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Structural variations of liquid crystalline polymers with phasmidic-type mesogens

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The fixation of phasmidic-type mesogens through spacer groups to polysiloxane backbones provided a method of obtaining liquid crystalline polymers with phasmidic mesogens as side groups. The polymer **6b** showed a bilayer structure in the mesophase range. The tendency to form liquid-crystalline phase depends on the number and the length of alkoxy substituents.

1. Introduction

The study of liquid-crystalline polymers has become of increasing interest because of their theoretical and technological aspects. Calamitic [1] and discotic [2, 3] liquid-crystalline polymers combine the orientability of low molecular weight liquid crystals with the ability of polymers to form stable glasses.

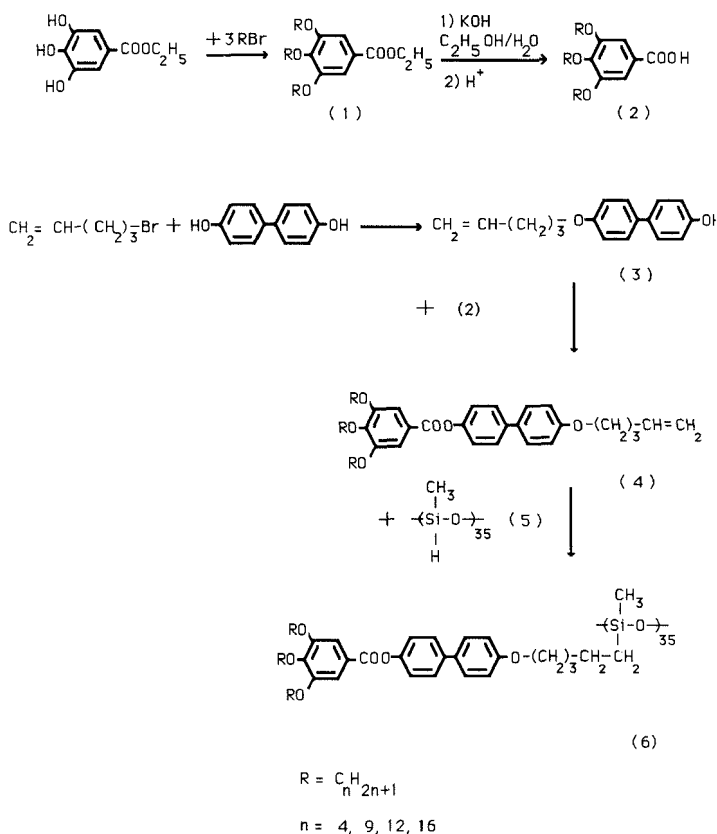
One of the most recent developments in the field of liquid crystals is the molecular engineering of systems with new and unconventional structures [4, 5]. Thus, low molecular weight plasmids were recently described as a new group of thermotropic liquid crystals [6]. They are obtained with molecules containing a central rod-like rigid core and four- to six-long aliphatic terminal groups. In this series both lamellar and columnar phases were found [7]. In connection with investigations of the molecular architecture of liquid-crystalline polymers it is interesting to fix phasmidic-type mesogens via spacer units to polymer backbones or to build them into main-chain polymers. In addition, it is also interesting to study the phase behaviour of these new phasmidic-type polymers and the structural influence of the mesophase.

2. Synthesis and phase behaviour of polymers with phasmidic-type mesogens

Side-chain polymers **6** were prepared by attaching trisubstituted rod-like mesogens ('half phasmidic') via spacers to a flexible polysiloxane backbone. The general reactions are shown in scheme 1.

The tetrasubstituted rod-like mesogen **4** was prepared by esterification of the trialkoxybenzoic acid **2** with the monoether of 4,4'-biphenyldiol (**3**). By addition of olefin **4** to the poly(methylhydrogen siloxane) **5** in toluene at 80°C, the side-chain polymers **6** were obtained.

The main-chain polymer **10** was prepared by solution polycondensation of the dicarboxylic acid **9** with diphenyldiol in a mixture of tetrachloroethane and pyridine as solvents. Scheme 2 shows this synthesis.

