

# Synthesis and characterization of liquid crystal polycarbosilanes: poly(1-methyl-1-silaethylene), poly(1-methyl-1-silabutane) and poly(1-silabutane) with pendant mesogenic groups

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The synthetic routes for preparation of side chain liquid crystal polycarbosilanes, with rod type mesogens, pending from every second and every fourth atom in the main chain, forming 'comb-like' and 'double comb-like' polymers, are described. Structure–property relationships were investigated. X-ray measurements of the smectic materials, oriented in a magnetic field, proved the  $S_{A1}$  phase to be a dominant one for these new mesomorphic polymers; however, generation of  $S_{Ad}$  and more ordered  $S_B$  phases was also detected. Polycarbosilanes present useful, highly thermally and chemically resistant materials, which provide useful models for studies of the influence of the main chain architecture on the properties of polymers with various pendant groups. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polycarbosilanes; ring-opening polymerization; side chain liquid crystal polymers)

## INTRODUCTION

Side chain liquid-crystalline polymers (SCLCPs) combine characteristic features of both low molecular mass liquid crystals and macromolecular systems<sup>1</sup>. Considerable interest in such materials has stimulated applied (e.g. opto-electronics, gas chromatography) as well as fundamental studies.

The properties of liquid crystal polymers can be varied not only via structural changes introduced into pendant mesogenic groups, but also as a result of the type of homo- or copolymer to which the mesogens are bonded. Side chain polysiloxanes may serve as good examples, indicating how one can affect the properties of a liquid crystalline polymer; the highly flexible –O–Si–O– units in the main chain lead to a significant decrease in transfer temperatures into the mesophase<sup>2</sup>.

A range of organosilicon SCLCPs has been already studied, covering mainly various types of polysiloxanes<sup>3</sup> and including, more recently, cyclosiloxane systems<sup>4</sup> as well as polysilanes with long alkyl pendant groups<sup>5</sup>.

During the last few years new types of organosilicon SCLCPs were synthesized, having their main chain composed of sequences containing carbon and silicon atoms<sup>6–9</sup>. Such polymers—polycarbosilanes—can be regarded as intermediate structural systems between organic and inorganic liquid crystal polymers. They offer not only a novel area for phase behaviour studies, but also an almost unique opportunity for synthesis and characterization of tailor-made SCLCPs with well defined structure.

In this paper we present a complete account of the synthetic routes leading to liquid crystal 'comb-like' (I and II) and 'double comb-like' (III) polycarbosilanes (Scheme 1).

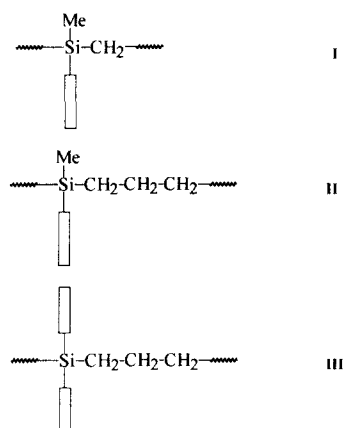
## EXPERIMENTAL

### Instrumentation

<sup>1</sup>H n.m.r. spectra were recorded at 200 and 300 MHz using, respectively, Bruker AC and Bruker MSL spectrometers (with residual benzene as internal reference).

I.r. spectra were obtained with a Specord M 80 spectrometer for polymer solutions in sodium-dried

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Scheme 1

toluene, stored over molecular sieve 4A. G.l.c. analyses were carried out with a Hewlett Packard 9890 chromatograph fitted with a flame-ionization detector; the packing was 10% OV-101 on Gas Chrom Q.

Thermal properties of the mesogenic alkenes and polymers were studied by differential scanning calorimetry (d.s.c.) (DuPont DSC-910), calibrated with an indium standard. The values of transition temperatures are from the second heating run, at  $10 \text{ K min}^{-1}$ . The samples were scanned from 0 to  $180^\circ\text{C}$ . Independently, mesophase textures were investigated by optical microscopy, using polarized light and a Linkam THNS 600 hot stage.

Molecular weight and heterogeneity indices of polymers were measured by gel-permeation chromatography (g.p.c.) on Waters columns 1000A and 500A using a Wyatt/Optilab 902 Interferometric Refractometer. The system was calibrated using monodisperse polystyrene standards.

