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## Liquid crystalline nature of poly(di-*n*-hexylsilane) (\*)

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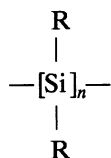
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**Résumé.** — Dans ce travail, on étudie par diffraction des rayons X et microscopie optique en lumière polarisée la structure en fonction de la température d'un poly(di-*n*-hexylsilane). Au-dessus de 42 °C, la structure correspond à une phase liquide cristalline colonnaire de type hexagonal, chaque colonne étant formée par une chaîne macromoléculaire. La période d'empilement des unités répétitives dihexylsilicium le long de l'axe colonnaire est voisine de 1.56 Å. Loin d'être toute trans comme dans le cristal à basse température, la conformation des chaînes d'atomes de silicium est vraisemblablement proche d'une conformation hélicoïdale toute-gauche.

**Abstract.** — Polarizing optical microscopy and X-ray diffraction were used to study the structure of poly(di-*n*-hexylsilane) as a function of temperature. Liquid crystalline in nature, the polymer above 42 °C shows hexagonal columnar symmetry, with the columns formed of single polymer chains. The stacking period of the dihexylsilicon repeat units along the columnar axis is of about 1.56 Å. Far from being all-trans as in the low-temperature crystal, the backbone conformation in the high-temperature mesophase is presumably close to an all-gauche helical conformation.

### Introduction.

Poly(disubstituted silanes) are polymers that contain only silicon atoms in the backbone :



The first polysilane derivative was synthesized more than sixty years ago [1]. But it was not until very recently that polysilanes with various substituents, in particular high molecular

(\*) This work was presented as a poster, outside the official program, at the Freiburg XII<sup>th</sup> International Liquid Crystal Conference, on August 17, 1988.

weight and soluble poly(dialkyl silanes), started to attract considerable attention, due in particular to their spectroscopic properties [2] : UV absorption, thermochromism, tendency for electron transfer to produce semi-conductors. A number of new promising applications were also discovered, notably in the field of silicon carbide ceramic precursors [3], photoconductivity [4] and microlithography [5]. The unusual properties of these materials, along with their complex photoelectron spectra, were interpreted as being closely related to the backbone conformation [6].

In order to study the relationship between the spectroscopic properties and the backbone conformation of poly(dialkyl silanes), X-ray diffraction studies have been carried out, especially for the dihexyl  $[R=CH_3-(CH_2)_5-]$  derivative (PDHS) [7]. This particular polymer was found to show a blue shift spectroscopic transition upon heating above 42 °C ; at the same temperature, differential scanning calorimetry revealed a strong endotherm, indicative of an abrupt thermodynamic phase transition [2]. At room temperature, the wide angle X-ray diffraction patterns displayed over forty distinct (and unusually sharp for a polymer) reflections characteristic of a well developed three-dimensional crystalline structure. Suitably indexed, the reflections could be interpreted in terms of a monoclinic cell ( $a = 13.75 \text{ \AA}$  ;  $b = 21.82 \text{ \AA}$  ;  $\gamma = 88.0^\circ$  ;  $c = 4.07 \text{ \AA}$ ) with two molecules per unit cell. The crystallographic analysis of the experimental data suggested a planar zig-zag (all-trans) conformation for the silicon backbone, and a slightly tilted orientation of the hexyl side chains with respect to the polymer chain [7]. Above the transition temperature at 42 °C, X-ray patterns showed an amorphous halo in the wide-angle region, at 4.6 Å, associated with the disordering of the hexyl side chains, and two sharp reflections in the small-angle region, at 13.5 Å and 7.6 Å respectively, interpreted to correspond to the polymer interchain distance. The thermochromic transition at 42 °C was considered, therefore, as being closely related to the disordering of the hexyl side chains with subsequent disordering of the polymer backbone itself. Analyzed according this same interpretation, further X-ray studies of PDHS simply added that the polysilane chains would be packed as cylinders on a hexagonal lattice [8].

The present paper is concerned with a more extensive study of the PDHS structure above 42 °C. It provides evidence showing that the structure of the polymer at high temperature is, in fact, liquid crystalline in nature, specifically of the columnar type.