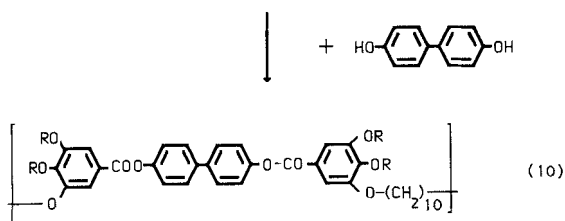
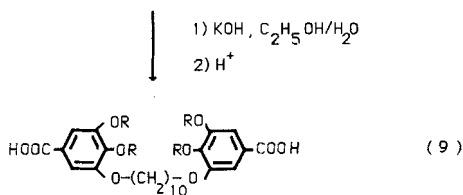
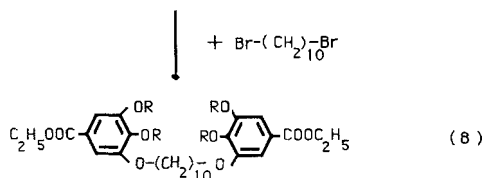
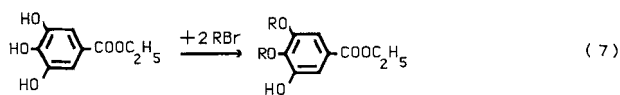


Scheme 1

The polyester **10** shows no mesophase. It has only a glass transition at 12°C. Its molecular weight was estimated to be above 18 000 (gel permeation chromatography, polystyrene as standard). The phase behaviour of the polysiloxanes was determined by means of differential scanning calorimetry (D.S.C.) and polarization microscopy (see table 1).

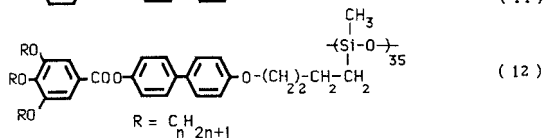
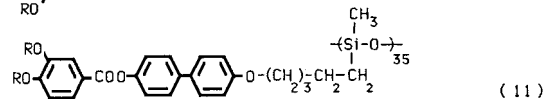
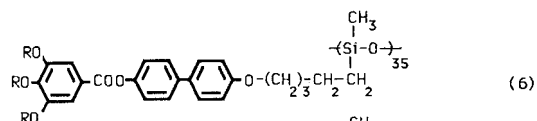
A polarizing microscope was used to observe the textures of two polysiloxanes **6a** and **6b**. For the polymer **6b** at room temperature, the texture shown in figure 1 was observed. For polymer **6a** crystallization at room temperature could be suppressed by rapid cooling to 0°C. After annealing at this temperature the polymer **6a** showed bâtonnet textures and cleared at 70°C (see figure 1).

As shown in table 1, the tendency of these polysiloxanes to form liquid-crystalline phases depends on the length and number of alkoxy substituents. As for other liquid-crystalline polymers, the clearing temperature of these side-chain polymers decreases with increasing alkyl chain length. If the alkyl chain is either too long or too short ($n = 4$ or $n = 16$, respectively), the tendency to crystallize increases. On the other hand, the phase width increases with chain length ($n < 12$). Beyond a critical length ($n > 12$) liquid-crystalline phase is suppressed by crystallization of hydrocarbon chains. The tendency to form liquid-crystalline phases increases with increasing number of alkoxy substituents (compare **6b** and **11b** as well as **6d** and **11d**).



Scheme 2

Table 1. Transition temperatures of polysiloxanes.



	n	Transition temperature/°C
6a	4	C 50 LC 70 I
6b	9	G 12 LC 62 I
6c	12	G - 12 LC 52 I
6d	16	C 53 I
11b	9	G 93 C 130 I
11c	12	G - LC 71 I†
12	9	G - 5 LC 63 I

C, crystalline; LC, liquid crystal; I, isotropic; G, glass transition.

† Glass transition could not be detected by D.S.C.



(a)



(b)

Figure 1. Textures of polysiloxanes (**6**), using crossed polarizers (magnification $136\times$), (a) after cooling from the isotropic melt of polymer **6b** at room temperature and (b) after annealing from the isotropic melt of polymer **6a**.

3. X-ray analysis

Structural information is derived from X-ray analysis of poorly aligned samples, apparently typical of low molecular weight phasmids [6]. The perfect alignment of polymer samples was not possible.

