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Structural transformations in poly(di-n-alkylsiloxane)s with alkyl side groups containing 7 to 10 carbon atoms

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Temperature dependent X-ray diffraction studies of poly(di-n-alkylsiloxane)s substituted with side chains containing 7 to 10 carbon atoms have been carried out in order to elucidate the crystalline structure of these materials. In contrast to their lower substituted homologues, no evidence for the presence of a hexagonal columnar mesophase could be found for the investigated materials. At low temperatures, far below the melting temperature, the polysiloxane backbones are assumed to pack in an orthorhombic lattice, with the n-alkyl side chains in a planar all-*trans* conformation and oriented perpendicularly to the backbone. The paraffinic n-alkyl side chains were found to crystallize in an orthorhombic lattice. The thermal behaviour of the investigated materials has been observed to show an odd-even effect. Whereas poly(di-n-heptylsiloxane) and poly(di-n-nonylsiloxane) were found to melt in a single step, an intermediate state of order was observed for poly(di-n-octylsiloxane) and poly(di-n-decylsiloxane) upon heating from the crystalline to the isotropic state. For this intermediate state, a pseudohexagonal packing of the n-alkyl side chains is proposed.

(Keywords: poly(di-n-alkylsiloxane)s; structure; side chains)

INTRODUCTION

Poly(di-n-alkylsiloxane)s with two to six carbon atoms per side chain are of particular interest since they are able to form a columnar liquid crystalline phase[1-4]. In contrast to rod-like, disc-like or amphiphilic molecules, for which mesophases of similar two-dimensional structures have been observed[5] the poly(di-n-alkylsiloxane)s do not contain any mesogenic moieties. Instead, the molecules are highly flexible and undergo in the first instance only dispersive interactions with each other. The organic/inorganic hybrid structure as well as the mesophase behaviour can be compared with that of poly(di-n-alkylsilylene)s[6-8] and polyorganophosphazenes[9-11]. It has been suggested that the stability of the mesophase depends on a delicate balance of intra- and intermolecular interactions, which changes upon an increase in temperature. The presence of the liquid-like conformational disorder of the macromolecular backbone and the side chains[2,3] motivated Wunderlich to coin the term CONDIS crystals[12,13]. Recently, it has been demonstrated that the shape dependence of the averaged molecular interaction potential can be modelled to explain quantitatively the thermodynamic stability of such defect saturated ordered states[14]. Thus, the interaction and packing of the side chains of the comb-type poly(di-n-alkylsiloxane)s is an essential factor for the determination of the ordered and mesomorphic chains. In this respect, it is of interest to study the influence of the length of the side chains on the crystallization and phase behaviour.

So far, structural investigations by means of X-ray analysis have been performed on polydimethylsiloxane (PDMS)[15], polydiethylsiloxane (PDES)[1] and poly(di-n-propylsiloxane) (PDPS)[16]. In order to determine the unit cell parameters, measurements have been performed on crosslinked oriented samples, or in the case of PDPS on a monocrystal. Polymorphism has been found for PDES at low temperature, i.e. a monoclinic and a tetragonal modification. PDPS was found to display a tetragonal unit cell at room temperature. The Si-O backbone conformation was proposed to be planar *cis-trans*, with an identity period of 4.72 Å for PDES.

In the present work, a series of higher homologues has been studied, with side chains containing 7 to 10 carbon atoms, i.e. poly(di-n-heptylsiloxane) (PDHepS), poly(di-n-octylsiloxane) (PDOS), poly(di-n-nonylsiloxane) (PDNS) and poly(di-n-decylsiloxane) (PDDS). The mechanical properties of the samples did not allow the preparation of oriented samples. However, the possibility to compare diffraction curves within the homologous series provided a means to assign the observed reflections and to find an interpretation for the structural changes upon heating.