## Results and discussion.

X-ray diffraction patterns of powder samples of PDHS in Lindemann capillaries were recorded photographically at several temperatures above 42 °C, using a Guinier focusing camera equipped with a bent quartz monochromator (copper  $K\alpha_1$  radiation from a Philips PW-1009 generator) and an electrical oven. In perfect agreement with previous observations [7, 8], they contain a diffuse ring at 4.6 Å, identical to that usually observed with alkanes in the molten state, and a series of sharp Bragg reflections in the small angle region, with reciprocal spacings in the ratio 1,  $\sqrt{3}$ ,  $\sqrt{4}$ ,  $\sqrt{7}$ , indicating a two-dimensional hexagonal lattice. The cell parameter of the hexagonal lattice at 54 °C is equal to 15.4 Å. The intensity sequence of the reflections is very strong, weak, very weak, very weak, respectively. The sharpness of the small-angle reflections was found to be comparable to that of the direct beam, suggesting a well developed two-dimensional ordering.

Such X-ray patterns are typical of the so-called columnar liquid crystals. These are obtained with a wide variety of substances, among which must be mentioned many alkaline earth metal soaps [9], and quite a few alkylsubstituted disk-like organic molecules [10]. The main feature of the columnar ordering is that the molecules pile up over one another so as to form infinitely long columns with the aliphatic chains spreading outwards in a disordered state. The columns

are then assembled according to two-dimensional crystal lattices, generally hexagonal in symmetry. It seems, therefore, that the structure of PDHS at high temperatures corresponds to nothing more than a classical columnar liquid crystalline ordering, the core of each column being formed by the silicon backbone of the polymer chain and the intracolumnar space being filled by the aliphatic chains in the disordered state.

Similar structures have also been obtained in concentrated solution with rigid rod-like polymers of biological interest, such as desoxyribonucleic acids [11] or polypeptides [12]. Here, the columns are formed by fully extended individual polymeric chains, instead of resulting from the stacking of small molecules. The columnar ordering must very likely originate in the important stiffness of the molecules, due either to the intramolecular stacking of the flat puric and pyrimidic residues (desoxyribonucleic acids), or to the intramolecular hydrogen bonding (polypeptides). This suggests a similar stiffness for PDHS in the columnar liquid crystalline state; incidentally, significant stiffness has already been claimed for PDHS on the grounds of the obvious severe steric crowding of the polymer due to the hexyl side chains on every backbone silicon atom [13].

It has already been reported that the strong birefringence of crystalline PDHS films decreases markedly upon heating above the transition temperature but does not vanish completely up to very high temperatures [7]. The persistence of the birefringence is consistent with the liquid crystalline nature of the material above 42 °C; it prompted us to look for optical textures characteristic of the columnar structure. The observations have been carried out with a Leitz polarizing microscope equipped with a Mettler FP82 hot stage. Thin films of PDHS, about 50 μm thick, as homogeneous as possible, were produced on glass slides by slow evaporation of relatively concentrated toluene solutions of the polymer. In order to get clear of the solvent and also to let the columnar structure develop completely, these were then annealed at a series of temperatures between 50 °C and 120 °C for several hours. The usual procedure to reveal characteristic textures of liquid crystals is to enter the mesomorphic state by cooling the sample slowly from the isotropic melt. With PDHS, this procedure is not applicable, since the product decomposes at 250 °C prior to melting. As a result, the microscopic observations of PDHS in this work were done using directly the films as prepared from evaporation. Nevertheless, the textures obtained (Fig. 1) were conclusively similar to those currently observed with columnar mesophases [14] and, consequently, confirmed the columnar liquid crystalline structure of PDHS.

With columnar liquid crystals, it has become customary to describe the structure more precisely by determining the stacking period,  $h$ , along the columnar axis. This parameter corresponds to the average projected length of one repeat unit on the axis of the columns. It can easily be deduced from the hexagonal cell parameter,  $D$ , provided the specific volume,  $v$ , of the material, and the molecular weight,  $M$ , of the repeat unit are known ( $N$  is Avogadro's number) [9]:

$$h = 2 Mv / (\sqrt{3} \cdot ND^2).$$

In the case of PDHS, the repeat unit of the polymer chain may be defined as formed of one dihexylsilane group ( $M = 198.4$ ). The specific volume,  $v$ , in the columnar state can be estimated ( $v = 0.971 \text{ cm}^3/\text{g}$ ) from the value of  $v$  determined in the crystalline state ( $v = 0.926 \text{ cm}^3/\text{g}$ ) using the cell parameters of the crystal [7] (as usual, a rough 5% increase of the specific volume was assumed to occur upon melting of the aliphatic chains). With these values, the stacking period  $h$  turns out to be equal to 1.56 Å at 54 °C. It is of interest to note that the double of this value (3.12 Å) is smaller than the length (3.84 Å) of one zig-zag of silicon atoms as deduced from the known diamond structure of silicon crystals [15]. That