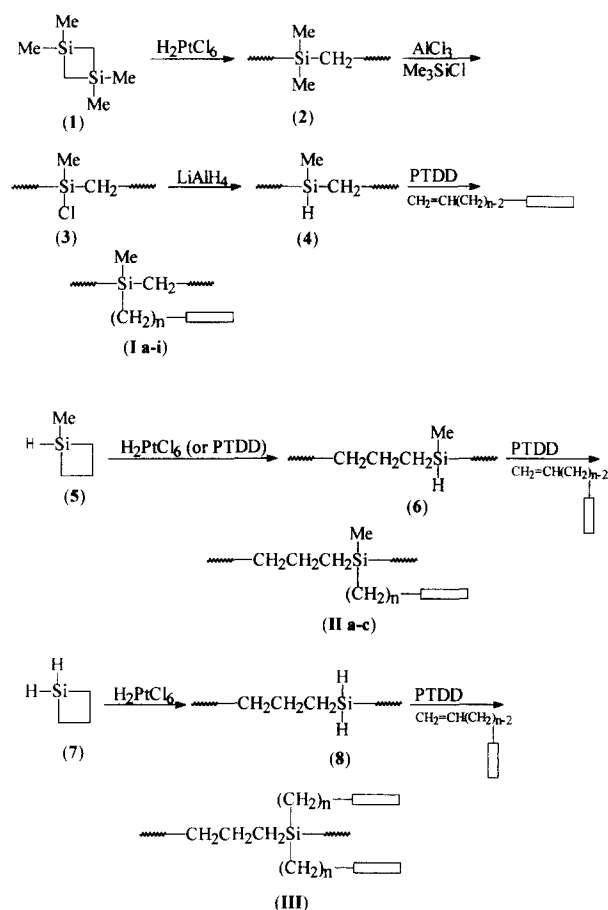
X-ray diffraction measurements have been performed on free standing samples. The layer spacings in smectic phases were determined with a high-temperature Guinier camera with  $\text{Co } K_\alpha$  monochromatic radiation. Diffraction patterns of magnetically oriented samples were also obtained in a flat camera ( $\text{Cu } K_\alpha$  radiation). Aligned samples were produced on slow cooling from the isotropic melt into the mesophase in a magnetic field of 1.5 T. Switching of the field at room temperature did not alter the alignment over the studied period of time (several days).

#### Synthesis of silacyclobutanes 1, 5 and 7

All solvents were dried by standard literature methods<sup>10</sup>. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane (1) was prepared according to the published data<sup>11,12</sup>; 1-methyl-1-silacyclobutane (5) and 1-silacyclobutane (7) were prepared as described, respectively, by Damrauer *et al.*<sup>13</sup> and Laane<sup>14</sup>. Magnesium turnings, for the Grignard type reactions were activated by stirring them for 24 h under nitrogen<sup>15</sup>. The silacyclobutane monomers were purified by distillation and were stored in Schlenk tubes under dry nitrogen.

#### Synthesis of linear polycarbosilanes 2-4, 6 and 8

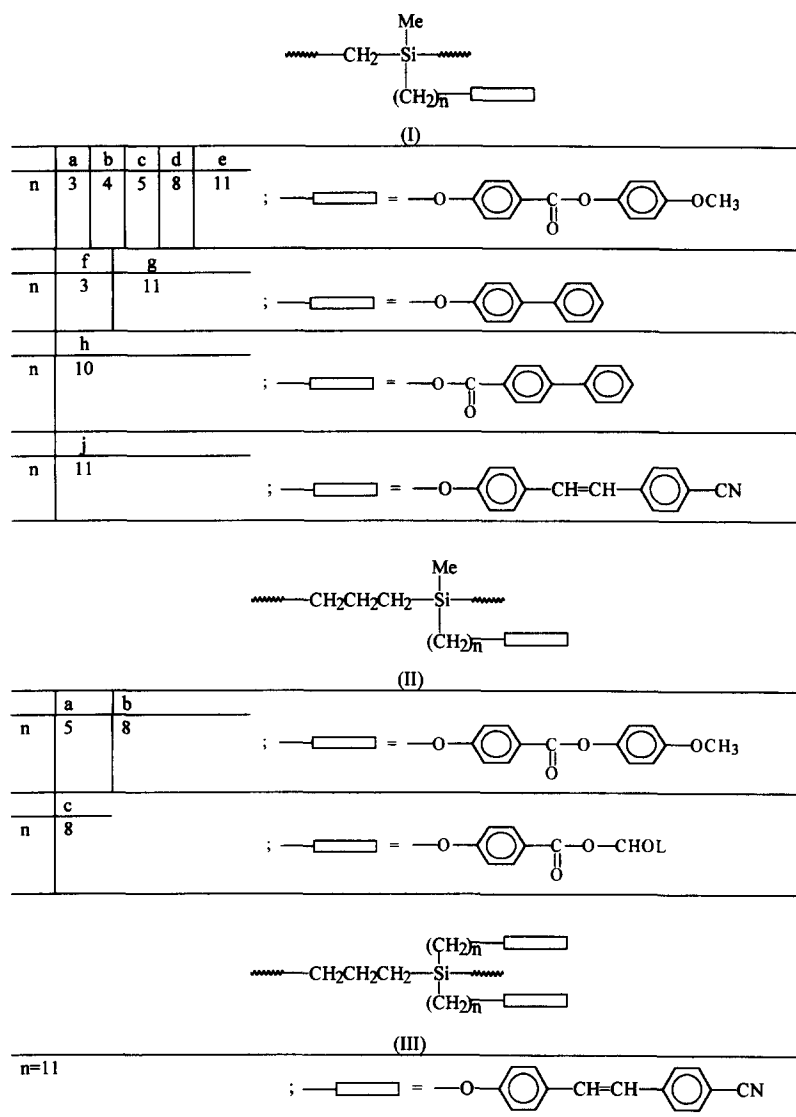
As shown in Scheme 2 poly(1-methyl-1-silaethylene) (4) was prepared by ring-opening polymerization of