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EXPERIMENTAL

Synthesis

Polymer synthesis has been carried out by cationic ring opening polymerization under argon as described before[2,17,18]. Crude polymeric products were precipitated twice in refluxing isopropanol in order to remove oligomeric side products and traces of the initiator. After fractionation in toluene/ethanol, the polymers were dried under vacuum at 110°C. High molecular weight fractions were selected for the study described here (*Table 1*).

Differential scanning calorimetry

A Perkin-Elmer DSC-7 equipped with a PE-7700 computer and TAS-7 software was used to monitor the thermal transitions of the bulk samples at a scan rate of $5\,\mathrm{K\,min^{-1}}$. Transition entropies were calculated assuming thermodynamic equilibrium, i.e. $\Delta H = T\Delta S$. Cyclohexane, gallium and indium were used as calibration standards. The onset of the recorded endotherm upon heating was taken as the transition temperature.

X-ray diffraction

Diffractograms of the bulk polymers were recorded at different temperatures using a Guinier-Simon camera with monochromatic CuKα radiation and a circular film. In order to detect scattering at angles as low as 1.5° (2θ), a slight adjustment of the beam stop was made. Flat samples with a thickness of 1 mm were obtained by pressing the polymers at 60°C. The specimen was mounted into the camera and the required temperature was attained by a constant flow of heated nitrogen gas, controlled by a thermocouple in the direct vicinity of the sample. The temperature gradient in the gas stream was checked at the end of the nozzle by means of an additional thermocouple, and it was found that the difference at the two opposite ends of the irradiated section of the sample was $<2\,\mathrm{K}$. Temperature variation of the nitrogen flow during the experiment was not more than $\pm 2\,\mathrm{K}$.

For temperature dependent measurements, the sample was cooled to the lowest required temperature at a rate of $5\,\mathrm{K\,min^{-1}}$. Before starting an exposure, the specimen was kept for 30 min at this temperature. After exposure, the specimen was heated at a rate of $10\,\mathrm{K\,min^{-1}}$, followed by annealing at the new temperature for 30 min before the next diffraction pattern was recorded. After attaining the highest required temperature, an additional diffractogram was recorded at ambient temperature in order to check whether the structural changes in the investigated materials were reversible. Optical density data were collected from the circular films using a linear microdensitometer LS20 controlled by SCANPI software.

RESULTS AND DISCUSSION

D.s.c. measurements are shown in *Figure 1* and summarized in *Table 1*. Samples were cooled from 333 to 193K at a rate of $5\,\mathrm{K\,min^{-1}}$, before recording a heating trace at the same rate. All samples exhibited at least one d.s.c. endotherm. Only one broad transition with a long low temperature shoulder was observed for PDHepS and PDNS with an onset temperature of 268 and 298K, respectively. For PDOS as well as PDDS two transitions were observed at 272/296 and 286/313K, respectively. By means of optical polarizing microscopy, it was observed that upon passing the single transition in the case of PDHepS and PDNS or the upper disordering transition in the case of PDOS and PDDS, the isotropic phase was formed. At this transition, the physical appearance of the materials changed from fairly tough solids to viscoelastic fluids, which were markedly different from the waxy semi-solid hexagonal columnar poly(di-n-alkylsiloxane)s[1,2]. No glass transition could be observed for all investigated polymers. Polarized optical microscopy indicated the appearance of birefringence only in the case of PDHepS, when a sample was slightly sheared or pressed between two microscope slides[18].

In order to elucidate the structural transformations upon heating, diffractograms of the bulk polymers have been recorded at temperatures which were relatively far from the actual transition temperatures (*Figures 2–5*).

