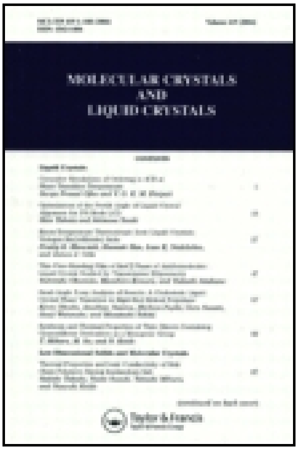

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Liquid Crystalline Main Chain Polysiloxane Esters and their Monomers Part II: Synthesis and Thermal Behaviour of Polysiloxane Esters with Linear and Tilted Aromatic Ester Moieties

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Liquid Crystalline Main Chain Polysiloxane Esters and their Monomers

Part II: Synthesis and Thermal Behaviour of Polysiloxane Esters with Linear and Tilted Aromatic Ester Moieties

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Liquid crystalline main chain polysiloxane esters have been formed by reacting bis[4-(ω-alkenyloxy)benzoic acid]esters containing 1,4-phenylene, 4,4′-biphenyldiyl, 2,7-fluorenediyl, and 2,7-fluorenonediyl units with α,ω-di-H-oligo(dimethylsiloxane)s. The chemical structure has been confirmed by elemental analyses, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Molecular weights have been measured by GPC. The thermal behaviour has been studied by polarising microscopy and by DSC. In general the phase transitions are lower with a decreasing length of the alkylene spacers and with an increasing number of siloxane units within the spacer while they increase with magnification of the mesogenic groups. X-ray diffraction measurements for one polymer confirmed the type of the liquid crystalline phases (N, S_C, S_F). Deuteration has no influence on the thermal behaviour.

Keywords: Liquid crystalline siloxane esters; polysiloxane esters; fluorene units as mesogenic groups; polysiloxanes with low clearing points; cybotactic structure

1. INTRODUCTION

Polymers, which exhibit in solution (lyotropic) or in melt (thermotropic) properties of solid crystals (order behaviour) and isotropic liquids (viscosity)

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*Corresponding author.

are called liquid crystalline or mesomorphic. These polymers are able to form in partially ordered solutions or melts materials with a high degree of molecular orientation and order. Interesting mechanical and optical properties, such as high tension strength, can result from this microscopic order.

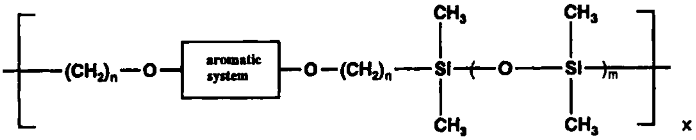
According to the different location of the mesogenic groups one has to differentiate between main chain and side chain polymers [1]. In addition one has to distinguish the form of the mesogenic group (calamitic or discotic), the characteristic of insertion (linear or lateral), the presence (directly) and the flexibility of spacer groups. For the multitude of possible liquid crystalline polymers Brostow *et al.* [2] have developed an additional nomenclature with the intention of attaining a more detailed characterisation of the different structures. Side chain polymers are of interest as storage materials [3]. Rigid rod liquid crystalline main chain polymers [4, 5] are used as high tension strength polymers.

Most of the semiflexible liquid crystalline main chain polymers (LCMCP) synthesised so far contain methylene or oxyalkylene groups in their chains as flexible segments.

It is well known, that the insertion of highly flexible siloxane groups results in a strong depression of the glass temperature and the transition temperatures of about 100°C [6]. This property of siloxane units supports the creation of polymers which could be investigated in direct and indirect ^2H-solid state NMR-spectroscopy at temperatures below 230°C.

The good solubility in common organic solvents allows a complete chemical and physical characterisation of the LCMCP, which is important to achieve a more detailed understanding of the relation between molecular structure and macroscopic properties of the LCMCPs.

In 1980 Ringsdorf *et al.* [7] published the first species of this type of liquid crystalline main chain polysiloxane esters, with the phenylene unit in the mesogenic group arising from hydroquinone as the diol. In the following years monosubstituted hydroquinone and various aromatic diols like 4,4′-dihydroxybiphenyl [7], 1,4-dihydroxycyclohexane or the chirale estradiol [8] were used for forming mesogenic groups.



$$\left[-(CH_2)_n-O-\boxed{\text{aromatic system}}-O-(CH_2)_n-\overset{CH_3}{\underset{CH_3}{Si}}-\left(O-\overset{CH_3}{\underset{CH_3}{Si}}\right)_m- \right]_x$$

FIGURE 1 Chemical structure of liquid crystalline main chain polyesters with linear mesogenic units and alkylene as well as siloxane spacers.

Similar polymers were studied by Kosfeld *et al.* [9, 10], who synthesized thermotropic liquid crystalline polyesters containing 4,4′-*p*-terphenylene or bis(1,4-phenylene) terephthalate as mesogenic units and flexible siloxane spacers in the main chain. Lenz *et al.* [11] and Blumstein *et al.* [12] varied the flexible main chain by copolymerisation.

A large number of liquid crystalline monomer compounds with 2,7-disubstituted fluorene as mesogenic groups have been synthesised by several groups [13]. Schulz *et al.* [14, 15] studied liquid crystalline side chain poly (dimethylsiloxane)s with fluorenediyl units as mesogenic groups. These polymers form highly ordered smectic phases.

The first liquid crystalline main chain polymer containing 2,7-substituted fluorene groups was synthesised in 1989 by Friedel-Crafts-acylation of fluorene with α,ω-dicarboxylic acids [16]. Polyesters from 2,7-fluorenediol or 2,7-fluorene dicarboxylic acid with different lengths of the alkylene spacers produce liquid crystalline behaviour [17].

This paper contains a description of semiflexible LCMCPs with siloxane spacers and different aromatic diols (hydroquinone **HC**, 4,4′-biphenyldiol **BPD**, 2,7-fluorenediol **FOD**, and 2,7-fluorenonediol **FODO**).

Our LCMCPs have been synthesised from esters of 4-(ω-alkenyloxy)-benzoic acid with four aromatic diols and oligo(dimethylsiloxane)s with α,ω-silane functions. The series of synthesised polymers are different concerning the length of their siloxane (m) and the methylene (n) units and the nature of their aromatic diols (see Tab. I). The main idea of our investigations was to find a correlation between size and symmetry with respect to the liquid crystalline behaviour of the polymers.

For the characterisation of the liquid crystalline behaviour of the described LCMCPs microscopy under polarised light and differential scanning calorimetry (DSC) were used. For one typical polymer (see Fig. 2, $n = 3$, $m = 1$, $R =$ 1,4-phenylene-d_4) X-ray measurements were performed additionally to get information about the type and structure of the formed liquid crystalline phases.

