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## Liquid Crystals

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P. Weber<sup>a</sup>; D. Guillon<sup>a</sup>; A. Skoulios<sup>a</sup>; R. D. Miller<sup>b</sup>

<sup>a</sup> Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, UM 380046, CNRS-ULP-EHICS, ICS, Strasbourg Cedex, France <sup>b</sup> IBM Almaden Research Center, San Jose, California, U.S.A.

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## Liquid-crystalline behaviour of a series of poly(di-*n*-alkylsilanes)

by P. WEBER, D. GUILLON and A. SKOULIOS

Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux  
de Strasbourg, UM 380046, CNRS-ULP-EHICS, ICS, 6, rue Boussingault,  
67083 Strasbourg Cedex, France

and R. D. MILLER

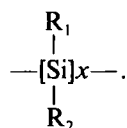
IBM Almaden Research Center, San Jose, California 95120-6099, U.S.A.

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A homologous series of poly(dialkylsilanes), with alkyl side chains from butyl to tetradecyl, has been studied using polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction. It was shown that these polymers undergo a first order transition from a low temperature crystalline to a high temperature columnar mesomorphic phase; the transition temperatures range from 9 to 82°C. As the length of the side chains is increased, the transition temperature initially drops drastically and then rises again. These two regimes are connected to the relative part played in the phase transition by the aliphatic side chains and the polymer backbone. The enthalpies also revealed two regimes. Starting from the butyl polymer the enthalpy first grows more and more rapidly and, beyond a chain length of about ten methylene groups, it then grows linearly. From the Y intercept of the corresponding curve it was inferred that the transition into the mesomorphic phase is followed by a stabilization of the backbone conformation. The structure of the columnar mesophase was described as a two dimensional hexagonal packing of columns consisting of straight polymer backbones surrounded by alkyl chains in a disordered conformation. From the slope of the square of the intercolumnar distance as a function of the number of methylene groups per silicon atom, and using the known value of the volume of one methylene group in the liquid state, the stacking period of the silicon atoms along the columnar axis was found to be 1.68 Å. This relatively small value indicates a coiled structure involving a significant number of gauche conformers. The Y intercept of the corresponding straight line, related to the volume of one silylene repeat unit deprived of all its methylene groups, suggests a great compacity of the atomic packing near the silicon backbone.

### 1. Introduction

Linear poly(dialkylsilanes) are polymers that contain only silicon atoms in the backbone



Their particular chemical structure leads to electron delocalization along the silicon backbone and gives rise to unusual electronic properties, suggesting significant interaction and delocalization within the  $\sigma$ -bonded silicon backbone [1-2]. They have already found promising applications in various industrial fields; for example

photoconductivity [3], microlithography [4] and the manufacture of silicon carbide ceramic precursors [5].

Of all the polysilane derivatives reported so far, the dihexyl derivative, PDHS (indicated in the following by PD-6-S), has been studied in detail by many experimental techniques. It was found to display a curious long wavelength electronic transition below 42°C, associated with a reversible strong thermal transition [6]. Infrared and Raman spectroscopy, together with differential scanning calorimetry and X-ray diffraction have been used to characterize the molecular conformation of both the main and side chains as a function of temperature. A mechanism involving the melting of the side chains with a subsequent disordering of the polymer backbone was thus proposed [7]. Evidence from X-ray diffraction was particularly clear in that connection. All of the Bragg reflections characterizing the crystalline form at room temperature vanished upon heating beyond the transition, while a broad halo appeared in the vicinity of 4.5 Å, characterizing the disordering of the hexyl side chains [7-9]. Regarding specifically the high temperature form, it is of interest to note that one or two additional equatorial reflections at 13.5 and 7.75 Å were detected in the X-ray patterns, first attributed to an overall short range order in the amorphous phase [7]. These were finally interpreted as indicating a large increase in intermolecular order, the polysilane chains being packed as cylinders on a hexagonal lattice [9].

The structural behaviour of PD-6-S has been studied by optical polarizing microscopy and X-ray diffraction [10]. It was shown that the first order transition at 42°C corresponds to a transition from a three dimensional crystal at low temperature to a liquid crystal at high temperature. The X-ray diffraction patterns and the optical textures observed above 42°C indicated not only that the structure at high temperature is liquid-crystalline in nature, but also that it belongs to the class of the well-known columnar mesophases. Indeed, the X-ray patterns and optical textures of PD-6-S were identical to those observed for organic compounds (with elongated or disc-like molecules such as metal soaps [11] or polyalkylated flat aromatic derivatives [12]), whose columnar molecular ordering was properly established and is now a matter of common agreement. By analogy, the core of the columns in PD-6-S was, therefore, described as being formed of extended silicon backbones of the polymer chains, and the intercolumnar space as being filled by the liquid-like hexyl chains.

The columnar nature of PD-6-S at high temperature having been established, it was straightforward to describe the columnar structure of PD-6-S in more detail, by using the concepts and methods of calculation defined for the general case of columnar liquid crystals. In particular; it was possible to calculate the stacking period,  $h$ , of the silicon atoms along the columnar axis, which corresponds to the average projected length of one dihexylsilylene repeat unit on the columnar axis. This was done knowing the intercolumnar distance ( $D = 15.4 \text{ \AA}$ ) measured from the hexagonal cell parameter of the columnar phase, and using a reasonable value for the specific volume of the mesomorphic material ( $v \approx 0.971 \text{ cm}^3 \text{ g}^{-1}$ ). Indeed, simple crystallographic arguments regarding the average value of the volume,  $V$ , of one repeat unit, determined from the value of the area of the hexagonal unit cell, show that

$$V = Mv/N_A = (\sqrt{3}/2)hD^2,$$

where,  $M$  is the molecular weight of the repeat unit (198.4) [11]. At  $1.56 \pm 0.12 \text{ \AA}$ , the stacking period proved much smaller than that ( $2.035 \text{ \AA}$ ) measured at room temperature for the stretched, planar zig-zag, all-trans silicon backbone of PD-6-S in the crystalline state [8]. Still more significantly, it is much smaller than that ( $1.92 \text{ \AA}$ )

calculated for an ideal planar zig-zag chain of silicon atoms, as in the diamond structure [13]. This evidence was interpreted to mean that the silicon backbone in the columnar liquid crystal is not fully extended in a planar zig-zag, all-trans conformation, but conclusively coiled in a strongly gauche conformation.