Scheme 2

1,1,3,3-tetramethyl-1,3-disilacyclobutane (1), chlorination of the resulting poly(1,1-dimethyl-1-silaethylene) (2) and subsequent reduction of poly(1-chloro-1-methyl-1-silaethylene) (3) with  $\text{LiAlH}_4$ . A modification of the procedure, published by Bacque *et al.*<sup>16</sup>, was used. In a typical experiment, 1,1,3,3-tetramethyl-1,3-disilacyclobutane (20 g, 0.14 mol) in dry toluene and  $\text{H}_2\text{PtCl}_6$  (Aldrich) (0.0515 g,  $7.1 \times 10^{-4} \text{ mol Pt mol}^{-1}$  of the cyclic monomer) in a solution of 1/1 benzene/isopropanol (2 ml) were degassed in a flamed out Schlenk tube and stirred under nitrogen at  $80^\circ\text{C}$ . After a violent polymerization, during which the temperature reached  $110^\circ\text{C}$ , the reaction mixture was stirred for 1 h at  $80^\circ\text{C}$ ; then 200 ml of hot cyclohexane was added and the solution was filtered under nitrogen. Solvents were stripped off under vacuum and the polymer was dried (1 mm Hg) at  $100^\circ\text{C}$  for 12 h to give 13 g (65%) of poly(1,1-dimethyl-1-silaethylene) (2). Chlorination and further reduction of the polymer 2 were then carried out as previously described<sup>16</sup>. The total yield, starting from 1,1,3,3-tetramethyl-1,3-disilacyclobutane, was 36%.

Poly(1-silabutane) (8) was prepared according to the general polymerization procedure given above. Thus, 1-silacyclobutane (7) (5 g, 0.069 mol) was polymerized in bulk in the presence of  $\text{H}_2\text{PtCl}_6$  ( $1.67 \times 10^{-4} \text{ mol mol}^{-1}$  of the monomer). The reaction took place immediately after addition of the catalyst to the degassed monomer at room temperature. The polymer was kept at  $80^\circ\text{C}$  for an additional hour, then dissolved in hot cyclohexane (20 ml), quenched with excess of hexamethyldisiloxane



Scheme 3

and filtered. The solvent was removed under vacuum and the material was dried at 1 mm Hg (80–100°C) for 12 h to give 4.2 g of poly(1-silabutane) (**8**) (yield = 84%).

Poly(1-methyl-1-silabutane) (**6**) was obtained via ring-opening bulk polymerization of 1-methyl-1-silacyclobutane (**5**). The monomer (15 g, 0.17 mol) was degassed in a Schlenk tube and 0.27 ml of platinum tetramethyldivinylsiloxane (PTDD) was added under nitrogen at room temperature as a 3% solution in xylene (Alfa Products) ( $1 \times 10^{-4}$  mol mol<sup>-1</sup> of 1-methyl-1-silacyclobutane).

As for poly(1-silabutane), the monomer polymerized rapidly at room temperature, and was kept for an additional hour at 80°C. It was then dissolved in 50 ml of heptane at 40°C, quenched with excess of hexamethyldisiloxane and filtered under nitrogen. Volatiles were removed under reduced pressure and the polymer was dried at 80–100°C for 6 h. The turbid viscous liquid was dissolved in 75 ml of heptane and filtered, using a transfer tube, the solvent was stripped off and poly(1-methyl-1-silabutane) (**6**) was dried on a vacuum line for 12 h at 1 mm Hg to give 8 g of transparent polymer (yield = 53%).

#### Mesogenic alkenes

4'-Methoxyphenyl-4-( $\omega$ -alkenyloxy)benzoates<sup>17</sup>, 4-( $\omega$ -alkenyloxy)biphenyls<sup>18</sup> and 4'-cyano-4-(10-undecenyl-oxy)stilbene<sup>19</sup> were prepared by literature procedures.

4-Biphenyl-(10-undecenate) was prepared in a typical esterification process of undecenoic acid (Janssen) (3.8 g, 0.02 mol) with 4-hydroxybiphenyl (Janssen) (3.4 g, 0.02 mol) in 80 ml of dry methylene chloride, in the presence of *N,N*-dicyclohexylcarbodiimide (Janssen) (51.5 g, 0.025 mol) and 0.3 g of 4-dimethylaminopyridine (Janssen). The reaction mixture was stirred for 24 h, then *N,N*-dicyclohexylurea was filtered off and, after removal of the solvent, the crude product was crystallized from ethanol. Further purification involved flash chromatography (silica gel/chloroform) to give a crystalline product (4.25 g, 60%).

An analogous procedure was used in the synthesis of cholesteryl-(7-octenoate), giving the ester with 64% yield.