^{2}H-solid-state NMR-spectroscopy was used to analyse the molecular order and motion states in the liquid crystalline phases.

TABLE I Characterisation of the used aromatic diols for the ester component

Aromatic diol		*Symmetry*	*Mesogenic group*
hydroquinone	**HC**	linear, rigid unit	three ring system
4,4′-biphenyldiol	**BPD**	linear, semiflexible unit	four ring system
2,7-fluorenediol	**FOD**	tilted (156°), rigid unit	four ring system
2,7-fluorenonediol	**FODO**	tilted (156°), rigid unit	four ring system

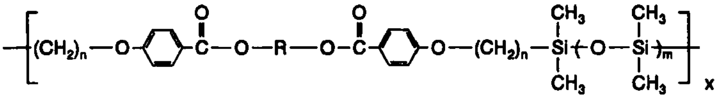


FIGURE 2 Chemical structure of the described polysiloxane esters.

2. SYNTHESIS

The hydrosilylation reaction is a well known method to connect monofunctional unsaturated mesogenic groups to a polymer backbone to build up side chain polysiloxanes (see lit. [18]).

One of the main questions of our work was whether it is possible to combine two bifunctional compounds to build up main chain polysiloxane esters in a similar manner. In literature there is no information whether the hydrosilylation reaction is a successful reaction to form liquid crystalline main chain polymers with a high degree of polymerisation.

Our synthetic work (see Fig. 3) describing the route to the polymers **1**–**16** demonstrates the usefulness of this reaction as a polymer forming reaction yielding oligomers and polymers with molecular weights up to 40.000 g/mol (estimated by GPC).

All polymers were synthesised in toluene or THF from bis[4-(ω-alkenyloxybenzoyl)oxy]-arenes (arising from the diols hydroquinone, 4,4′-biphenyldiol, 2,7-fluorenediol, and 2,7-fluorenonediol and α,ω H-terminated oligo(dimethylsiloxane)s catalysed by hexachloroplatinic acid. The bis[4-(ω-alkenyloxybenzoyl)oxy]arenes were prepared by a reaction of 4-(ω-alkenyloxy)benzoyl chloride with four different aromatic diols (see Tab. I and Fig. 3). The synthesis and thermotropic properties of these compounds are described in an earlier paper [19].

The synthesised polymers are characterised by their molecular weight between 5,000 and 40,000 g/mol (measured by GPC against polystyrene as standard), which is typical for oligomers and polymers. From the molecular weight we can calculate the chain length, which is approximately 8 to 50 repeating units per chain. The influence of shorter chains is provable by X-ray measurements of fibres.

We assume that the formation of longer polymer chains is hindered by unknown side reactions of the catalytic mechanism of the hydrosilylation reaction.

Liquid crystalline polyesters with linear mesogenic units and siloxane spacers in the main chain, described in literature [20, 7, 9] are similarly products with molecular weights of about 10,000 g/mol.

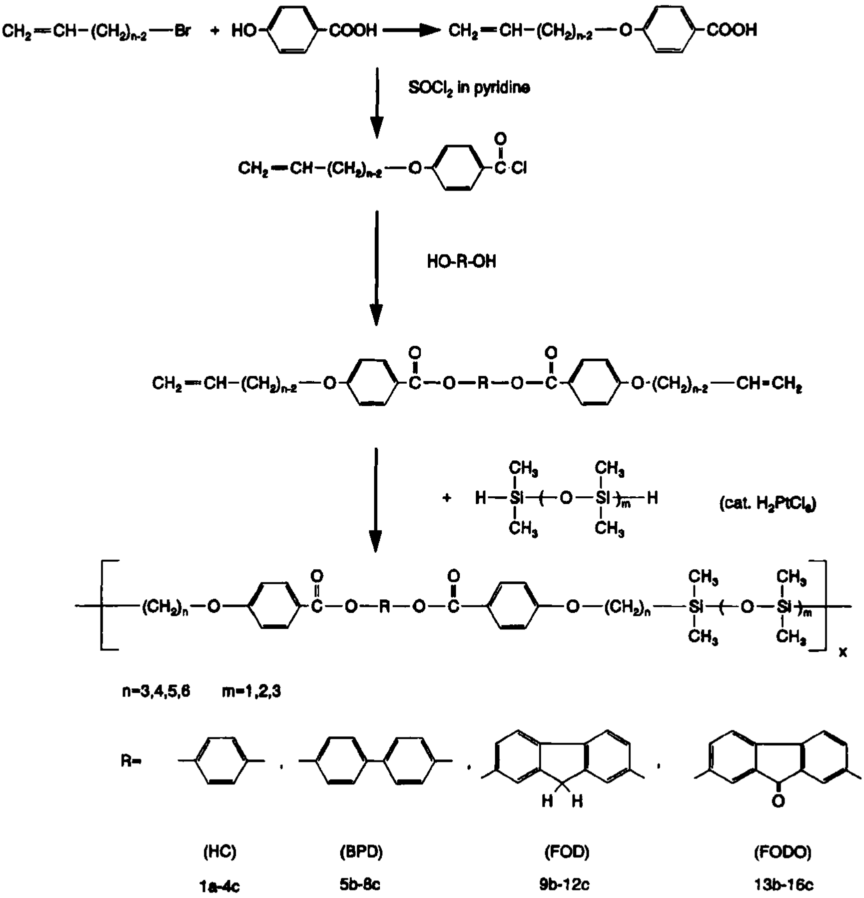


FIGURE 3 Synthesis of the liquid crystalline polysiloxane esters.

Table II shows the number of polymers with different lengths of methylene (*n*) and siloxane (*m*) spacers. For instance the acronym 5EBEBPDSi3 (**7b**) means 5 ($n=5$) methylene groups, 3 ($m+1$) siloxane atoms in the spacer and 4,4′-biphenylene (BPD) in the middle of the mesogenic unit.

Two deuterated polymers (**3EBEHCSi2-d$_4$**, $n=3$, $m=1$(**1a-d$_4$**), **3EBEHC-Si2-d$_8$**, $n=3$, $m=1$(**1a-d$_8$**)) were synthesised in the same way as described in Figure 3. The educts necessary for this synthesis were obtained by a deuteration reaction to H. Zimmermann [21] (see Fig. 4).

The rate of deuteration is higher than 95 %. No signals of the residual protons can be seen in the ^{1}H-NMR spectrum. These polymers were used for ^{2}H-solid-state NMR-measurements [22].