We note that the value used for the specific volume of the mesomorphic material was not measured experimentally, by dilatometry as usual. Because of the thermal degradability of polysilanes, it was impossible to degas the samples efficiently by heating them in the melt as required. To overcome this difficulty, an estimate of  $v$  was calculated instead [10] by just applying an approximate 5 per cent increase to the specific volume of the crystal ( $v_{cr} = 0.926 \text{ cm}^3 \text{ g}^{-1}$ , deduced from the volume of the monoclinic cell [8]). Although reasonable, this approach might seem too arbitrary and hence be subject to discussion. To avoid this question, it seemed necessary to obtain the stacking period in a different way which is independent of any preliminary knowledge of the specific volume of the material in the mesomorphic state. This is the main objective of the present work.

Here, a systematic study of a series of polysilanes is described. Apart from providing a different method of obtaining a more reliable estimate of the stacking period, this work also generalizes the results obtained with PD-6-S to other members of the homologous poly(di-*n*-alkylsilane) series and to analyse the rôle of bulk alkyl substituents on the conformation of the silicon backbone. It will also give valuable information about the general problem of the structural behaviour of long chain polymers [14]. The polysilane derivatives used carried alkyl substituents of various lengths. In addition to the dihexyl derivative [PD-6-S], six other high molecular weight ( $M > 10^5$ ) poly(di-*n*-alkylsilanes), indicated by the general symbol PD-*p*-S, were considered: poly(di-*n*-butylsilane) [PD-4-S], poly(di-*n*-pentylsilane) [PD-5-S], poly(di-*n*-octylsilane) [PD-8-S], poly(di-*n*-undecylsilane) [PD-11-S], poly(di-*n*-dodecylsilane) [PD-12-S], and poly(di-*n*-tetradecylsilane) [PD-14-S].

## 2. Thermotropic polymorphism

Optical studies of thin films of material were carried out with a Leitz polarizing microscope equipped with a Mettler FP 82 hot stage. Upon slow heating, the strong birefringence of the solid, crystalline films at room temperature decreased markedly, but did not disappear completely, at a given temperature, indicating a phase transition toward a highly viscous, weakly birefringent, mesomorphic phase. The textures observed at high temperature were all similar to those reported for PD-6-S in the mesomorphic state (see figure 1 in [10]), suggesting a similar columnar liquid-crystalline structure.

Miscellaneous thermal properties, including enthalpies of transition when observable, have already been reported in the literature for several polysilane derivatives (see table 11 in [2]). In order to analyse the thermal behaviour of the whole set of polysilanes under consideration here, the temperatures and enthalpies of the crystal to liquid crystal phase transitions were all redetermined by differential scanning calorimetry. Measurements were performed at a heating rate of  $10 \text{ K min}^{-1}$ , with a Perkin-Elmer DSC 4 instrument using sealed aluminium pans. Great care was taken, especially with the PD-8-S derivative which was soft and waxy in consistency, to rid the samples of any residual solvent by heating at  $60^\circ\text{C}$  under vacuum for a long time (over 1 week). The thermal properties were studied by starting at temperatures ( $-50^\circ\text{C}$ ) well below the respective transition temperatures. A typical DSC thermogram of PD-8-S is

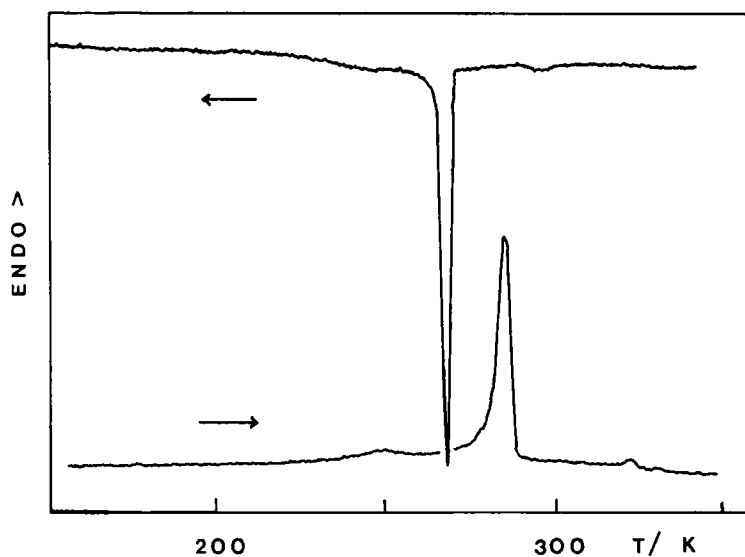


Figure 1. Differential scanning calorimetry scan of PD-8-S, upon heating and cooling at a rate of 10 K/min.

Temperature and enthalpy† of crystal to mesophase phase transition in poly(di-*n*-alkylsilanes) [*n*-alkyl chains: CH<sub>3</sub>(CH<sub>2</sub>)<sub>*p*-1</sub>-].

Polymer	<i>p</i>	<i>T</i> /°C	$\Delta H$ /kJ mol <sup>-1</sup>
PD-4-S	4	76/82‡	2
PD-5-S	5	60/65‡	2
PD-6-S	6	42	7
PD-8-S	8	9/45‡§	10
PD-11-S	11	53	21
PD-12-S	12	45/56‡	25
PD-14-S	14	53	34

† Enthalpies refer to dialkylsilylene repeat units.