#### Synthesis of side chain LC polycarbosilanes **Ia–j**, **IIa–c** and **III**

Polymers of **Ia–i**, **IIa–b** and **III** type (see Scheme 3) were

made via hydrosilylation of mesogenic alkenes with linear polycarbosilanes. Polymer **IIc** was obtained in a one-pot process—directly from a cyclic carbosilane, without separation of linear poly(1-methyl-1-silabutane) (**6**).

In a typical hydrosilylation reaction, 1.0 g (2.82 mmol) of 4'-methoxyphenyl-4-(octenyloxy)benzoate was dissolved under nitrogen in 20 ml of dry (sodium mirror) toluene and then 147 mg (2.54 mmol of  $-\text{[CH}_2\text{Si(Me)H]-}$  units) of poly(1-methyl-1-silaethylene) (**4**) was added into a Schlenk tube containing the solution. After addition of a catalyst—8 ml of 3% PTDD solution in

xylene ( $2 \times 10^{-4}$  mol Pt mol $^{-1}$  of the Si-H)—the reaction was carried out for 24 h, with magnetic stirring, at room temperature. During that time the colourless solution turned pale brown due to the formation of colloidal platinum. The temperature was then raised and the process was continued for another 72 h at 60–65°C. The polymer was then centrifuged from the reaction mixture and purified by several dissolutions (methylene chloride) and precipitations (methanol) until it was free from the excess of mesogen (t.l.c.); 1 g (63%) of **Id** was obtained: DP = 85;  $M_w/M_n = 3.03$  (g.p.c.).

The same procedure was applied for the synthesis of

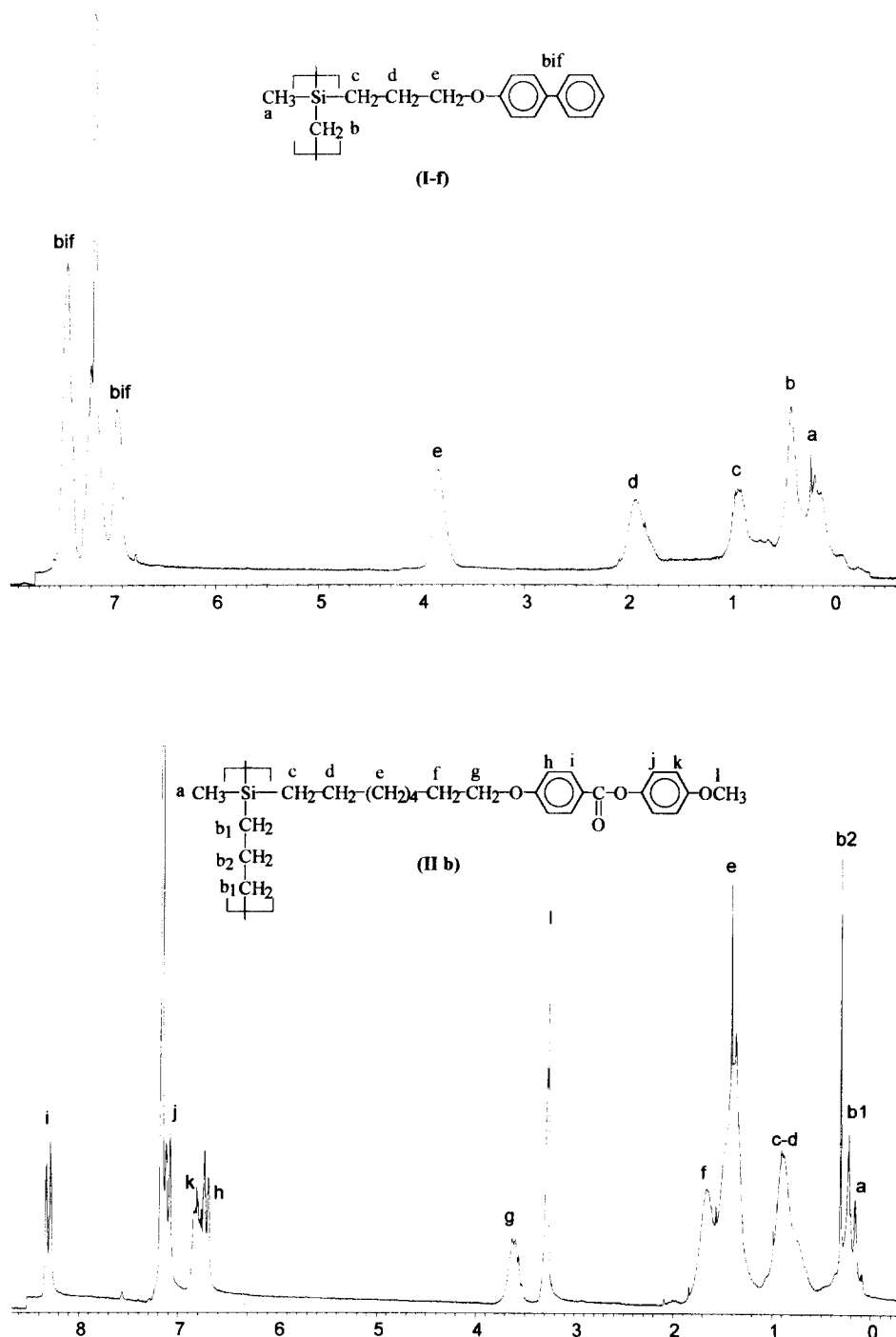


Figure 1 Examples of <sup>1</sup>H n.m.r. spectra of side chain polycarbosilanes (structure types I, II and III)