Diffractograms which were obtained below the d.s.c. transitions exhibited few reflections with a pronounced difference in intensity and characterized by a large halfwidth. Apparently, the crystallographic ordering in

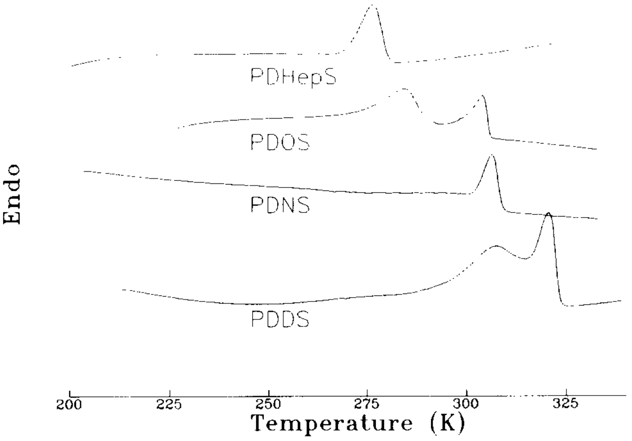

Figure 1 D.s.c. heating scans (rate $5\,\mathrm{K\,min^{-1}}$) of poly(di-n-heptylsiloxane), poly(di-n-octylsiloxane), poly(di-n-nonylsiloxane) and poly(di-n-decylsiloxane)

Table 1 Thermal behaviour of poly(di-n-alkylsiloxane)s as observed by d.s.c.

Polymer	DP^a	T_{d1} (K)	ΔH_{d1} ($\mathrm{kJ\,mol^{-1}}$)	ΔS_{d1} ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T_{d2} (K)	ΔH_{d2} ($\mathrm{kJ\,mol^{-1}}$)	ΔS_{d2} ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T_i^b (K)
DPHepS	18 450		-		268	12	45	648^c
PDOS	1 617	272	15.8	58	296	4.1	13.7	301
PDNS	3 829	-		-	298	20	68	304
PDDS	2 750	286	21	72	313	9	29	320

[a] Based on M_w from g.p.c. according to universal calibration
[b] Disappearance of birefringence
[c] Birefringence is only observed under slight pressure

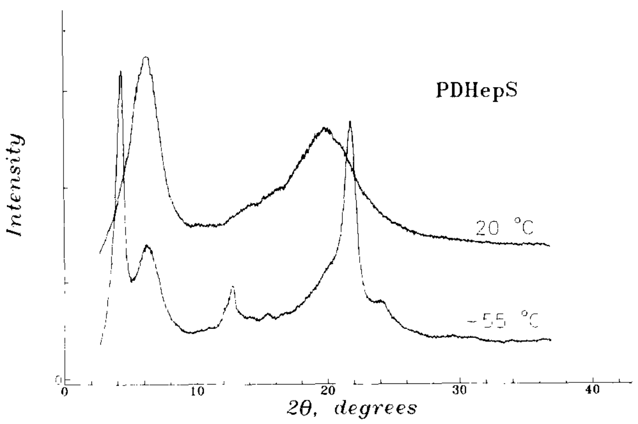

Figure 2 Diffractograms of bulk poly(di-n-heptylsiloxane) at different temperatures. The diagrams have been offset vertically for clarity

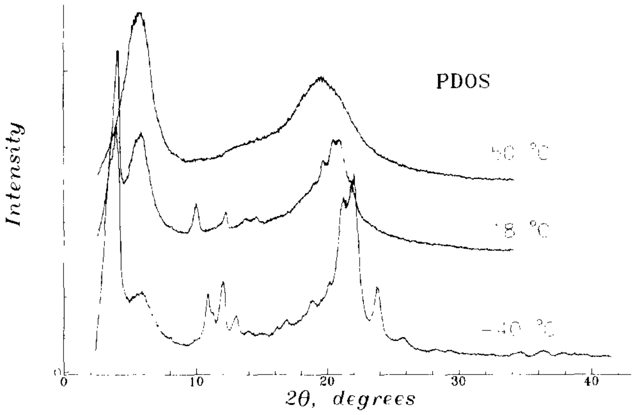

Figure 3 Diffractograms of bulk poly(di-n-octylsiloxane) at different temperatures. The diagrams have been offset vertically for clarity