‡ Double DSC peaks upon heating, and single upon cooling.

§ Peak at 45°C is very weak (0.2 kJ mol<sup>-1</sup>).

shown in figure 1. Although reversible, the transitions showed a marked hysteresis of about 20 to 30°C upon cooling. This is simply related to the induction period of the crystallization process. The table summarizes the experimental data obtained. It should be noted, that, for PD-4-S, PD-5-S, and PD-12-S, while the transition peaks are slightly split into two peaks upon heating, they are clearly single peaks upon cooling. However, the total enthalpy change measured either upon heating or cooling is always the same, suggesting the occurrence of an additional polymorphic form, intermediate between the low temperature crystalline and the columnar mesomorphic phase; this additional form may possibly be crystalline in nature because, as is usual for crystals, it fails to appear without delay upon cooling through the transition temperature.

As the length of the alkyl side chain is increased from butyl, the transition temperature initially drops significantly then increases again (see figure 2). This behaviour may be compared to that commonly observed with alkyl side chain

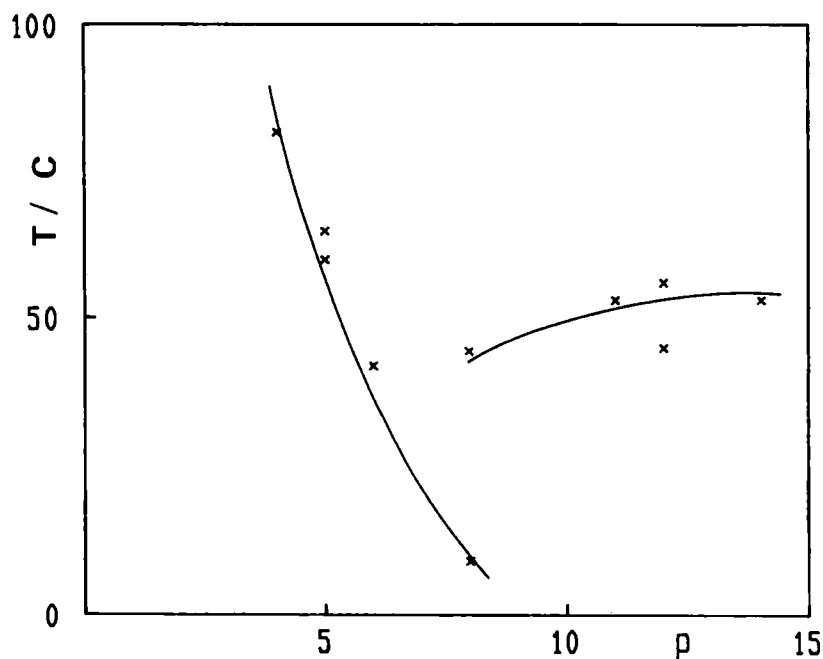


Figure 2. Crystal to mesophase transition temperatures as a function of the number of carbon atoms in the alkyl chains.

polymers (see figure 3 in [14]). The two regimes detected are obviously related to the relative rôles played in the phase transition by the aliphatic side chains and the polymer backbones. The decreasing regime, observed with short alkyl chains, corresponds to the lowering of the thermal stability of the crystals, whose structure is determined mainly by the polymer backbones and perturbed by the short side chains. On the other hand, the increasing regime, observed with long alkyl chains, corresponds to the enhancement of the thermal stability of the crystals, whose structure is dominated mainly by the crystallization of the long paraffin side groups.

With this regard, the thermal behaviour of PD-8-S deserves the following comment. Because of the intermediate length of its alkyl side chains, this particular polymer seems governed simultaneously by the two transition regimes. Indeed, as shown in figure 1, both regimes are present at 9 and 45°C, even though the decreasing regime is dominant. As evidenced by the UV shift, which generally accompanies the transition [6], the occurrence of the high temperature transition in PD-8-S seems favoured when the polymer is cast in the form of a thin film and annealed under vacuum. Maybe there is a thin film effect (a skin effect in bulky specimens), where a particular crystalline form is favoured by the effect of the substrate (of the free surface).

These two regimes are also obvious when considering the enthalpies of transition (see figure 3). Starting from the butyl polymer with a value of about  $2 \text{ kJ mol}^{-1}$ , the enthalpy change increases more and more rapidly with increasing length of the alkyl side chains until it begins to increase linearly for the higher members of the series ( $p = 11, 12$  and  $14$ ).

Considering the thermal behaviour of polysilanes with short alkyl chains, we note that, independent of the experimental error, the enthalpy values are rather scattered

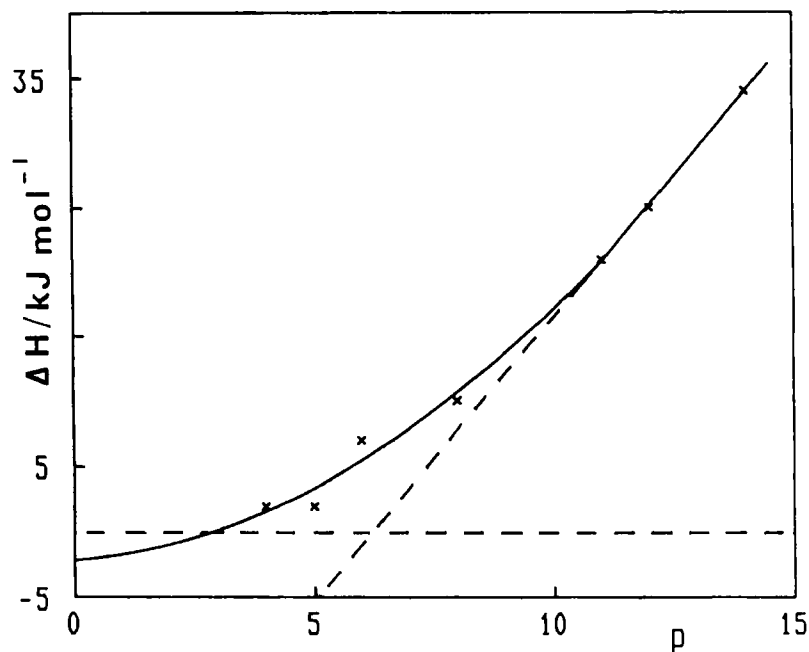


Figure 3. Crystal to mesophase transition enthalpies as a function of the number of carbon atoms in the alkyl chains.