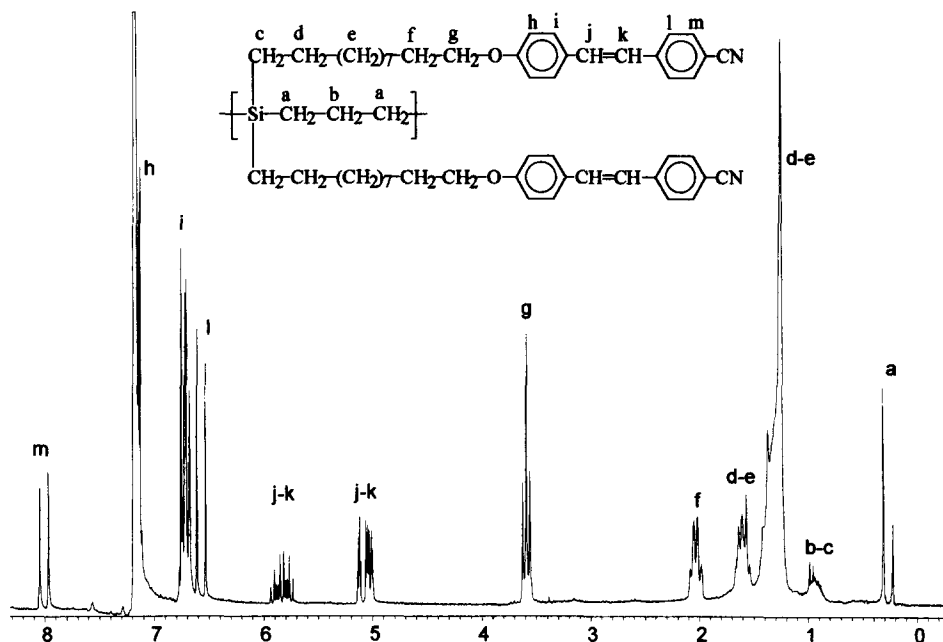


Figure 1 (Continued)

polymer **III** with a *E*-4-(undecyloxy)-4'-cyanostilbene pendant group. After 96 h the standard precipitation method gave 0.1 g (23%) of **III**: DP = 35;  $M_w/M_n = 2.81$  (g.p.c.).

The one-pot ring-opening polymerization and hydrosilylation was used for the preparation of polymer **IIc**, starting from 1-methyl-1-silacyclobutane (**5**). It was carried out as follows.

A degassed solution of 1-methyl-1-silacyclobutane (0.36 g, 4.07 mmol) in 1 ml of dry toluene was stirred under nitrogen in a Schlenk flask at 80°C, in the presence of 18  $\mu$ l of a 3% solution of PTDD in xylene (2.7  $10^{-4}$  mol Pt mol $^{-1}$  of 1-methyl-1-silacyclobutane). After a vigorous exothermic reaction took place, increasing the viscosity of the mixture, the solution was stirred for a further 4 h at 80°C. The solution of the resulting linear polycarbosilane was then cooled down to room temperature and 2.8 g (4.5 mmol) of cholesteryl-4-(7-octenyloxy) benzoate in 20 ml of toluene was added. The system was degassed and hydrosilylation was initiated with 10  $\mu$ l of PTDD (1.6  $10^{-4}$  mol Pt mol $^{-1}$  of Si-H). The reaction mixture was stirred for 24 h at room temperature and for a further 48 h at 60°C. The end groups were introduced using excess of hexamethyldisiloxane and the polymeric material was precipitated with methanol giving a white polymer which was purified by dissolution in methylene chloride, precipitation with methanol and finally dried under vacuum (1  $10^{-3}$  mm Hg) for 12 h at 100°C. The yield, based on 1-methyl-1-silacyclobutane, was 45%; DP = 35,  $M_w/M_n = 1.45$  (g.p.c.).

## RESULTS AND DISCUSSION

Scheme 3 presents the three types (**I**, **II** and **III**) of polycarbosilanes with various mesogenic groups and spacers of the [-O(CH $_2$ ) $_n$ -] type. Typical  $^1$ H n.m.r. spectra of the polycarbosilanes with characteristic mesogenic cores are shown in Figure 1.

In all the cases the first synthetic step involves ring-opening polymerization of the respective silacyclobutanes.

A similar approach was also applied, by Sargeant and Weber<sup>9</sup>, in the synthesis of liquid crystal poly(1-silapent-3-ene)s with pendant aryloxy substituents, namely an anionic ring opening of 1-methyl-1-silacyclopent-3-ene.