TABLE II Number and acronymes of the non-deuterated polymers

	HC *hydroquinone* *as diol*			*BPD* *4,4′-biphenyldiol* *as diol*		*FOD* *2,7-fluorendiol* *as diol*		*FODO* *2,7-fluorenonediol* *as diol*	
	$m = 1$ Si-2	$m = 2$ Si-3	$m = 3$ Si-4	$m = 2$ Si-3	$m = 3$ Si-4	$m = 2$ Si-3	$m = 3$ Si-4	$m = 2$ Si-3	$m = 3$ Si-4
$n = 3$	**1a**	**1b**	**1c**	**5b**	**5c**	**9b**	**9c**	**13b**	**13c**
$n = 4$	**2a**	**2b**	**2c**	**6b**	**6c**	**10b**	**10c**	**14b**	**14c**
$n = 5$	**3a**	**3b**	**3c**	**7b**	**7c**	**11b**	**11c**	**15b**	**15c**
$n = 6$	**4a**	**4b**	**4c**	**8b**	**8c**	**12b**	**12c**	**16b**	**16c**

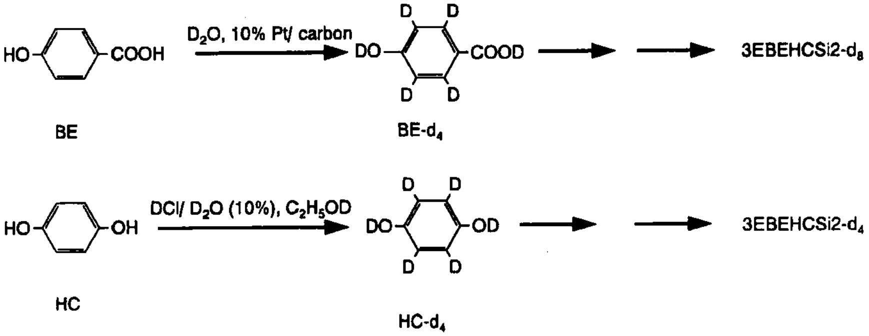
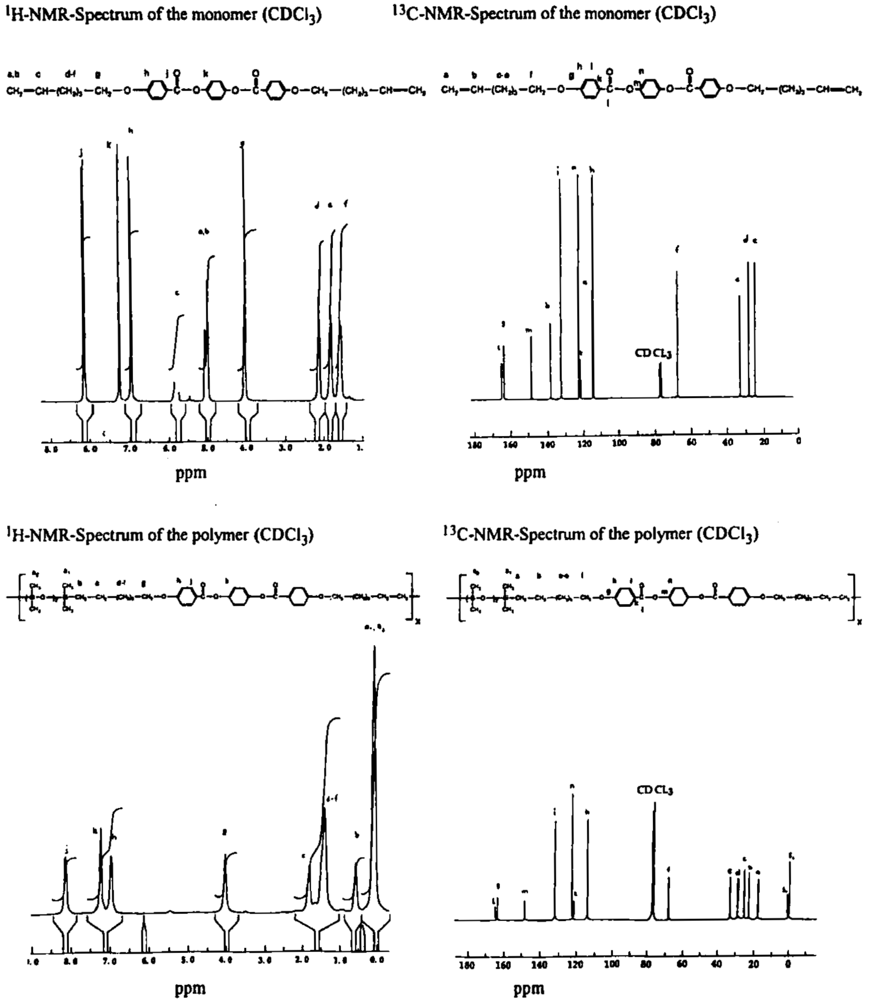


FIGURE 4 Synthesis of the labeled benzoic acid (BE), hydroquinone (HC) and their polymers.

All polymers show good solubility in the commonly used organic solvents (THF, chloroform, methylene chloride, toluene), and therefore it is easy to characterise them by spectroscopic methods. An example for the changes of ^{1}H-NMR- and ^{13}C-NMR-signals by the conversion from monomer 6EBEHC to polymer 6EBEHCSi3 (**4b**) can be seen in Figure 5. The typical signals of the starting materials (^{1}H-NMR: 5,8 ppm- $-C\underline{H}{=}CH_2-$; 5,0 ppm- $-CH{=}C\underline{H}_2-$; ^{13}C-NMR: 137 ppm- $-\underline{C}H{=}CH_2-$; 115 ppm- $-CH{=}\underline{C}H_2-$) disappeared during the reaction. The polymers are characterised by following signals: ^{1}H-NMR: 0,05 ppm- $-Si-(C\underline{H}_3)_2$; 0, 8 ppm- $-Si-C\underline{H}_2-$; ^{13}C-NMR: 0 ppm- $-Si-(\underline{C}H_3)_2$; 18 ppm- $-Si-\underline{C}H_2-$; 23 ppm- $-Si-CH_2-\underline{C}H_2-$. After the reaction we observed the disappearance of the protons of the double bond, indicating the effort of the hydrosilylation reaction.

Table IV shows the typical signals of the structural unit in the ^{1}H-NMR- and ^{13}C-NMR-spectra.

SPECTROSCOPIC CHARACTERISATION


¹H-NMR-Spectrum of the monomer (CDCl₃)

¹³C-NMR-Spectrum of the monomer (CDCl₃)

¹H-NMR-Spectrum of the polymer (CDCl₃)

¹³C-NMR-Spectrum of the polymer (CDCl₃)

FIGURE 5 ^{1}H-NMR- and ^{13}C-NMR-signals from monomer 6EBEHC and polymer 6EBEHCSi3 (**4b**).

Complete addition was controlled with the help of IR-spectroscopy. After the reaction $\nu(C{=}C)$ at 1641 cm^{-1} and $\nu(Si{-}H)$ at 2140 cm^{-1} disappear. In all polymers we find new broad peaks at 1031 cm^{-1} $\nu(Si{-}O{-}Si)$ and 1257 cm^{-1} $\nu(Si{-}CH_3)$.