The X-ray scattering diagram of a non-oriented sample of polymer **6b** shows two sharp reflections in the small-angle region corresponding to distances of 49 and 25.6 Å (see figure 2). The broad halo corresponding to a distance of 4.3 Å in the side-angle region is caused by the aliphatic chains of the half disc-like ends. Considering the fact that the calculated side-chain length of polymer **6b** is 29 Å, the measured distance of 49 Å points to a layer structure with slightly interlaced alkyl chains.

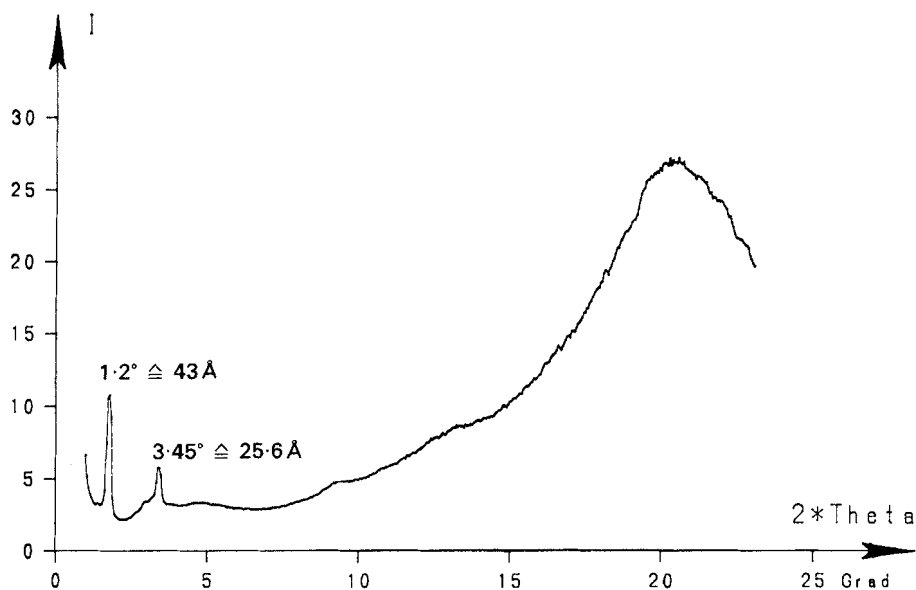


Figure 2. Wide-angle X-ray scattering diagram of polymer **6b** at room temperature.

4. Experimental

4.1. 3,4,5-Trialkoxybenzoic acid (2)

Into a 500 ml single-necked, round-bottomed flask were placed 0.02 mol of bromalkane and 0.07 mol of 3,4,5-trihydroxybenzoic acid ethyl ester, 0.15 mol (30 g) of powdered potassium carbonate, catalytic amounts of potassium iodide and 150 ml of acetone. The reaction mixture was refluxed for 48 h, then cooled and filtered to remove potassium bromide and excess potassium carbonate. The acetone was removed using a rotary evaporator. The yields of crude product ranged from 70 to 91 percent. After purification by flash chromatography using a mixture of petroleum ether and ethyl acetate (10:1), the product **1** was dried in a vacuum oven.

Saponification of the resulting triether **1** was carried out in 150 ml of 80 per cent ethanol with 20 per cent excess of potassium hydroxide at 100°C for 4 h. The acids were crystallized from ethanol. Elemental analyses are listed in table 2.

For example **2b**: EI-MS: M^+ (100 per cent) = 548.

400 MHz ^{13}C -N.M.R. (CDCl_3): δ (in p.p.m.) = 153, 153, 124, 109 (arom. C); 74, 69 (Ar-O-C).

Table 2. Elemental analyses of low molecular weight compounds.