Polymers **Ia-j** were prepared from 1,1,3,3-tetramethyl-1,3-disilacyclobutane (**1**) in the presence of hexachloroplatinic acid. The same catalyst was also used for polymerization of 1-silacyclobutane (**7**), whereas ring opening of 1-methyl-1-silacyclobutane (**5**) was also accomplished in the presence of PTDD in a one-pot process. Linear polycarbosilanes **6** and **8** could be used directly in hydrosilylation of mesogenic alkenes. Poly(1,1-dimethyl-1-silaethylene), had to be first modified in order to obtain, via chlorination and subsequent reduction, Si-H bonds containing system **4**. Side chain polymers with methoxybenzoate, biphenyl, cholesteric and cyanostilbene cores were, as already mentioned, synthesized by hydrosilylation of the respective rigid mesogenic alkene terminated compounds.

Phase transition temperatures (determined from d.s.c. measurements) as corresponding to the minima of endothermic peaks, isotropization entropy changes and interlayer smectic spacings for these new mesogenic polymers are presented in Table 1 (in the scanned temperature range, glass transitions were not detected). The effect of molecular mass on phase transition temperatures for a series of polymers with poly(1-methyl-1-silaethylene) backbone bearing methoxyphenyl benzoate cores is illustrated in Figure 2.

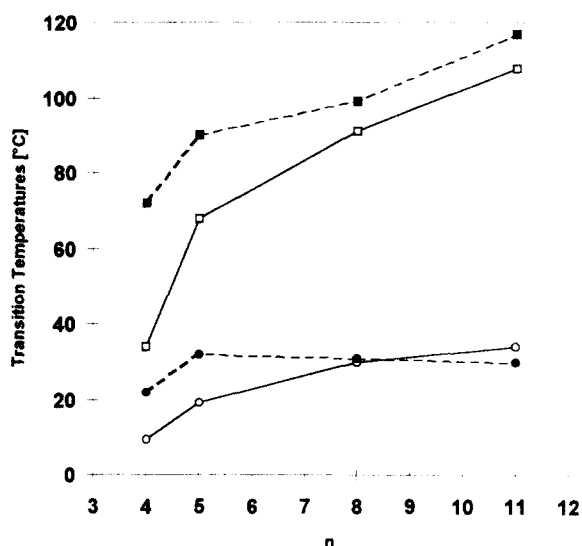
As shown in Figure 2, the general trend of changes in liquid crystalline properties is similar to that observed for analogous side chain polysiloxanes<sup>20</sup>. The degree of polymerization (DP) results in expanding the range of the mesophase. The data collected in Table 1 correspond to DP = 85 for polymers **I** and DP = 460 for polymers **II** and **III**.

As can be clearly seen from Table 1 the transition temperatures follow the usual structural dependence—short methylene spacers lead to nematic phases, while the longer ones generate smectic phases.

**Table 1** Phase transition temperatures (°C), isotropization entropy changes ( $\Delta S$ ), interlayer spacings ( $d$ ) and temperature range of mesophases ( $\Delta T$ ) of polycarbosilanes

Polymer	Spacer length ( $n$ )	Transition temperatures (°C)	$\Delta S$ ( $J \cdot \text{mer}^{-1} \cdot \text{K}^{-1}$ )	$d$ (nm)	$d/l$	$\Delta T$ (K)
Ia	3	K 42 I	25.3	—	—	—
Ib	4	K 22 N 72 I	1.4	—	—	50
Ic	5	K 32 S <sub>A</sub> 90 I	3.3	2.23	0.96	58
Id	8	K 30 S <sub>A</sub> 99 I	8.9	2.90	1.08	69
Ie	11	K 34 S <sub>A</sub> 117 I	13.9	3.36	1.06	83
If	3	K 80 I	24	—	—	—
Ig	11	K 49 S <sub>A</sub> 88 I	50.5	2.95	1.11	39
Ih	10	K 53 S <sub>B</sub> 85 I	43.7	2.85	1.10	32
Ii	11	K 49 S <sub>A</sub> 144 I	8.3	3.63	1.23	95
IIa	5	K 61 I	7.2	—	—	—
IIb	8	K 48 S <sub>A</sub> 82	6.1	3.12	1.16	34
IIc	8	K 38 S <sub>A</sub> 110 N* 123 I	10.2	3.31	0.97	85
IIIa	11	K 14 S <sub>A</sub> 44 I	6.4	3.09	1.17	30

K, crystal; S, smectic; N, nematic; N\*, twisted nematic; I, isotropic;  $l$ , calculated length of side chain



**Figure 2** The dependence of transition temperatures on molecular mass and length ( $n$ ) of flexible spacer  $-(\text{CH}_2)_n-$ . (○)  $T_{K-\text{mesophase}}$ , DP = 8; (□)  $T_{\text{isotropization}}$ , DP = 8; (●)  $T_{K-\text{mesophase}}$ , DP = 85; (■)  $T_{\text{isotropization}}$ , DP = 85

A polycarbosilane backbone provides the same useful feature as other linear polymers in promoting liquid crystalline properties for originally non-mesogenic, rigid low molecular mass compounds<sup>8</sup>. An important role in the case of this new liquid crystal system is being played by the main chain itself in varying the mesophase temperature span.