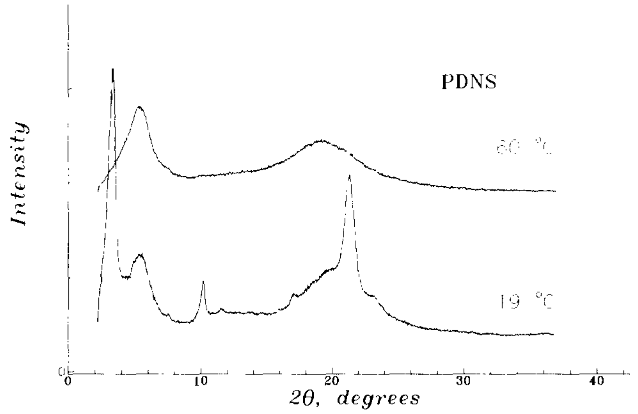

Figure 4 Diffractograms of bulk poly(di-n-nonylsiloxane) at different temperatures. The diagrams have been offset vertically for clarity

these polymers is rather poor, even at low temperatures. This is in strong contrast to the results for poly(di-n-hexylsiloxane), which indicated a well organized three-dimensional crystallographic ordering in the low temperature state[2]. There are three basic features to be noted in the diffractograms of this low temperature state:

1. When the diffractograms of polysiloxanes with an even or an odd number of carbon atoms in the side chains are compared, it is evident that the number of reflections is higher for the even numbered cases.
2. There is a strong small-angle reflection, which shifts to smaller angles upon extension of the side chain length. In all cases, reflections are observed which correspond to the 3rd and 5th order of this small angle reflection.
3. A strong reflection at 21.5° (2θ) corresponding to $d = 4.15$ Å is observed at constant position for all poly(di-n-alkylsiloxane)s within the investigated series. In addition a weaker reflection appeared at 24.0° (2θ) corresponding to $d = 3.75$ Å.

The higher number of reflections for the even substituted poly(di-n-alkylsiloxane)s can be correlated with the fact that two endothermic transitions were observed for the polymers with an even number of side chain carbons, whereas only one d.s.c. transition was monitored for PDHepS and PDNS.

Regarding the second point, all polysiloxanes are characterized by a high electron density along the Si–O main chain relative to the side chain. Taking into account the rather poor ordering of the polymers at low temperatures, it seems reasonable to assign the low angle reflection to the scattering from the regularly arranged main chains.

When the Bragg distance corresponding to this small angle reflection is plotted against the number of carbon atoms in the side chains, a linear dependence is observed (*Figure 6*). For comparison and completeness, the data for

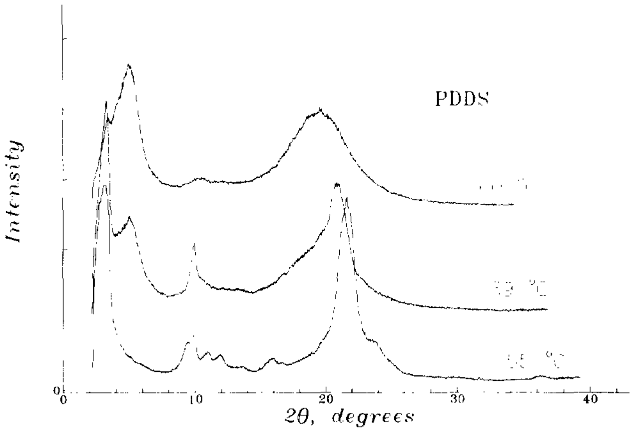

Figure 5 Diffractograms of bulk poly(di-n-decylsiloxane) at different temperatures. The diagrams have been offset vertically for clarity