and hence are difficult to analyse quantitatively. This is due to the fact that, in the crystalline state at low temperature, the conformation of the silicon backbone (planar zig-zag or helical) and the structure of each individual polymer depend strongly on the length of the alkyl side groups [2]. The general trend of the enthalpy variation is, however, perfectly clear. It can be represented by a simple curve which, intersects the *X* axis at about 2.5 and the *Y* axis at about  $-2 \text{ kJ mol}^{-1}$  (see figure 3). The order of magnitude of the *Y* intercept, which is related essentially to the silicon backbone, is in agreement with the energy differences involved in *trans-gauche* conformational changes in organic materials [15] and in silicon polymers [2]. Its negative sign, on the other hand, suggests that, whatever the crystalline structure at low temperature, the transition into the columnar mesophase is presumably followed by a stabilization of the backbone conformation.

From the slope ( $4.357 \text{ kJ mol}^{-1}$ ) of the straight line representing the thermal behaviour of the higher members of the series (see figure 3)—for which a least square fit gives the equation:  $\Delta H/\text{kJ mol}^{-1} = 4.357 p - 27.1$ —we find an enthalpy increment of  $156 \text{ J g}^{-1}$  of methylene group. This is smaller than that found for normal paraffins ( $289 \text{ J g}^{-1}$  [16]) or smectic liquid crystals ( $272 \text{ J g}^{-1}$  [17]). The same deficiency in the transition enthalpy has also been found for the columnar copper alkanoates ( $196 \text{ J g}^{-1}$  [18]) and for long alkyl side chain polymers in general [14]. For the columnar copper alkanoates [18], the enthalpy deficiency observed might be related to the fact that the aliphatic chains are either only partially disordered in the columnar mesophase or only partially ordered in the crystalline state. Another quite plausible interpretation, particularly appropriate for the description of side chain polymers, suggests that, due to their anchoring on the backbone, the alkyl side chains crystallize only partly, especially for the portion located farthest from the silicon atoms; in

addition, that it is certainly possible that the polymer side chains do not necessarily crystallize with the same low energy local structure as the pure paraffins (orthorhombic, monoclinic, or triclinic form). For these reasons, we can readily rationalize that the melting enthalpy of these alkyl chains might very well be smaller than expected.

From the position in the  $X, Y$  plane of the straight line representing the  $p$  dependence of the transition enthalpy, we might be led to certain conclusions based on the following arguments [14]. With the assumption that all of the methylene groups in the alkyl chains play the same part in the crystal to mesophase transition, the negative, non-zero  $Y$  intercept might be taken as reflecting the energy gain of the system related to the conformational change of the silicon backbone at the transition. If we assume that some of the methylene groups are not involved in the transition (as would already be the case if there was disorder in the low temperature crystal), the non-zero  $X$  intercept might be indicative of the number of disordered methylene groups. Clearly, both interpretations are somewhat exaggerated. The first results in a completely unrealistic value for the enthalpy associated with the conformational change of the backbone at the transition. More importantly, it implicitly assumes that all methylene groups melt and crystallize with the same ease, as with normal paraffins. The latter assumption disregards the fact that each silicon atom on the polymer carries two alkyl side chains and, as a result, the methylene groups near the polymer backbone are severely overcrowded and subject to strong geometrical constraints. Experimental support for the steric crowding of the methylene groups near the silicon core is given by the restricted mobilities measured by  $^{13}\text{C}$  NMR [19]. The second proposal assumes that the conformational change of the backbone surrounded by several disordered methylene groups at the transition temperature, if it occurs at all, is athermal. The truth obviously lies somewhere between these two extremes.

Perhaps, a more reasonable way to analyse the DSC data on the poly(dialkylsilanes) is the following. Considering the small negative value of the  $Y$  intercept of the enthalpy variation with  $p$  (see figure 3) suggests that the transition from the crystal to the mesophase proceeds with a stabilization of the silicon backbone conformation. This suggestion seems reasonable as the partial melting of the aliphatic chains can only relieve the steric stresses exerted on the backbone and allow it to relax to some extent. It is proposed that the alkyl chains are composed of two distinct regions. The terminal regions, comprising those methylene groups that are placed far from the polymer backbone (for convenience these might be called *distal*), crystallize and melt normally, with each methylene group contributing equally. The initial regions, perhaps comprising a number up to ten methylene groups located near the polymer backbone (for convenience these might be called *proximal*), on the other hand, melt and crystallize only partially. The further they are from the polymer backbone, the less the methylene groups are sterically strained and the more they participate in the transition process as shown by the increasing slope of the  $\Delta H(p)$  curve (see figure 3).

### 3. Structural behaviour of the columnar mesophases

The structural behaviour of the mesomorphic poly(dialkylsilanes) was studied by X-ray diffraction. X-ray patterns of powder samples in Lindemann capillaries were recorded photographically using two different diffraction cameras. The columnar nature of the samples was established using a Guinier focusing camera equipped with an electrical oven and a bent-quartz monochromator (copper  $\text{K}\alpha_1$  radiation from a



Philips PW-1009 generator). To investigate the temperature dependence of the structure, runs of small angle diffraction patterns were recorded automatically, as a function of temperature; the camera used for that purpose was equipped with a bent, gold-plated glass mirror (nickel filtered copper radiation from an Elliott GX 20 rotating anode generator) and a computer assisted electrical oven.