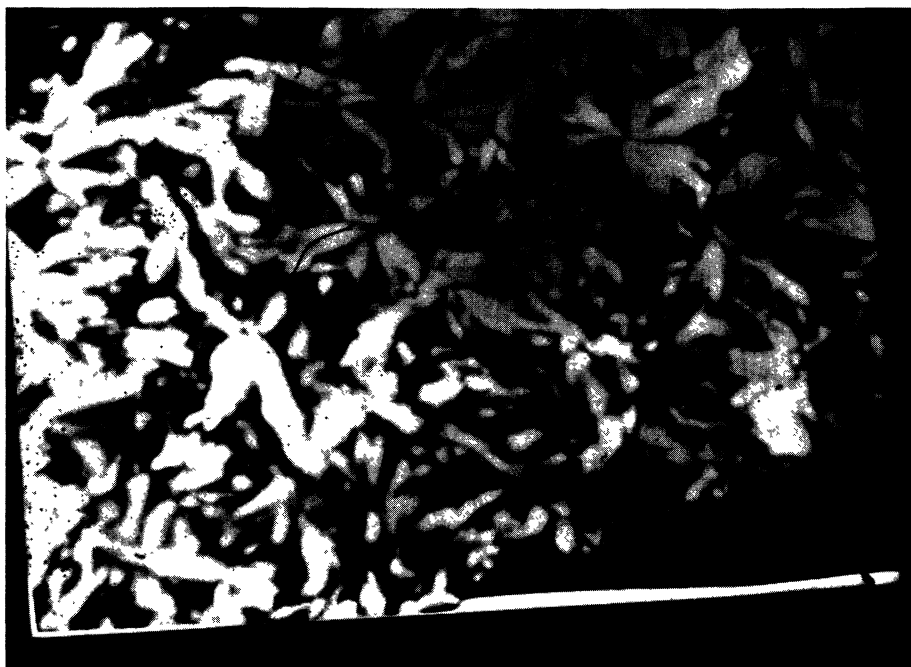


Fig. 1. — Optical texture of the PDHS columnar mesophase at 80 °C.

means that, in the liquid crystalline state, the silicon backbone of PDHS is not fully extended to reach a planar all-trans conformation but coiled.

For the columnar liquid crystals obtained with alkaline earth metal soaps, the stacking period along the columnar axis is found to be independent both of the temperature and the length of the aliphatic chains in the molecules. This independence was interpreted as an indication of a compact and regular packing of the polar heads within the columnar cores, in close connection with the coordination geometry of each metal atom considered [9]. In the particular case of copper (II) soaps, this was recently confirmed by EXAFS spectroscopy [16]. To investigate the thermal behavior of the stacking period in the columnar phase of PDHS, a series of small-angle X-ray diffraction patterns were recorded automatically as a function of temperature. The custom-made X-ray camera used was equipped with a bent gold-plated glass mirror (nickel-filtered copper radiation from an Elliott GX20 rotating anode generator) and a computer-assisted electrical oven. As shown in figure 2, the hexagonal cell parameter increases very slightly with temperature. From a linear least-square fit of the experimental data ( $D(\text{Å}) = 15.41 + 4.13 \times 10^{-3} T(^{\circ}\text{C})$ ), one finds a relative expansion coefficient of  $(1/D) \delta D / \delta T = 2.7 \times 10^{-4} \text{ K}^{-1}$ . By assuming a relative volume expansion coefficient of  $(1/v) \delta v / \delta T = 7 \times 10^{-4} \text{ K}^{-1}$  (which is a common value for liquid crystals [17]), one finds for the stacking period of PDHS a thermal coefficient of  $(1/h) \delta h / \delta T = (1/v) \delta v / \delta T - 2(1/D) \delta D / \delta T = 1.6 \times 10^{-4} \text{ K}^{-1}$ , in good agreement with values usually found with polymeric crystalline solids [18]. By analogy with the above mentioned columnar soaps, this result strongly suggests the idea of a regular and temperature independent arrangement of the silicon atoms for the PDHS backbone.