3. THERMAL PROPERTIES

The thermal behaviour of the polysiloxane esters was studied by microscopy under polarised light, differential scanning calorimetry (DSC), and X-ray diffractometry. To make sure that thermal degradation does not affect these results we performed thermogravimetry (TGA), supposing that structural changes of these polymers are indicated by the formation of volatile products. The TGA showed that the weight loss starts far above the clearing point. All polymers exhibit a weight loss of about 1% at temperatures higher than 350°C.

Microscopy Under Polarised Light

Only for some polymers it is possible to characterise a phase transition by the textures found by microscopy under polarised light (Figs. 6a–d). The transition from the isotropic to the nematic phase constitutes an exception. It is characterised analogously to the low molecular weight compounds by the appearance of droplets (Fig. 6a). In the nematic mesophase an undifferentiated "sand structure" (Fig. 6b) develops, which becomes cloudy at the transition from the nematic to the smectic phase. This effect is known for polymers and is explained by a state of higher viscosity [23]. The liquid crystalline systems that are described in this paper show comparable characteristics in spite of its oligomeric character.

The polymers with hydroquinone as the central diol component and with the shortest siloxane chain ($m = 1$) have an exceptional position. Besides exhibiting smectic phases below the nematic phase, when inspected under polarised microscopy they show distinctive interpretable textures already after 4 h annealing (6c, d).

Differential Scanning Calorimetry (DSC)

The transition peaks of the polymers in the DSC-curves (measured with a heating rate of 10 K/min) are very broad because of the polydispersity of the samples. For this reason we indicate the maximum of the peak as the transition temperature. Table III shows a summary of the liquid crystalline behaviour of the described polymers.

Dealing with polymers with hydroquinone in the middle of the mesogenic group the second and third heating curves of the cycles are perfectly reproducible (Fig. 7).

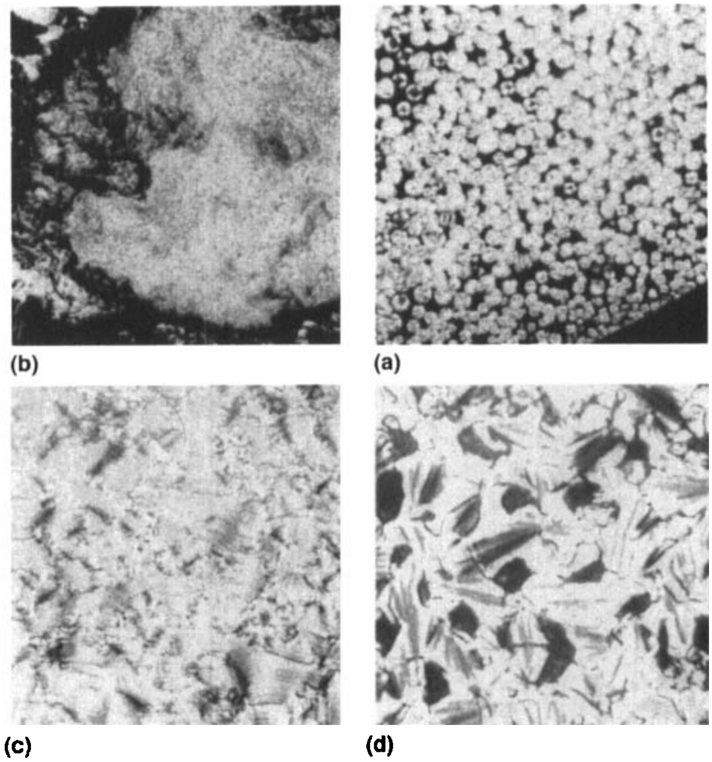


FIGURE 6 a) nematic droplets (**6EBEFODSi3 (12b)**, 210°C, ×100) b) "sand-like" texture (**6EBEBPDSi4 (8c)**, 100°C, ×100) c) S_C-phase, (**3EBEHCSi2-d$_4$ (1a-d$_4$)**, 100°C, ×100) d) S_F-phase, (**3EBEHCSi2-d$_4$ (1a-d$_4$)**, 68°C, ×100). (See Color Plate I).

In case the mesogenic group is lengthened by 4,4′-biphenyldiol, 2,7-fluorenediol or 2,7-fluorenonediol the DSC-curves of the polymers show special features such as the shifting of the transition temperatures when repeating the cycles to lower temperatures, and the widening of the peaks until the disappearance of the transition peak from the nematic to the isotropic phase (Fig. 8 compares first and second heating of the polymer (**6c**)).

The glass transition which shows up as a jump of the DSC-curves is not measurable by our polymers. The same effect was observed for other liquid crystalline polyesters with oligosiloxane spacers of a comparable structure [24, 25]. By some polymers the glass transition can be seen as an endothermic peak during the first heating (see peak at 60°C in Fig. 8, first heating), an effect which is described in the literature [26] as enthalpy relaxation.

TABLE III Characterisation and thermal behaviour of the synthesised polymers

Polymer	*Nr.*	*Yield* [%]	*Mol. weight* [*g/mol*]	*Elemental analysis*		*Phase transition temperatures* [°*C*]	*Phase width* [°*C*]
				C_c [%] C_f [%]	H_c [%] H_f [%]		
3EBEHCSi2	**1a**	80	5,619	63.80	6.42	g/49.9/S_F/70/S_C/103/N/145, 6/i	95
				60.51	6.21	i/144/N/97/S_C/68/S_F/g	
3EBEHCSi3	**1b**	90	8,911	60.15	6.62	g/38* /N/110/i^b	72
				58.97	6.46	i/110/N/g	
3EBEHCSi4	**1c**	93	9,941	57.26	6.78	g/28* N/91/i^c	63
				55.52	6.47	i/86 N/g	
4EBEHCSi2	**2a**	61	7,297	64.83	6.80	g/62* /S_F/86/S_C/110/N/174/i	112
				62.98	6.50	i 173/N/109/S_C/76/S_F/g	
4EBEHCSi3	**2b**	75	13,733	61.22	6.95	g/0* /S/50/N/123/i	123
				59.21	6.73	i 104/N/40/S/g	
4EBEHCSi4	**2c**	70	22,076	58.34	7.07	g/30* /S/42/N/108 i	78
				55.67	6.75	i/100/N/36/S/g	
5EBEHCSi2	**3a**	97	23,035	65.77	7.14	g/40* /S_F/129/S_C/161/N/171/i	131
				64.55	7.02	i/168/N/158/S_C/118/S_F/g	
5EBEHCSi3	**3b**	84	22,936	62.21	7.25	g/50* /S/128/N/153/i	103
				64.96	6.95	i/128/N/98/S/g	
5EBEHCSi4	**3c**	95	21,342	59.33	7.34	g/55* /S/121/N/132/i	78
				57.63	7.14	i/126/N/102/S/g	
6EBEHCSi2	**4a**	70	9,152	66.63	7.46	g/60* /S_F/113/S_C/165/N/186/i	126
				67.54	6.96	i/183/N/161/S_C/102/S_F/g	
6EBEHCSi3	**4b**	89	17,131	63.19	7.54	g/60* /S/88/N/154/i	94
				61.04	7.16	i/150/N/82/S/g	
6EBEHCSi4	**4c**	93	11,227	60.26	7. 58	g/57* /S/94/N/147/i	90
				59.03	7.25	i/143/N/85/S/g	
3EBEBPDSi3	**5b**	88	7,173	63.86	6.44	g/60* /S/71/N/226/i^d	166
				61.65	6.21	i/223/N/70/S/g	
3EBEBPDSi4	**5c**	97	13,388	60.91	6.34	g/50* /S/66/N/167/i^e	117
				59.55	6.13	i/159/N/60/S/g	
4EBEBPDSi3	**6b**	40	9,465	64.69	6.74	g/50* /S/113/N/248/i	198
				62.07	6.50	i/241/N/107/S/g	