The X-ray patterns registered above the crystal to liquid crystal transition were all the same as those already described for PD-6-S. On the one hand, they contain one diffuse ring around 4.6 Å, indicative of the molten state of the alkyl chains; and on the other hand, they contain a series of sharp Bragg reflections in the small angle region, with reciprocal spacings in the ratio 1,  $\sqrt{3}$ ,  $\sqrt{4}$ ,  $\sqrt{7}$ . The corresponding structure consists, therefore, of a hexagonal packing of columns, formed by the silicon backbone of the polysilane molecules and surrounded by the alkyl chains spreading outwards in a disordered conformation.

The hexagonal cell parameters of all the polysilanes studied here, and hence the corresponding distance,  $D$ , between the axes of adjacent columns, increase only very slightly with temperature, up to 200°C. The value of the relative thermal expansion coefficient of the intercolumnar distance,  $(1/D)\delta D/\delta T \approx 3 \times 10^{-4} \text{ K}^{-1}$ , is one-half that of the relative expansion coefficient of the volume of fluid organic materials in general, and of columnar liquid crystals in particular [18]. It suggests that the volume thermal expansion of the columnar system is continued entirely to the two dimensional crystal lattice, with the linear density (or the overall length) of the columns kept constant.  $D$  was found to increase considerably with the length of the alkyl chains. The values measured at 100°C, that is above the crystal to liquid crystal transition temperature, are: 12.9, 14.2, 15.6, 18.0, 20.9, 21.9, and 23.5 Å and PD-4-S, PD-5-S, PD-6-S, PD-8-S, PD-11-S, PD-12-S and PD-14-S, respectively.

As pointed out some time ago, and successfully used for the columnar mesophases of alkaline earth metal soaps [11, 18], another way to secure the value of  $h$  from  $D$ , without preliminary knowledge of the specific volume of each columnar sample, is to analyse the dependence of  $D^2$  upon the number  $p$  of methylene groups in the repeat unit. Transposed to the case of poly(dialkylsilanes), this method amounts to using

$$(\sqrt{3}/2)hD^2 = V_0 + 2pV_m,$$

where  $V_m$  is the volume of one methylene group and  $V_0$  the volume of one dialkylsilylene repeat unit deprived of all its methylene groups (including those in the terminal methyl groups of the alkyl chains). This equation is founded on the reasonable assumption that the partial molar volumes of the constituent parts of the molecules are additive. If  $h$  were exactly the same for all the terms of the polysilane homologous series, and  $V_m$  exactly the same for all the methylene groups, then  $D^2$  should, of course, depend linearly upon  $p$

$$D^2 = \frac{2V_0}{h\sqrt{3}} + \frac{4V_m}{h\sqrt{3}}p.$$

As shown in figure 4, this is clearly the case in the present work, at least with  $ps$  ranging from 4 to 14. To analyse the linear dependence of  $D^2$  upon  $p$  in a quantitative way, a least-square fit gave

$$D^2/\text{Å}^2 = 9.6 + 39.04p.$$

with a reliability factor of 99.99 per cent. The standard deviations were respectively of 2.3 for the Y intercept and of 0.25 for the slope of the straight line. From the slope

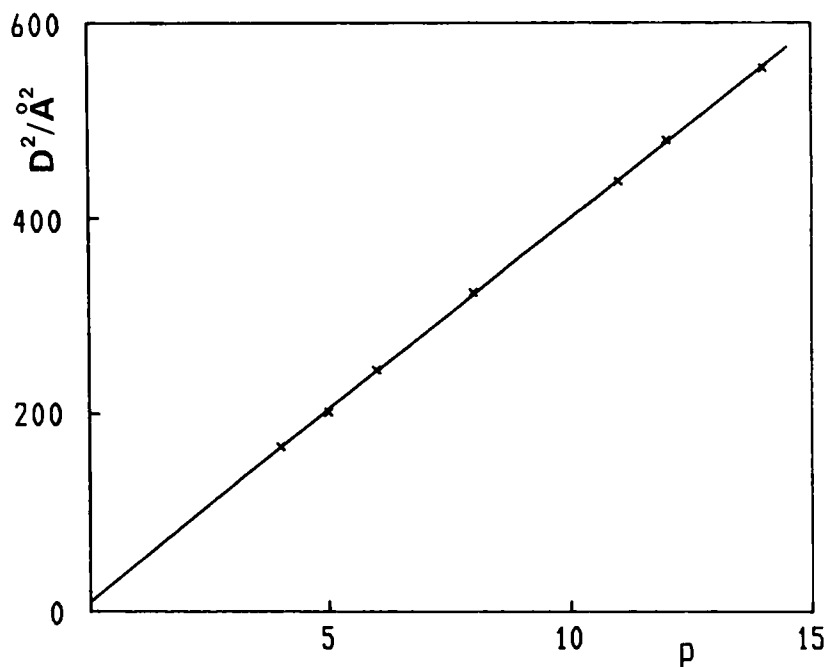


Figure 4. Square of the intercolumnar distance as a function of the number of methylene groups in the alkyl side chains for the columnar mesophase of poly(di-*n*-alkylsilanes) at 100°C.

of  $D^2$  versus  $p$ ,  $4V_m/(h\sqrt{3}) = 39.04 \text{ \AA}^2$ , and the volume of one methylene group in a disordered alkyl chain, of  $28.4 \pm 0.5 \text{ \AA}^3$  at 100°C (see Appendix), we find:  $h = 1.68 \pm 0.04 \text{ \AA}$ . Within the experimental error, this value compares well to that ( $1.56 \pm 0.12 \text{ \AA}$ ) previously reported for PD-6-S [10]. This agreement is all the more significant as the latter value was calculated through an entirely different method using the molar volume of one dihexylsilylene group, estimated from the crystallographic volume of the unit cell ( $\pm 3$  per cent) increased by 5 per cent to take into account the volume expansion occurring on melting.