The simplest possible regular arrangement for the silicon atoms in the backbone is probably the helical arrangement with all atoms being equivalent [19]. These would all be located at a constant distance  $\rho$  from the axis, experiencing the same displacement  $h$  and the same

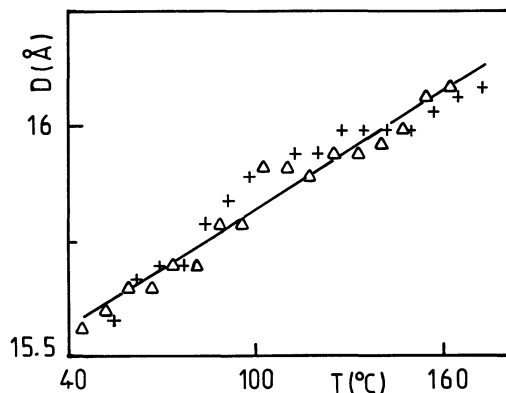


Fig. 2. — Intercolumnar distance of PDHS as a function of temperature : (+) and ( $\Delta$ ) correspond to spacings measured upon heating and cooling, respectively ; full line represents a linear least-square fit of the experimental data.

rotation  $\theta$  about the axis on passing from one atom to the next. Each helical arrangement obviously goes parallel with a particular conformation of the silicon backbone, defined by the Si-Si bond length,  $\sigma$ , the Si-Si-Si bond angle,  $\varphi$ , and the internal rotation angle,  $\tau$  (Fig. 3). Simple geometrical considerations show that [20] :

$$\cos (\theta / 2) = \cos (\tau / 2) \sin (\varphi / 2)$$

$$h \sin (\theta / 2) = \sigma \sin (\tau / 2) \sin (\varphi / 2)$$

$$2 \rho^2 (1 - \cos \theta) + h^2 = \sigma^2 .$$

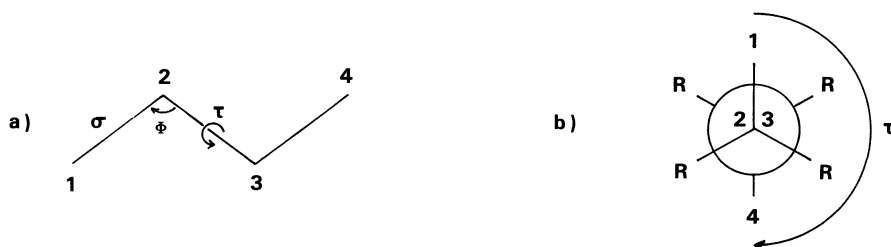


Fig. 3. — (a) Schematic view of polysilane backbone conformation ;  $\sigma$  is the Si-Si bond length,  $\varphi$  is the Si-Si-Si bond angle,  $\tau$  is the dihedral angle of the Si-Si-Si-Si bond system ( $\tau = 180^\circ$  corresponds to the angular deviation from the trans planar zig-zag conformation), running numbers correspond to successive Si atoms. (b) Newman representation [22] of the poly(di- $n$ -alkylsilane), viewing the atoms along bond 2-3 with 2 nearer the observer than 3 : R is the alkyl group.

The helical order,  $n = 2 \pi / \theta$ , the dihedral angle of the Si-Si-Si-Si bond system,  $\tau$ , and the radial distance of the silicon atoms from the axis,  $\rho$ , can easily be deduced from the above equations and calculated as a function of  $\varphi$ ,  $\sigma$ , and  $h$  :

$$\cos^2 (\pi / n) = \frac{\sigma^2 \sin^2 (\varphi / 2) - h^2}{\sigma^2 - h^2} \quad (1)$$

$$\sin^2 (\tau/2) = \frac{h^2}{(\sigma^2 - h^2) \operatorname{tg}^2 (\varphi/2)} \quad (2)$$

$$|\rho| = \frac{(\sigma^2 - h^2)}{2 \sigma \cos (\varphi/2)}. \quad (3)$$

By taking for  $\sigma$  the standard value of a Si-Si bond (2.355 Å) and for  $h$  the experimental value found in this work (1.56 Å), one finds that  $n$  lies consistently in the range from 3.05 to 5.24 when  $\varphi$  goes from 100 to 130° (Fig. 4). Clearly, this result is at variance with the suggestion of a  $7_3$  helix ( $n = 7/3$ ) found to correspond to the lowest conformational energy of PDHS for  $\varphi = 120^\circ$  [13]. It is essential to note that the calculated value of the helical order is little affected ( $\leq 5\%$ ) by the dubiousness ( $\leq 5\%$ ) of the specific volume of PDHS in the mesomorphic state and hence of the axial displacement of the silicon atoms. As for the