4EBEBPDSi4	**6c**	60	9,353	58.82 56.99	6.86 6.54	g / 60 [*] / S / 80 / N / 226 / i i / 204 / N / 65 / S / g	166
5EBEBPDSi3	**7b**	76	13,456	65.45 63.46	7.01 6.79	g / 50 [*] / S / 129 / N / 244 / i i / 232 / N / 116 / S / g	194
5EBEBPDSi4	**7c**	68	34,144	62.56 61.03	7.11 6.98	g / 55 [*] / S / 108 / N / 252 / i i / 231 / N / 100 / S / g	197
6EBEBPDSi3	**8b**	98	12,919	66.16 65.46	7.27 6.96	g / 60 [*] / S / 126 / N / 261 / i i / 238 / N / 100 / S / g	201
6EBEBPDSi4	**8c**	96	17,470	63.30 62.43	7.34 6.97	g / 60 [*] / S / 107 / N / 235 / i i / 221 / N / 96 / S / g	175
3EBEFODSi3	**9b**	68	6,876	64.43 65.03	6.38 6.04	g / 70 [c] / S / 140 / N / 205 / i	135
3EBEFODSi4	**9c**	75	10,325	61.47 60.98	6.54 6.21	g / 54 [c] / LC / 170 [f] / i	116
4EBEFODSi3	**10b**	62	5,134	65.22 65.78	6.67 6.98	g / 40 / S / 114 / N / 232 [f] / i	192
4EBEFODSi4	**10c**	65	15,926	62.28 63.10	6.80 6.42	g / 40 [c] / S / 142 / N / 214 [f] / i	174
5EBEFODSi3	**11b**	78	8,628	65.95 66.50	6.95 7.21	g / 70 [c] / S / 145 / N / 232 [f] / i [b]	162
5EBEFODSi4	**11c**	81	9,735	63.03 62.64	7.06 7.61	g / 65 [c] / S / 107 / N / 202 [f] / i	137
6EBEFODSi3	**12b**	84	18,444	66.61 66.95	7.21 7.65	g / 70 / S / 157 / N / 245 [f] / i	175
6EBEFODSi4	**12c**	87	18,103	63.76 64.21	7.29 7.05	g / 90 / S / 130 / N / 210 [f] / i	120
3EBEFODOSi3	**13B**	91	5,573	63.22 63.02	5.98 6.21	g / 90 [c] / LC / 190 [f] / i	100
3EBEFODOSi4	**13c**	79	4,435	60.41 61.05	6.18 6.47	g / 80 / S / 105 / N / 170 [f] / i	90
4EBEFODOSi3	**14b**	82	25,478	64.03 64.21	6.29 6.48	g / 60 / S / 115 / N / 215 [f] / i	155
4EBEFODOSi4	**14c**	91	40,378	61.25 60.89	6.54 6.89	g / 40 / S / 112 / N / 192 [f] / i	152

TABLE III (Continued)

Polymer	*Nr.*	*Yield* [%]	*Mol. weight* [*g/mol*]	*Elemental analysis* C_c [%] C_f [%]	H_c [%] H_f [%]	*Phase transition temperatures* [°*C*]	*Phase width* [°*C*]
5EBEFODOSi3	**15b**	92	19,517	64.78 65.12	6.57 6.82	g / 50 / S / 130 / N / 220 [f] /i	170
5EBEFODOSi4	**15c**	91	38,747	62.02 62.81	6.71 6.51	g / 75 [c] / S / 117 / N / 218 [f] /i	143
6EBEFODOSi3	**16b**	93	21,456	65.48 65.46	6.84 6.99	g / 75 [c] / S / 116 / N / 236 [f] /i	161
6EBEFODOSi4	**16c**	88	6,572	62.77 62.02	6.95 7.28	g / 70 [a] / S / 129 / N / 220 [f] /i	150
3EBEHCSi2-d_4	**1a-d_4**	93	10,422			g / 50 / S_F / 72 / S_C / 104 / N / 146 / i i / 144 / N / 100 / S_C / 70 / S_F / g	96
3EBEHCSi2-d_8	**1a-d_8**	85	8,594			g / 50 / S_F / 71 / S_C / 105 / N / 148 / i i / 147 / N / 101 / S_C / 68 / S_F g	98

[a] enthalpy relaxation.
[b] Ref.[7]: T_i = 130°C, T_m = 35°C.
[c] Ref.[7]: T_i = 114°C, T_g = 5°C.
[d] Ref.[7]: T_i = 274°C, T_m = 95°C.
[e] Ref.[7]: T_i = 228°C, T_g = 43°C.
The deviation of the phase width from the lit. could result from the distribution of the molecular weights.
[f] Maximum of the second heating curve.
*under the polarising microscope.
g = glassy state; i = isotropic phase.
N = nematic phase; S = smectic phase.