From the Y intercept,  $2V_0/(h\sqrt{3})$  of  $9.6 \text{ \AA}$ , we can calculate the area of the hexagonal unit cell of the fictitious columnar mesophase obtained with PD-0-S, i.e. a poly(dialkylsilane) deprived of all its methylene groups:  $V_0/h = 8.3 \pm 2.0 \text{ \AA}^2$ . This area is closely related to the cross-section of the silicon core of the columns; it represents the cross-section of the silicon backbone itself, enlarged to include the cross-sectional area corresponding to two methyl groups deprived of their methylene part. We can also deduce the diameter of the silicon core (assumed circular):  $\sqrt{(4V_0/\pi h)} = 3.3 \pm 0.8 \text{ \AA}$ . Although lacking in precision, the value of all these additional geometrical parameters is consistent with the backbone and the atomic van der Waals dimensions.

We can further calculate  $V_0$  as  $14 \pm 4 \text{ \AA}^3$ , which, corresponds to the volume occupied in the columnar state at 100°C by one di(alkylsilylene) repeat unit depossessed of all its methylene groups:  $V_0 = V_{\text{Si}} + 2(V_{\text{CH}_3} - V_{\text{CH}_2})$ . To discuss its value, we have to consider the volume of one silicon atom and the excess volume of one disordered methyl over one disordered methylene group. The former ( $\approx 15 \text{ \AA}^3$ ) may be deduced by analogy with the known diamond structure of silicon ( $V_{\text{Si}} = 20.0 \text{ \AA}^3$

[13]), carbon ( $V_C = 5.6 \text{ \AA}^3$  [13]), and silicon carbide ( $V_{\text{SiC}} = 21.9 \text{ \AA}^3$  [24]); the latter (of about 10 to 20  $\text{\AA}^3$ ) may be approximately estimated by considering the volume of one methyl group in a variety of organic compounds (see Appendix). The expected value ( $\approx 15 + 2 \times 15 = 45 \text{ \AA}^3$ ) of  $V_0$  significantly exceeds (by about 30  $\text{\AA}^3$ ) that (14  $\text{\AA}^3$ ) deduced from the Y intercept of  $D^2(p)$ . It is important to note, however, that the volume shortage observed is merely due to the way  $V_0$  was calculated by extrapolating  $D^2$  using for the volume of all the methylene groups the unique value of 28  $\text{\AA}^3$ . Characteristic of methylene groups in a liquid matrix, this value is exaggerated for the proximal methylene groups which are overcrowded in the immediate neighbourhood of the silicon core.

No doubt, the volume shortage observed indicates an increased compactness in the spatial arrangement of the proximal methylene groups. By sharing out the volume shortage uniformly among the three proximal methylene groups, we find for each of them an effective volume of about 23  $\text{\AA}^3$ . This is slightly smaller than the volume (24.3  $\text{\AA}^3$ , see Appendix) of one methylene group in the crystalline state, but much larger than the corresponding covolume (17.1  $\text{\AA}^3$  [22]). With a density ( $17.1/23 = 74.3$  per cent of space filling) comparable to that of a face centred cubic periodic packing of spheres, such a compact arrangement is perfectly plausible for many reasons. First of all, the orthorhombic, monoclinic, and triclinic crystalline structures of paraffins, from which the 24.3  $\text{\AA}^3$  value of  $V_{\text{CH}_2}$  was deduced, do by no means count among the densest possible long range periodical arrangements in space [22]. Second, if the proximal methylene groups are allowed just to pack around the columnar axis densely but without the geometrical constraints of long range translational symmetry suited to a macroscopic crystal, then they presumably [25] can reach local densities larger than those of a crystal [26]. Finally, the very fact of their chemical bonding to, and of their radial arrangement outwards from, the silicon backbones makes it only natural that the alkyl chains are, of necessity, severely constrained in the neighbourhood of the columnar axis; at radial distances  $r$  shorter than 3.8  $\text{\AA}$  (which probably correspond to the radial distances of the first two proximal methylene groups), their average molecular area ( $S = 2\pi rh/2 \approx 5.3r$ ) is smaller than that ( $\approx 20 \text{ \AA}^2$  [25]) of paraffins in the crystalline state.

#### 4. Conclusion

The present investigation has shown that the columnar mesomorphic behaviour first observed with PD-6-S is also found with a wide variety of PD- $p$ -S, from the butyl to the tetradecyl derivative ( $4 \leq p \leq 14$ ). These polymers undergo a first order thermal transition from a low temperature crystalline to a high temperature columnar mesomorphic phase. Thermotropic columnar mesophases have so far been known to occur with low molecular weight, organic and organometallic materials such as discotic mesogens, soaps, and metal-including substituted phthalocyanines [12]; however, they can also be obtained with polymers, like those containing disc-like pendant mesogenic groups [27]. It is useful to add that columnar mesophases have already been reported in the literature to occur with rigid chain polymers, such as nucleic acids and polypeptides [28], but these are then lyotropic in nature, as they can only be produced in the presence of an appropriate solvent.