In the homologous series **Ia–e**, the nematic phase exists only for  $n = 4$ , while the other members of this series form smectic phases. The values of the smectic interlayer spacing  $d$  and the length  $l$  of the side chains are comparable:  $d \sim l$  (by the length of the side chain we mean the length of the pendant group in the most extended conformation with addition of the length of the Si–Me group of the backbone). This suggests the presence of an orthogonal disordered smectic

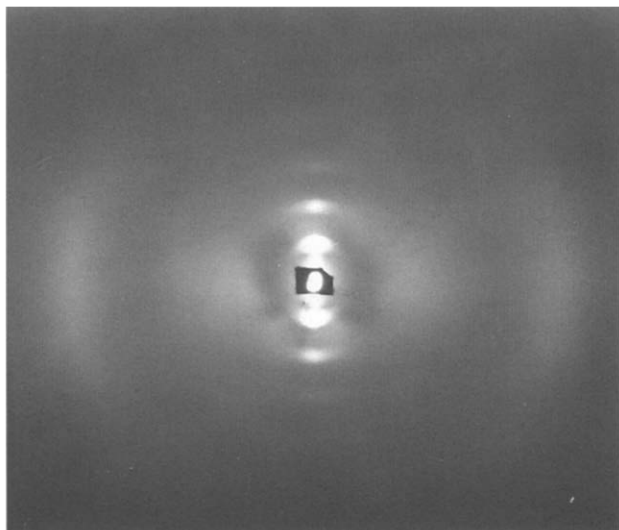
mesophase, such as a smectic A<sub>1</sub> phase. Such monolayer structure has not been observed for similar organosilicon polymers—polysiloxanes with mesogenic groups in which the spacer is longer than an aliphatic tail<sup>17</sup>. It exists, however, in polysiloxanes with mesogenic groups incorporating fluoroalkyl tails<sup>21</sup>. The values of  $d/l < 1$ , observed for **Ic** and **IIc** polymers, indicate that the mesogenic groups are not fully extended and are able to pass through a loose network of the backbones. No appreciable dependence of the interlayer spacing on temperature has been detected.

In the series **Ia–e**, the clearing temperature as well as the entropy change increase with the increase of the spacer length. This effect results from increase of the flexibility of the pending chain, since more flexible side groups can be more easily distorted. Therefore, a higher degree of ordering in a mesomorphic state should be expected, leading to higher temperature and entropy change of isotropization.

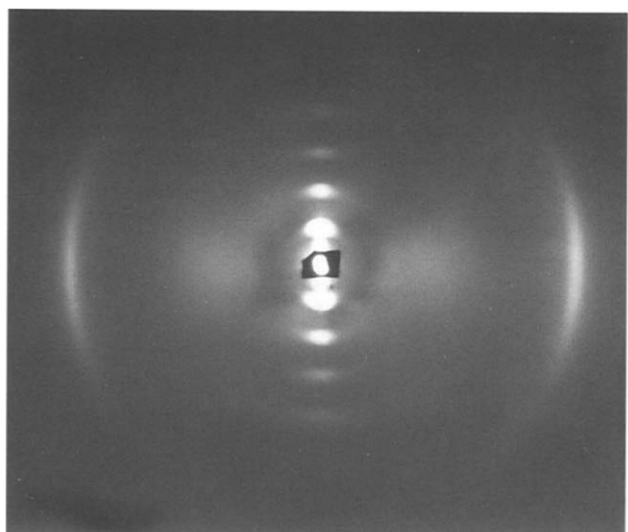
Compared to polysiloxanes, the increase of the spacer length affects to a smaller extent the temperature of the mesophase generation, but exerts a reverse effect on the temperature of transfer into isotropic liquid<sup>20</sup>.

If a mesogen has a strong electric dipole as a terminal fragment (such as a CN group), the dipole induces the formation of antiparallel pairs of partly overlapping cores. Consequently, a partial bilayer smectic S<sub>Ad</sub> phase is observed for **Ij** polymer. Substitution of a methyl group in a tail of a mesogenic rod of the polymer **IIb** by a cholesteric fragment leads to a significant increase of the temperature span of the mesophase. It generates, as expected, a chiral nematic phase due to incorporation of an asymmetric centre into the mesogen structure.