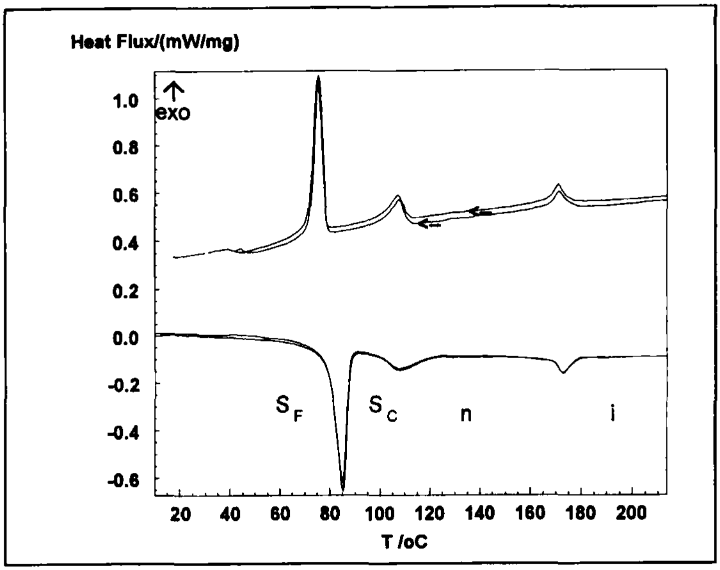


FIGURE 7 Second and third heating and cooling curves for **4EBEHCSi2 (2a)**.

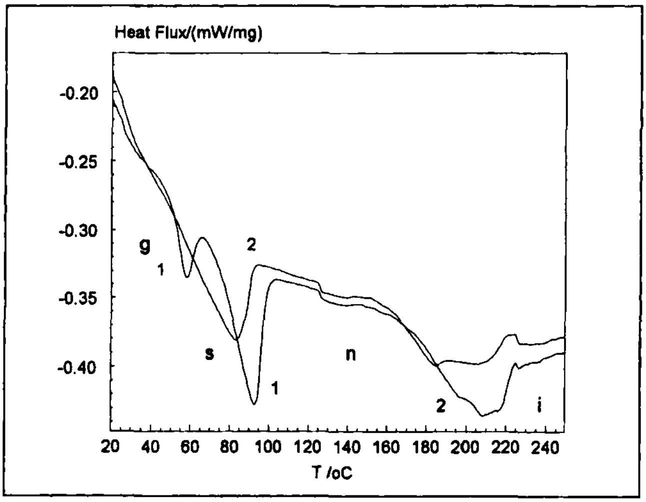


FIGURE 8 DSC-curves for **4EBEBPDSi4 (6c)** – first (1) and second (2) heating. (The step at 130°C results from the DSC-apparatus).

Under the microscope one can observe the softening of the contours of the amorphous polymers in this range of temperature.

Trying to give an answer to this problem one gets assistance by the direct and indirect ^{2}H-solid state NMR. It is well known that small aromatic guests (for example benzene-d_6) to host polymers change the spin-relaxation characteristics near the glass transition [27, 28].

In principle this peak can be explained by the formation of partly crystalline domains. We want to exclude this by X-ray diffraction measurements.

X-ray Diffraction for Polymer 3EBEHCSi2-d_4 (1a-d_4)

Polymer **3EBEHCSi2-d_4** (**1a-d_4**) was selected to confirm the nature and liquid crystalline properties of the observed mesophases by additional X-ray studies.

To make a precise phase assignment the polymers must be oriented. This was done by two different methods. The first was to investigate a sample, oriented in a magnetic field. The second was to use a mechanically oriented fibre.

The main intention of X-ray diffraction was to rule out the existence of different smectic phases at lower temperatures than the glass point.

The X-ray pattern at 123°C (Fig. 9a) results from a nematic phase and shows reflections from "cybotactic" groups [29] . The lateral distance between the mesogenic groups is 4.81 Å The diffraction patterns below the nematic phase at 95°C confirm an S_C arrangement with a spacing value of *d* = 22.5 Å for the layers, a lateral distance of 4.61 Å and a tilt angle of ≈ 37° (Fig. 9b). This angle corresponds to the theoretical angle of 43°, as calculated from the length of the repeating units (30.85 Å) and the layer thickness (22.5 Å).

Figure 9c shows the X-ray pattern of the mechanically oriented fibre at 70°C. It confirms a S_F structure with a *d*-value of 22.1 Å and a lateral distance between the mesogenic groups of 4.48 Å. Additionally we detect wide angle reflections for the siloxane units with a lateral distance of ≈ 6 Å. Since in this case we find layer reflections in equatorial direction we have to assume that the layers are in the same direction as the fibre axis. In the tilted S_F phase the wide angle reflections show the angle between the mesogenic groups and the layer direction (≈37°).

In the glassy state the magnetically oriented sample exhibits the typical reflexes of S_F phases (see Fig. 9d). In this sample typical characteristics of crystalline fractions can not be found.

In Figure 10 the resulting arrangement of the mechanically oriented fibre is displayed. The layer formation can be attributed to the interaction of the permanent dipoles of the carbonyl group linking the spacer with the

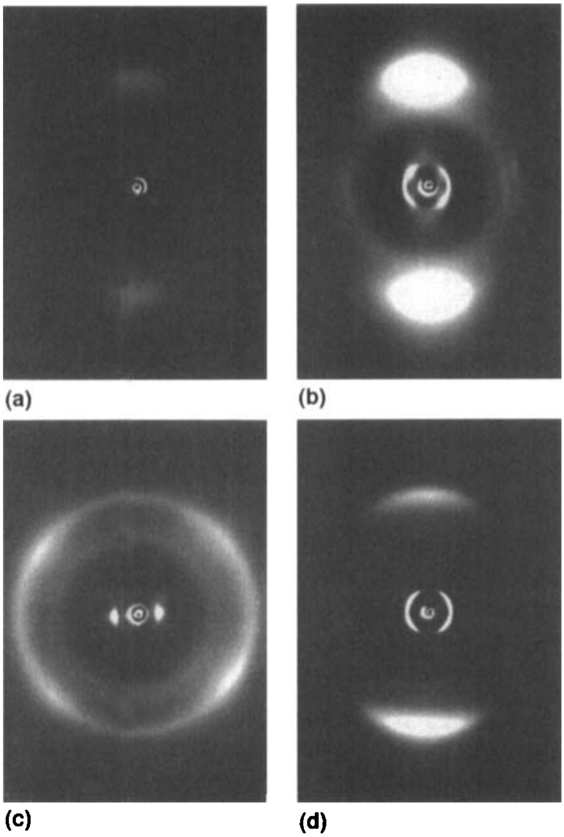


FIGURE 9 X-ray diffraction pattern of polymer **3EBEHCSi2-d$_4$** (**1a-d$_4$**). a) at 123°C, nematic phase with "cybotactic" reflexes b) at 95°C, $_C$-phase, oriented in magnetic field c) at 70°C, meachanically oriented fibre, $_F$-phase d) at 27°C, oriented in magnetic field, glassy $_F$-phase.

mesogenic groups and the electrical dipoles induced in the π-electron system of the aromatic ring of the lateral neighbouring groups.