	C/percent		H/percent	
	Calculated	Found	Calculated	Found
2b	74.40	74.20	11.02	10.88
2c	76.50	75.88	11.65	11.43
4b	78.01	78.36	9.76	9.19
4c	79.07	79.36	10.40	10.34
4d	80.09	80.07	11.02	10.82

4.2. 4-Hydroxy-4'-(4-pentenyl-oxy)-biphenyl (3)

To 0.01 mol of 5-bromopentene, 0.01 mol of 4,4'-biphenyldiol in 100 ml of absolute ethanol were added 0.012 mol of sodium in 50 ml of absolute ethanol. The reaction mixture was refluxed for 8 h. The ethanol was partially removed using a rotary evaporator, and the reaction mixture was washed with water. The crude product was filtered and washed with water and finally dried in a vacuum oven. Purification of the product was achieved using flash chromatography with an eluent of petroleum ether to ethyl acetate (3:1): yield 30 per cent.

4.3. 4-(Pentenyl-oxy)-4'-(3,4,5-tris(alkoxy)-1-phenylcarboxy)-biphenyl (4)

To 10 mmol of carboxylic acid 2, 10 mmol of 3 in 20 ml of absolute CH_2Cl_2 and 10 mmol of 4-(1-pyrrolidinyl)-pyridine were added 11 mmol of DCC (dicyclohexylcarbodiimide)-pyridine at 0°C . The reaction mixture was warmed at room temperature and stirred for 5 h. After filtering, CH_2Cl_2 was removed using a rotary evaporator. The product was recrystallized from absolute ethanol after purification by flash chromatography (petroleum ether to ethyl acetate 10:1). Yields ranged from 40 to 64 per cent.

For example 4b: EI-MS:
$$\frac{I(M)}{I(M + 1)} \quad \text{calculated} \quad \text{found}$$

$$\quad \quad \quad 1.71 \quad 1.74$$

4.4. Polysiloxanes 6

The compounds 4 were added to poly(methylhydrogen siloxane) 5 according to the literature procedure [8].

For example 6b: 400 MHz ^{13}C -N.M.R. (CDCl_3): δ (in p.p.m.) = 159, 153, 150, 143, 139, 133, 128, 127, 122, 115, 109 (arom. C); 74, 69, 68 (Ar-O-C).

Elemental analysis	% C	% H
calculated	73.72	9.55
found	73.39	9.92

4.5. 3-Hydroxy-4,5-dioctyloxylbenzoic acid ethyl ester (7)

This compound was prepared as described above for compound 1 except that 3,4,5-trihydroxybenzoic acid ethyl ester was reacted with only two equivalents of *n*-octyl bromide: yield 15 per cent.

EI-MS: M^+ (28 percent) = 422. 400 MHz ^{13}C -N.M.R. (CDCl_3): δ (in p.p.m.) = 151, 149, 138, 126, 109, 106 (arom. C); 74, 69 (Ar-O-C).

4.6. 1,10-((Bis(2,3-dioctyloxy)-5-carboxy)-phenyloxy)decan (9)

The ester **8** was obtained by etherification of **7** with 1,10-decandibromide analogously to the procedure described for compound **1**: yield 81 per cent. Saponification of the ester **8** was carried out in ethanol with potassium hydroxide as in the procedure for compound **2**. The acid **9** was recrystallized for ethanol: yield 77 per cent, m.p. 96°C.

Elemental analysis:	% C	% H
calculated	71.69	10.11
found	71.91	10.49

$^{13}\text{C-N.M.R.}$ (CDCl_3): δ (in p.p.m.) = 153, 143, 124, 108 (arom. C).

4.7. Polyester **10**

The polyester was prepared from the diacid chloride of **9** by esterification with 4,4'-biphenyldiol according to the procedure in [9]: yield 82 per cent.

$M_w = 18\,200$, $T_g = 12^\circ\text{C}$.

Elemental analysis:	% C	% H
calculated	75.80	9.36
found	75.24	9.64

4.8. Characterization methods

All polymers as well as the precursors revealed correct elemental analyses. The infrared, ^{13}C - and ^1H -N.M.R. spectra of all products are in agreement with the proposed structures. The thermal behaviour of the compounds was investigated using a Perkin-Elmer DSC-2C differential scanning calorimeter. The peak maxima were taken as phase transition temperatures. Textures were obtained with a Leitz POL-BK II polarizing microscope equipped with a Mettler FP 52 hot stage. X-ray analysis was performed with a wide-angle goniometer (Siemens, X-D-500). CuK_α radiation with wavelength 0.154 nm was used.

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