Regarding the thermal stability of the crystal in relation to the liquid crystal, it was found that, as the length of the alkyl side chains is increased from butyl, the transition temperature first drops dramatically and then rises again. This behaviour is typical of

alkyl side chain polymers, in general [14]. For short side chains, the crystal structure is dominated by the backbone conformation, the side chains acting essentially as a defect, only perturbing the molecular interactions and the stability of the system. However for long side chains, the structure is controlled by the side chains themselves, which tend to stretch out and come together side by side in lateral register. It is instructive to recall here the main features of the crystalline structure of alkyl side chain polymers in general. When the alkyl chains are short, the structure generally corresponds to the packing of the polymer molecules with a helical conformation; in return, when the alkyl chains are sufficiently long, the structure fundamentally corresponds to the alternate stacking of backbone and paraffin sublayers, with the alkyl chains fully extended and oriented at an angle with respect to the layer normal.

These two ordering regimes in the crystal also show through the enthalpies involved in the phase transitions to the liquid crystal. The variation of these enthalpies as a function of the side chain length reveals that the methylene groups are not all equivalent to one another. Those far off the silicon backbone are fairly free to crystallize or melt; located in distinct sublayers when crystallized, they all contribute the same heat of melting to the transition enthalpy. On the other hand, those next to the silicon atoms are strongly affected by the backbone conformation; sterically disordered below the transition temperature and appreciably immobilized [29], they play a modest part in the melting process; their contribution to the transition enthalpy grows, however, with their chemical distance from the backbone.

The columnar nature of the mesomorphic phases at high temperature was established by using polarizing optical microscopy and X-ray diffraction. Their structure consists of a two dimensional hexagonal packing of elongated silicon backbones surrounded by aliphatic chains spreading outwards in a disordered conformation. The squared distance between the axes of neighbouring columns, deduced from the experimental hexagonal cell parameters increased linearly with the number of carbon atoms in the alkyl chains. This was interpreted to mean, first, that on and after the fourth methylene group starting from the silicon atom, the molar volume of all the disordered methylene groups is exactly the same and, second, that the mean stacking period of the silicon atoms along the columnar axis is a constant for the whole series of polymers considered here, from the dibutyl up to the ditetradecyl polysilane. This made it possible to calculate the stacking period of the silicon atoms using the known value of the molar volume of methylene groups in a liquid paraffin. The value found (1.68 Å) is in agreement with that calculated for the dihexyl derivative using a different method involving the molar volume of the whole polymer estimated from the density of the crystal at room temperature [10].

Such a low value for the silicon period along the columnar axis is by far too small to be compatible with an all-trans conformation for the silicon backbone. It rather points, as suggested for the dihexyl polymer [10], to an all-gauche conformation, or at least to a conformation containing a large number of gauche conformers. It is important to recall that the stacking period of the silicon atoms is the same for the whole series of polysilanes considered and also independent of temperature. This means that the conformation of the polymer backbone is not affected by the bulkiness and the thermal agitation of the pendant alkyl groups, having presumably reached an enhanced stability upon the transition into the columnar liquid-crystalline phase (as supported in another connection by the small negative transition enthalpy found by extrapolation to  $p = 0$ ).

From the (extrapolated) value of the squared intercolumnar distance of (fictitious) polydialkylsilanes with less than three methylene groups in their alkyl side chains, it is evident that the methylene groups near the silicon backbone occupy a volume much smaller than in the liquid state. This is consistent also with the rather small contribution of the (four to ten) proximal methylene groups to the overall transition enthalpy from the crystal to the liquid crystal. The number of methylene groups which are found to be proximal from the transition enthalpy is larger than that found from the molar volume; this is due merely to the fact that, even though the volume of the methylene groups just beyond the third is comparable to that in a liquid, the thermal (translatory, rotatory, and perhaps also vibratory) motions of the groups is probably not yet completely free to contribute efficiently to the averaging of the interactions.

### Appendix

The molar volume of *n*-alkanes, calculated from the densities measured at a variety of temperatures [20], is found to depend linearly upon the number of carbon atoms in the chain. A least-square fit of the experimental values at 100°C leads to a value of 28.7 Å<sup>3</sup> for the volume of one methylene group, and to a value of 61.5 Å<sup>3</sup> for one methyl group. A similar analysis carried out with smectic liquid crystals leads for the methylene groups at 100°C to a value of 28.0 Å<sup>3</sup> [21].

In *n*-alkanes at 100°C, the volume of one methyl group is of 61.5 Å<sup>3</sup>; much larger than the minimum volume or covolume (23.5 Å<sup>3</sup> [22]) of methyl groups in strict contact with adjacent molecules, this volume takes into account the high mobility (translatory, vibratory and rotatory motions) of the methyl groups when carried by the ends of free flexible alkyl chains. For stearic acid in the crystal B form [23], the volume of the methyl (30.9 Å<sup>3</sup>) and methylene (24.3 Å<sup>3</sup>) groups can be directly deduced from the atom coordinates in the unit cell. Finally, from the density at room temperature [15] and the molecular volume of 2,2-dimethylpropane (195.4 Å<sup>3</sup>) and 2,2,3,3-tetramethylbutane (230.2 Å<sup>3</sup>), and using the known value (5.0 Å<sup>3</sup> [22]) for the covolume of quaternary carbon atoms, it is easy to calculate the volume of the methyl groups: 47.6 and 36.7 Å<sup>3</sup>, respectively. Clearly, the scatter in these values is connected with the mobility of the methyl groups in the material and the free volume attributed to their neighbouring atoms and groups (sharing of the free volume). Considering that the mobility of the alkyl chains in the columnar polysilanes is rather reduced (owing to their rigid attachment to the silicon hard cores and to their overcrowding around the columnar axes) and that the binary contacts between methyl end groups are presumably more frequent than expected from the chemical composition of the liquid paraffin matrix (owing to the reduced interpretation of the alkyl chains belonging to adjacent columns), it seems reasonable to assume for the volume of the methyl end groups a value in the range from 40 to 50 Å<sup>3</sup>.