4. RESULTS AND DISCUSSION

One intention for doing this research was to examine the influence of the length of the alkylene and oligo(dimethylsiloxane) spacers on the phase behaviour of liquid crystalline materials. All the polymers described in this paper form liquid crystalline phases and show besides a nematic phases at least one smectic phase. Although the starting materials have only nematic phases (with one exception [19]), the same mesogenic groups incorporated in

FIGURE 10 Geometric arrangement resulting from X-ray-measurement of the mechanically oriented fibre. (The polymer strand is perpendicular to the fibre direction). (See Color Plate II).

a polymer chain induce also smectic phases. Our studies have shown that flexible oligo(dimethylsiloxane) spacers enable the mesogenic units to form highly ordered phases. The behaviour of the polymers with the shortest oligo(dimethylsiloxane) spacers (Si2) and the hydroquinone as the central diol in the mesogenic unit are remarkable, because these polymers always show several smectic phases at temperatures below the nematic phase (see Tab. III and Fig. 11). The clearing temperature rises, as a rule, according to the increasing length of the alkylene chain. The diagram shows that the influence of the alkylene chain on the liquid crystalline behaviour is stronger for shorter mesogenic units (hydroquinone as a central diol, Fig. 11) than for longer mesogenic groups (4,4′-dihydroxybiphenyl, 2,7-fluorenediol, 2,7-flourenonediol, Fig. 12). A slight "even-odd"-effect occurs. In contrast to the monomers we find higher clearing temperatures for these polymers with an even number of methylene groups.

The widths of the liquid crystalline phases fluctuate betwen 95 and 113°C. The nematic phases tend to become smaller with an increasing number of methylene groups up to $n = 5$, while the smectic phases become broader. The widths of the smectic phases decrease for the polymers with 6 methylene groups.

The orientations of the mesogenic units increase through the incorporation of the mesogenes in the polymer chains. Because of this we can observe already two smectic phases in substances with only few methylene units.

In general, for polymers with the same mesogenic group the extension of the siloxane chain leads to a lowering of the clearing temperatures. The influence on the glass temperatures is small. Through the replacement of the three ring system by a four ring system in the mesogenic unit (1,4-phenylene replaced by 2,7-fluorenonediyl, 2,7-fluorenediyl, 4,4′-biphenyle) the clearing temperatures rise and the liquid crystalline phases widen (Fig. 12).

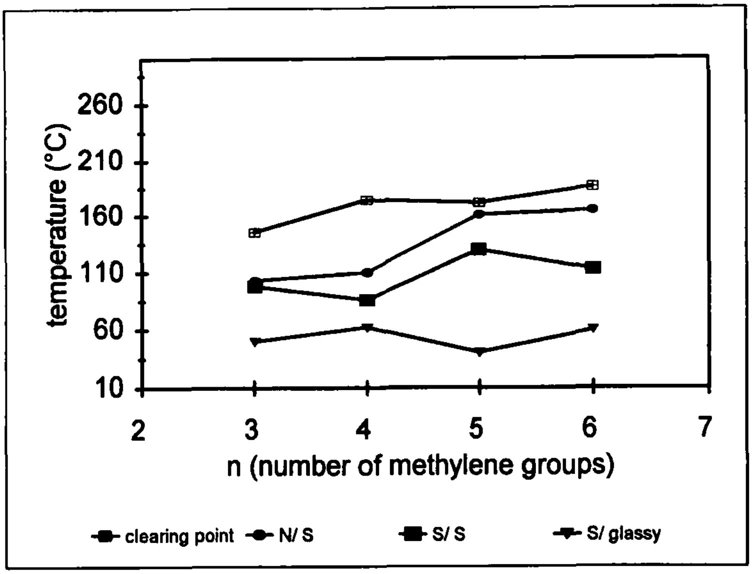


FIGURE 11 Influence of the length of the alkylene spacer on the transition temperatures of the liquid crystalline polyesters **3EBEHCSi2-6EBEHCSi2** (**1a-4a**).

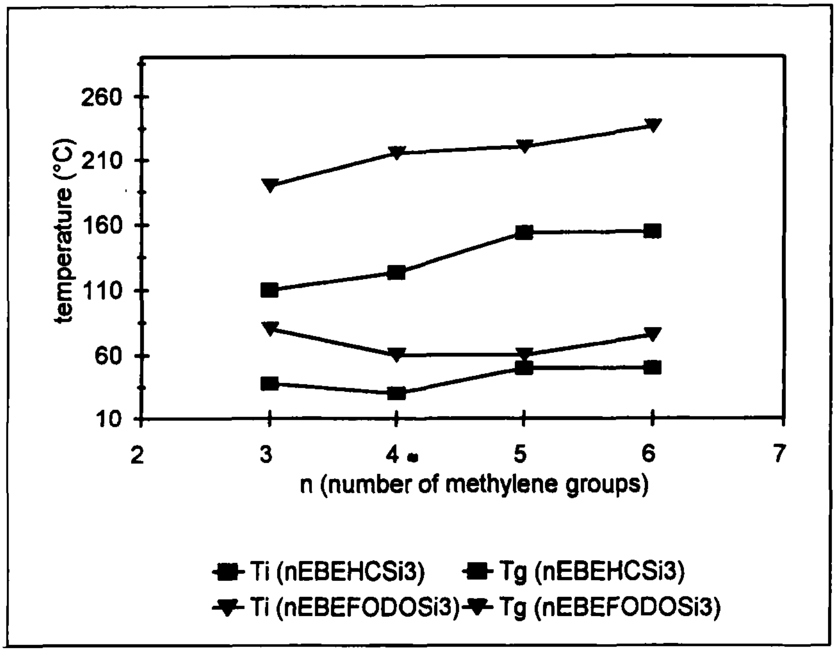


FIGURE 12 Influence of the aromatic diol on the transition temperatures of the liquid crystalline polyesters **nEBEHCSi3** (**1b**, **2b**, **3b**, **4b**) and **nEBEFODOSi3** (**13b**, **14b**, **15b**, **16b**).

The widths of the liquid crystalline phases vary for the polymers **1b-4b** from 72 to 123°C and for the polymers **13b-16b** from 100 to 170°C. A widening of the liquid crystalline phases up to 70°C results from the enlargement of the aromatic system.

We observe a slight increase of the glass temperatures for the polymers **13b-16b**.

In contrast to linear mesogenic units (arising from e.g., 4,4′-biphenyldiol) the formation of tilted mesogenic units from 2,7-fluorenediol or 2,7-fluorenonediol ((158°) decreases the clearing temperatures (Fig. 13) and reduces the range of the liquid crystalline phase.

5. EXPERIMENTAL PART

Measurements

Fourier transform nuclear magnetic resonance spectra were recorded with a Bruker WH 270/AC 250, using TMS as an internal standard. Infrared spectra were performed on a Perkin Elmer 580-B spectrometer.