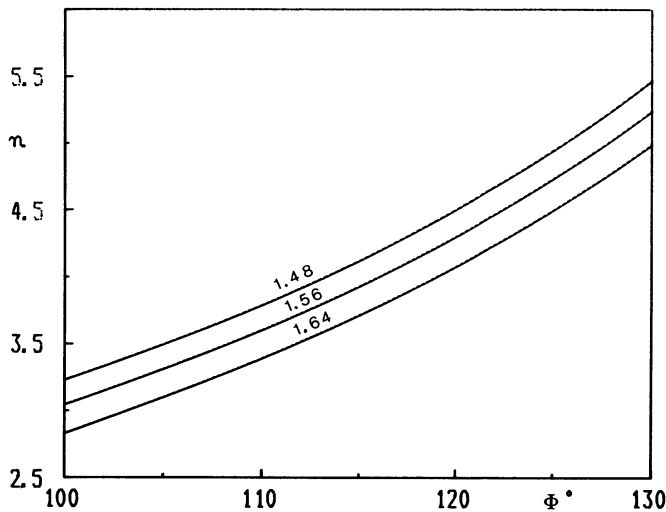


Fig. 4. — Order of the helical axis  $n$  as a function of  $\varphi$ , calculated with equation (1) for three values of  $h$  ( $1.56 \text{ \AA} \pm 5\%$ ).

dihedral angle of the Si-Si-Si-Si bond system, one finds that  $\tau$  varies from 95.58 to 48.70° when  $\varphi$  goes from 100 to 130° (Fig. 5). This suggests a strongly gauche conformation for the silicon backbone. Here again, the torsion of the backbone out of the all-trans planar zig-zag conformation is little affected by the experimental error on  $h$ . Finally, regarding the radial distance of the silicon atoms from the columnar axis, one finds that it ranges from 1.03 to 1.56 Å when  $\varphi$  goes from 100 to 130° for  $h = 1.56 \text{ \AA}$  (Fig. 6). The average radius of the columnar silicon core would then be of about  $R = \rho + \sigma/2 = 2.36 \text{ \AA}$ . The intensity of the small-angle Bragg reflections of the columnar mesophase (as the radial distance of the silicon atoms from the columnar axis is of the same order of magnitude as the radius of the silicon atoms themselves, one can safely compare the columnar cores with solid rods of radius  $R$ ) being proportional to  $[J_1(2 \pi R s)/2 \pi R s]^2$  where  $J_1$  is the first order Bessel function and  $s = 2 \sin \theta / \lambda$  the Bragg reciprocal spacing [21], the calculated intensity sequence of the reflections is in the ratio 600 : 21 : 3 : 6, in perfect agreement with the experimental observations (see above).

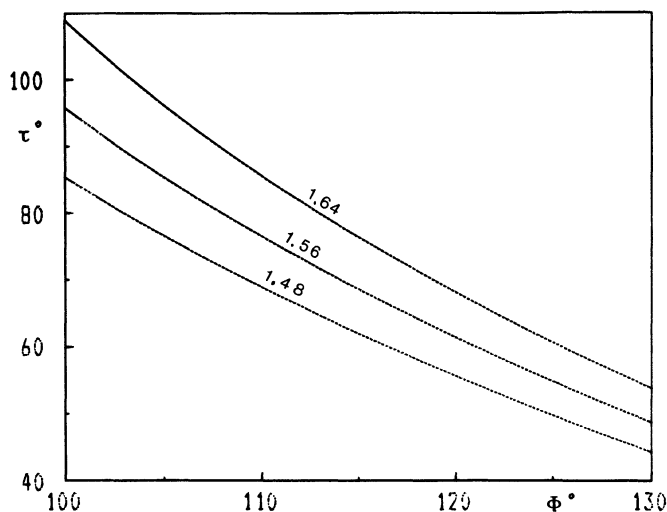


Fig. 5. — Internal torsion  $\tau$  of the Si-Si-Si-Si bond system as a function of  $\phi$ , calculated with equation (2) for three values of  $h$  ( $1.56 \text{ \AA} \pm 5\%$ ).