### References

- [1] MILLER, R. D., RABOLT, J. F., SOORIYAKUMARAN, R., FLEMING, W., FICKES, G. N., FARMER, B. L., and KUZMANY, H., 1988, *Inorganic and Organometallic Polymers*, edited by M. Zeldin, J. Wynne and H. R. Allcock, ACS symposium Series No. 360 (American Chemical Society).
- [2] MILLER, R. D., and MICHL, J., 1989, *Chem. Rev.*, **89**, 1359.
- [3] KEPLER, R. G., ZEIGLER, J. M., and HARRAH, L. A., 1984, *Bull. Am. phys. Soc.*, **29**, 504.

- [4] MILLER, R. D., MCKEAN, D. R., HOFER, D., WILLSON, C. J., WEST, R., and TREFONAS, P. T., 1984, *Materials for Microlithography*, edited by L. F. Thomson, C. G. Willson and J. M. J. Fréchet, ACS Symposium Series No. 266 (American Chemical Society).
- [5] WEST, R., 1986, *J. organomet. Chem.*, **300**, 327.
- [6] MILLER, R. D., HOFER, D., and RABOLT, J., 1985, *J. Am. chem. Soc.*, **107**, 2172.
- [7] RABOLT, J. F., HOFER, D., MILLER, R. D., and FICKES, G. N., 1986, *Macromolecules*, **19**, 611.
- [8] KUZMANY, H., RABOLT, J. F., FARMER, B. L., and MILLER, R. D., 1986, *J. chem. Phys.*, **85**, 7413.
- [9] LOVINGER, A. J., SCHILLING, F. C., BOVEY, F. A., and ZEIGLER, J. M., 1986, *Macromolecules*, **19**, 2657.
- [10] WEBER, P., GUILLON, D., SKOULIOS, A., and MILLER, R. D., 1989, *J. Phys., Paris*, **50**, 793.
- [11] SPEGT, P., and SKOULIOS, A., 1965, *J. Chim. Phys.*, **62**, 377; 1963, *Acta crystallogr.*, **16**, 301; *Ibid.*, **17**, 198.
- [12] CHANDRASEKHAR, S., SADASHIVA, B. K., and SURESH, K. A., 1977, *Pramana*, **9**, 471. DESTRADE, C., GASPAROUX, H., FOUCHER, P., NGUYEN, H. T., MALTHETE, J., and JACQUES, J., 1983, *J. Chim. phys.*, **80**, 137. GUILLON, D., WEBER, P., SKOULIOS, A., PIECHOCKI, C., and SIMON, J., 1985, *Molec. Crystals liq. Crystals*, **130**, 223.
- [13] ASHCROFT, N. W., and MERMIN, N. D., 1976, *Solid State Physics* (Holt-Saunders International Editions).
- [14] PLATÉ, N. A., and SHIBAEV, V. P., 1974, *J. Polym. Sci. Macromolec. Rev.*, **8**, 117.
- [15] WEAST, R. C. (editor), *Handbook of Chemistry and Physics*, 64th edition (CRC Press).
- [16] CAREY, F. A., and SUNDBERG, R. J., 1984, *Advanced Organic Chemistry, Structure and Mechanisms*, second edition (Plenum Press).
- [17] SEURIN, P., GUILLON, D., and SKOULIOS, A., 1981, *Molec. Crystals liq. Crystals*, **65**, 85.
- [18] ABIED, H., GUILLON, D., SKOULIOS, A., WEBER, P., GIROUD-GODQUIN, A. M., and MARCHON, J. C., 1987, *Liq. Crystals*, **2**, 269.
- [19] SCHILLING, F. C., BOVEY, F. A., and ZEIGLER, J. M., 1986, *Macromolecules*, **19**, 2309. SCHILLING, F. C., BOVEY, F. A., LOVINGER, A. J., and ZEIGLER, J. M., 1986, *Macromolecules*, **19**, 2660.
- [20] DOOLITTLE, A. K., 1951, *J. appl. Phys.*, **22**, 1471.
- [21] GUILLON, D., SKOULIOS, A., and BENATTAR, J. J., 1986, *J. Phys., Paris*, **47**, 133.
- [22] KITAIGORODSKY, A. I., 1973, *Molecular Crystals and Molecules* (Academic Press).
- [23] VON SYDOW, E., 1955, *Acta crystallogr.*, **8**, 557.
- [24] WYCKOFF, R. W. J., 1964, *Crystal Structures* (Interscience Publishers, J. Wiley and Sons).
- [25] ROBERTSON, J. M., 1953, *Organic Crystals and Molecules* (Cornell University Press).
- [26] BERNAL, J. D., 1959, *Nature, Lond.*, **183**, 141. SCOTT, D. G., 1960, *Nature, Lond.*, **188**, 908. COXETER, H. S. M., 1958, *Illinois J. Math.*, **2**, 746.
- [27] KREUDER, W., and RINGSDORF, H., 1983, *Makromolek. Chem. rap. Commun.*, **4**, 807. PERCEC, V., and PUGH, C., 1989, *Side Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Blackie).
- [28] FEUGHELMAN, M., LANGRIDGE, R., SEEDS, W. E., STOKES, A. R., WILSON, H. R., HOOPER, H. C. W., WILKINS, M. H. F., BARKLAY, R. K., and HAMILTON, L. D., 1955, *Nature, Lond.*, **175**, 834. LUZZATI, V., 1963, *Prog. Nucleic Acid. Res.*, **1**, 347. SALUDJIAN, P., and LUZZATI, V., 1967, *Poly- $\alpha$ -aminoacids*, edited by G. D. Fasman (Marcel Dekker).
- [29] SCHILLING, F. C., LOVINGER, A. J., ZEIGLER, J. M., DAVIS, D. D., and BOVEY, F. A., 1989, *Macromolecules*, **22**, 3055.