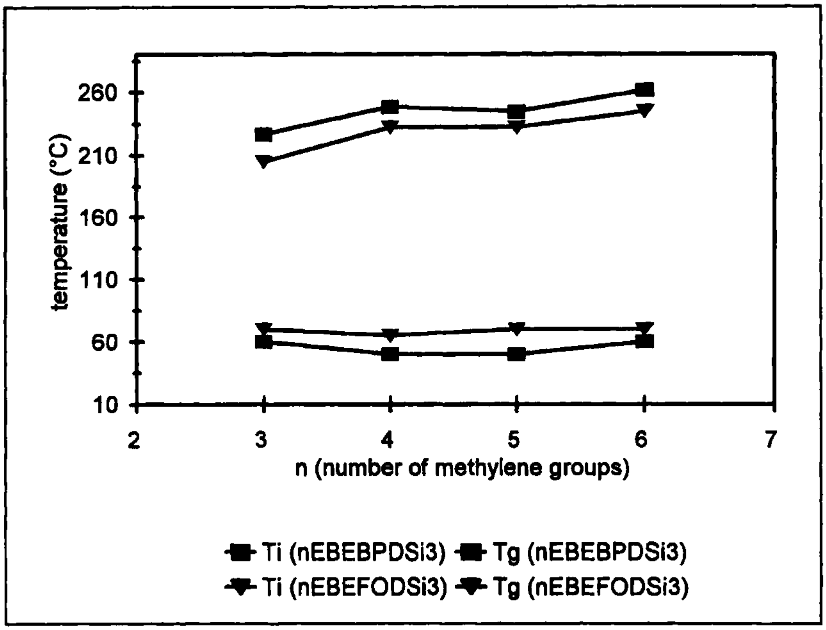
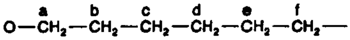
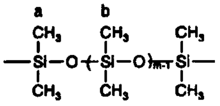
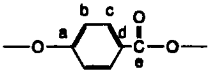
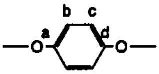
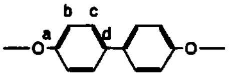
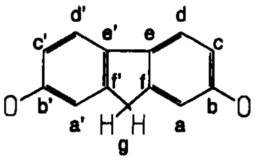
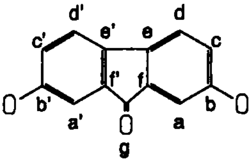


FIGURE 13 Comparison between the transition temperatures of the polymers prepared with the linear aromatic diol 4,4′-biphenyldiol (**nEBEBPDSi3-5b, 6b, 7b, 8b**) and the non-linear 2,7-fluorenediol (**nEBEFODSi3-9b, 10b, 11b, 12b**) in the mesogenic group.

TABLE IV ^{1}H-NMR- and ^{13}C-NMR signals of single structural units of the described polymers (the numbering is not identical with the numbering in Fig. 5)

fragment	^{13}*C-NMR* [*ppm*]	^{1}*H-NMR* [*ppm*]
 $O-\overset{a}{C}H_2-\overset{b}{C}H_2-\overset{c}{C}H_2-\overset{d}{C}H_2-\overset{e}{C}H_2-\overset{f}{C}H_2-$ 6(n)E	$C_a = 68$ $C_b = 33$ $C_c = 28$ $C_d = 25$ $C_e = 23$ $C_f = 18$	$H_a = 3{,}9$ $H_b = 1{,}8$ $H_c = 1{,}4$ $H_d = 1{,}4$ $H_e = 1{,}4$ $H_f = 0{,}6$
 Si-(m+1)	$C_a = 0{,}18$ $C_b = 1{,}20$	$H_a = 0{,}05$ $H_b = 0{,}01$
 EBE	$C_a = 163$ $C_b = 114$ $C_c = 132$ $C_d = 121$ $C_e = 165$	$H_b = 7{,}0$ $H_c = 8{,}2$
 HC	$C_a = 148$ $C_b = 123$	$H_b = 7{,}2$
 BPD	$C_a = 150$ $C_b = 122$ $C_c = 128$ $C_d = 138$	$H_b = 7{,}7$ $H_b = 7{,}3$
 FOD	$C_a = 121$ $C_b = 150$ $C_c = 120$ $C_d = 120$ $C_e = 139$ $C_f = 145$ $C_g = 36$	$H_a = 7{,}4$ $H_c = 7{,}7$ $H_d = 7{,}2$ $H_g = 4{,}0$
 FODO	$C_a = 120$ $C_b = 153$ $C_c = 114$ $C_d = 128$ $C_e = 138$ $C_f = 141$ $C_g = 194$	$H_a = 7{,}3$ $H_c = 7{,}5$ $H_d = 7{,}6$

For phase assignment, the samples were studied with a polarising microscope (Fa. Olympus) combined with a hot stage (Fa. Linkam THM 600).

X-ray diffraction was carried out in a custom made, temperature controlled ($\Delta T = \pm 0.1$ K) vacuum chamber with a flat film camera at a distance of 81.5 mm from the sample. Monochromatic Cu-K_α radiation ($\lambda = 0.15418$ nm, graphite monochromator) was focused by a glass capillary. The polymer sample was oriented inside the chamber in a magnetic field (2.4 Tesla) perpendicular to the incident beam. Additional fibres drawn out of the anisotropic melt at 75°C were studied, to confirm whether another smectic phase exists. Size exclusion chromatography was performed on a Waters chromatograph using THF as eluent and polystyrene standards (PS 4000, PS 10000 from Pressure Chemical Company) for calibration.

The phase transition temperatures of the polymers were determined by differential scanning calorimetry (DSC) using a Netzsch DSC 200 apparatus at a scanning rate of 10 K/min. Indium was used for calibration. The maxima of the DSC enthalpy peaks of the second heating were taken as the phase transition temperatures.

Thermogravimetric analyses were done with a Netzsch TGA 200.

Synthesis of the Polysiloxane Esters

Bis[4-(ω-alkenyloxy)benzoic acid]esters were prepared as reported in a previous paper [19]. Polyaddition of 0.005 mol bis[4-(ω-alkenyloxy)benzoic acid]esters to 0.005 mol α,ω-di-H-oligo(dimethylsiloxane)s (molar ratio exactly 1:1) was carried out by stirring in a nitrogen atmosphere in 30 ml dry toluene at 80°C with a 2 ml H_2PtCl_6-solution (0.031 g H_2PtCl_6 in 9.47 g diethyleneglykol dimethylether). A concentrated solution containing both components was used. After complete addition (24 h, disappearance of the Si—H-absorption at 2140 cm^{-1}), the polymer is precipitated by cold methanol and reprecipitated several times from CH_2Cl_2/methanol.

See Figures 2 and 3 for the structure of the educts, Table III for elemental analyses, molecular weights, and yields, Table IV for the spectroscopic data, Table III for melting points and phase transition temperatures.

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