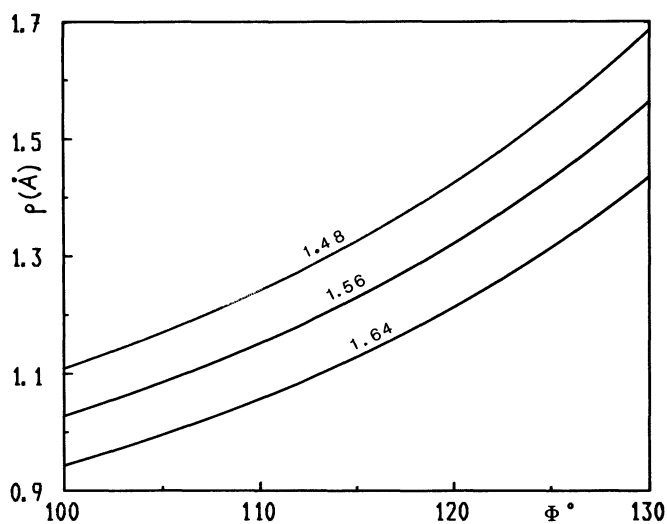


Fig. 6. — Radial distance  $\rho$  of the silicon atoms from the helical axis as a function of  $\phi$ , calculated with equation (3) for three values of  $h$  ( $1.56 \text{ \AA} \pm 5\%$ ).

The strongly gauche conformation of the silicon backbone suggested in the present work raises, of course, the important question of whether or not this conformation is realistic from the energetic point of view. All-gauche or nearly all-gauche conformations have indeed been obtained with a variety of polymers; poly(oxyethylene) in the orthorhombic ( $G_4 - 2/1$ ) or in the trigonal ( $G'_{18} - 9/5$ ) form is a classical example of such a behavior (see p. 14 in Ref. [20]). Quite interestingly, however, all these polymers are significantly deprived of pendant groups. In substituted polymers, such as polyvinyls or polyacrylates, all-gauche conformations are highly energetic for steric reasons, and hence disfavored. The length of the Si-Si bonds is



importantly larger than that of the C—C or the C—O bonds ; considerably relieved as a result, the hard core repulsive interactions of the pendant groups play a much less decisive part in polysilanes than in usual polymers. This fact makes it possible for the polymer backbone in poly(di-*n*-alkylsilanes) to adopt an all-gauche helical conformation quite easily, as shown in figure 7.

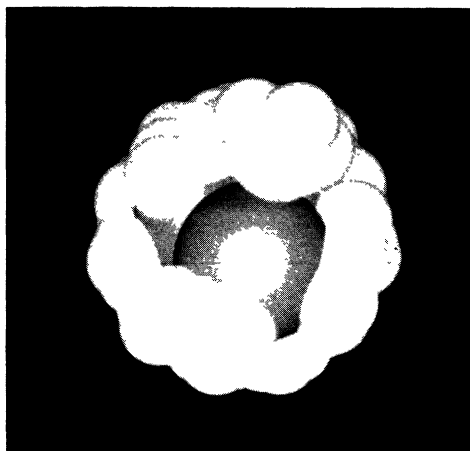


Fig. 7. — Axial view of a poly(dimethylsilane) molecule with a  $3_1$  all-gauche helical conformation. Large, medium and small spheres stand for silicon, carbon and hydrogen atoms, respectively. Sybyl-software graphic simulation obtained by Mrs Maia of Evans and Sutherland (France) :  $\sigma = 2.355 \text{ \AA}$ ,  $\varphi = 109.323^\circ$ .

A systematic study of the columnar liquid crystalline phases of poly(dialkylsilanes) with a variety of alkyl residues is currently in progress to definitely establish the all-gauche helical conformation suggested in the present work, with a helical order  $n = 2 \pi / \theta$  very likely in the range from 3.5 to 4 ; and to analyze the influence of the bulkiness of the alkyl substituent in the exact conformation of the silicon backbone.

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