*Figure 3* shows a typical X-ray diffraction pattern of the magnetically oriented sample in the smectic phase (polymer **Id**). It consists of small angle Bragg reflections and a wide angle diffuse halo characteristic of a liquid-like smectic mesophase. The intermesogenic mean distance,  $D$ , calculated from the equation



**Figure 3** Flat camera X-ray diffraction pattern of **Id** in the SmA phase (55°C). The direction of the magnetic field is vertical



**Figure 4** Flat camera X-ray diffraction pattern of **Ih** in the SmB phase (70°C). The direction of the magnetic field is vertical

$2D \sin(\Theta) = 1.117\text{\AA}$  (where  $\theta$  is the angle of the diffused diffraction) is about 0.54 nm for all the polymers. In all studied cases the Bragg reflections 001 decrease with increase of the order  $l$  and only 2–3 reflections are visible

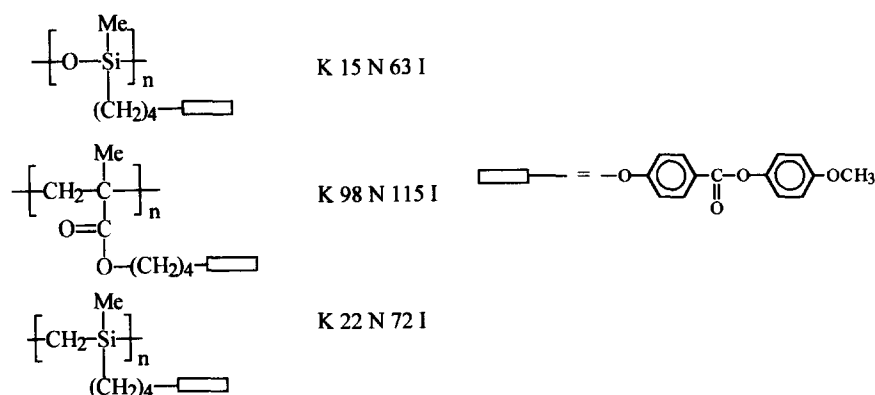
on overexposed films. According to Davidson and Levelut<sup>22</sup> it may indicate that the backbones are not affected to a significant extent by the smectic field, i.e. are not located in sublayers squeezed between adjacent layers of mesogenic cores.

Smectic B phase has been observed only for the **Ih** polymer. *Figure 4* shows the X-ray diffraction spectrum of a magnetically ordered sample. Contrary to the wide angle diffuse scattering, observed for  $S_A$ , the  $S_B$  phase exhibits one sharp reflection at a wide angle, confirming the existence of a characteristic long range ordering within each layer. The absence of the reflections with  $h \neq 0, k \neq 0$  and  $l \neq 0$  may be interpreted as the lack of a long range three-dimensional positional correlation. It seems that the backbones tend to decorrelate adjacent smectic layers and they prevent the propagation of the crystalline order along a director as it occurs for low molecular mass liquid crystals.

An important role in the case of these new liquid crystal polymers is being played by the main chain itself in varying the mesophase temperature range. Polymers of silaethylene type **I** already generate liquid crystallinity (nematic phase) with a rather short butyloxy spacer **Ib**. For the silabutane type polymer **II**, the even longer pentyloxy spacer **IIa** does not give rise to a material with liquid crystal properties. The polymer of **IIb** type with the same octyloxy link to the methoxyphenyl benzoate core, as polymer **Id**, has lower clearing temperature and isotropization entropy change. It also exhibits a more narrow temperature range of the mesophase. Such a 'dilution' of mesogenic groups by introducing two additional  $-\text{CH}_2-$  groups into the type **I** backbone suppresses mesomorphic properties. Additionally the 'dilution' modified the smectic A layer in such a way that the layer thickness increases with the decreasing proportion of mesogenic side groups. A similar effect was observed also for comb-like polysiloxanes<sup>23</sup>.

Mesogenic properties of polycarbosilanes **I** with short spacers fall between those for side chain polysiloxanes<sup>24</sup> and polyolefins<sup>25</sup>, as indicated by phase transition temperatures (*Scheme 4*).

Although small discrepancies are possible here as we compare polymers with slightly different polymerization degree, it is accepted that with DP close to 100 there is almost no significant change of properties on further increase of molecular mass<sup>26</sup>. It should not thus affect much the general picture presented in *Scheme 4*.



**Scheme 4**

## CONCLUSIONS

Side chain polycarbosilanes present a new useful type of liquid crystal polymer, where mesomorphic properties can be additionally varied by regular structural changes in the main chain.

Although copolycondensation of different mesogenic and non-mesogenic chlorosilanes may also modify the liquid crystal properties of recently widely studied polysiloxanes, the resulting polymer is of purely random structure. Thus, it becomes difficult to attribute the influence of real local changes in mesogen 'density' on the properties of such systems. Polycarbosilanes, on the other hand, offer a clear polymeric model for further studies of the effect of structure of the side chains on the properties of mesomorphic materials.

Synthetic routes leading to comb-like polycarbosilanes present a simple set of ring-opening polymerization and hydrosilylation processes, which can be further simplified by applying a one-pot approach.

X-ray studies indicate that side chain liquid crystal polycarbosilanes form predominantly  $S_{A1}$  phases (with methoxyphenyl benzoate type cores), while for more polar rod-like systems  $S_{Ad}$  and  $S_B$  phases are also observed.

The 'double comb-like' liquid crystal polycarbosilane **III**, based on a poly(1-silabutane) linear chain, has been described here for the first time (a previous report on a structurally similar system concerned a polymer that did not preserve mesomorphic properties once heated above the clearing point<sup>27</sup>).

## ACKNOWLEDGEMENT

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