ester–imide)s forming a smectic type of layer structure in the solid state were then prepared from these deuterated spacers. ^{13}C n.m.r. CP/MAS spectroscopy and ^{2}H n.m.r. line shape analysis of the spacers suggest the following conformational and dynamical properties. The spacers adopt a relatively high fraction of *trans–trans* conformations up to 100°C. However, the mobility of the middle segments increases dramatically when heated from −100°C to +100°C, and finally they undergo a quasi-isotropic motion although embedded in a solid layer structure.

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