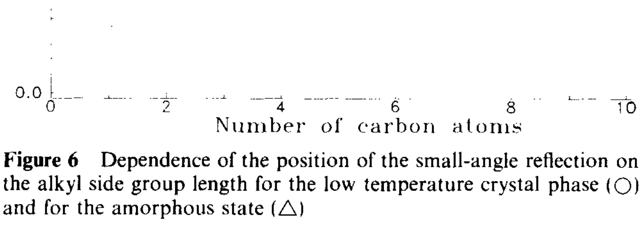

Figure 6 Dependence of the position of the small-angle reflection on the alkyl side group length for the low temperature crystal phase (○) and for the amorphous state (△)

poly(di-n-pentylsiloxane) and poly(di-n-hexylsiloxane)[2] are also shown. The slope yielded an increment of 2.55 Å which correlates well with the repeating distance for a planar all-*trans* sequence of methylene units. Extrapolation to zero side chain length yielded a value of 2.1 Å, which might be correlated to the diameter of the macromolecular backbone and is consistent with the van der Waals diameter of the silicon atoms of 2.34 Å[19]. In order to obtain a linear dependence on the side chain length with an increment of 2.55 Å, the macromolecules have to adopt a planar sheet structure with the alkyl side chains oriented perpendicularly to the backbone. Under the assumption of an all-*trans* side group conformation and a planar structure of the main chain, the experimental *d*-spacings correlated with the calculated distance between opposite methyl groups to within an accuracy of 0.5 Å.

As the position of the 4.15 and 3.75 Å reflections appeared to be practically independent of the side group length, these reflections can be assigned to the packing of the side chains. The same two reflections are observed for the orthorhombic unit cell of polyethylene (PE) or paraffins, in which case they are characterized by Miller indices 110 and 200. Hence, a similar packing of the alkyl side chains might be proposed for the investigated poly(di-n-alkylsiloxane)s. This type of crystallization seems to be plausible in view of the paraffin-like nature of the n-alkyl side groups and the similarity existing between the identity period of the siloxane backbone and the *b*-edge of the rhombic unit cell in paraffins or PE.

Figure 7 depicts the proposed packing. The interlayer distance equals the value of $a = 7.5$ Å, where a is the PE unit cell parameter. The all-*trans* arrangement of the side chains does not fit perfectly, because of insufficient separation between the nearest side chains along the *a*-direction. However, this can be easily accommodated by a slight conformational change, e.g. by introduction of one *gauche* conformer into each side chain. Assuming that the main chain conformation for all investigated homologues is similar to that of PDES, for which a *cis–trans* conformation has been proposed[1], the identity period along the *c*-axis for all investigated homologues has been estimated to be 5 Å. The *b*-parameter of the solixane unit cell is equal to the experimental *d*-spacing.

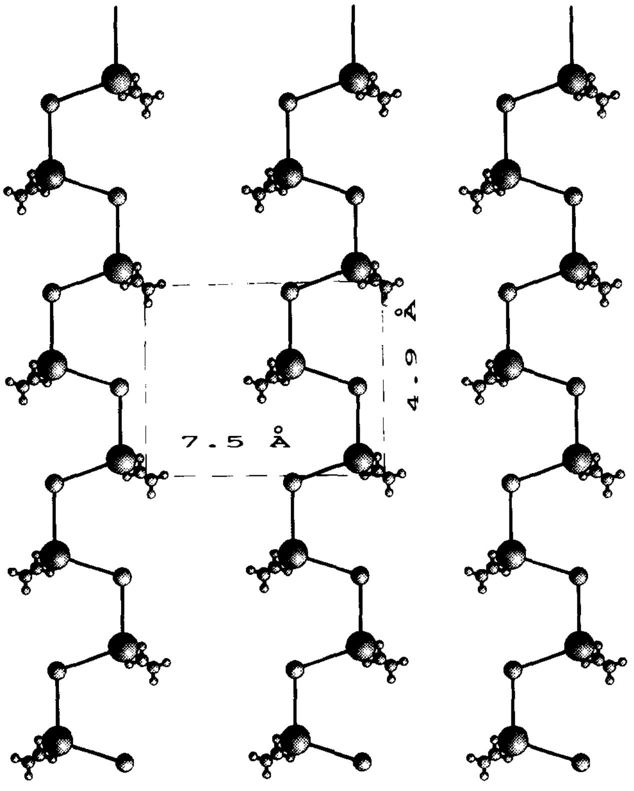

Figure 7 Schematic presentation of the proposed structure of poly(di-n-alkylsiloxane)s in the low temperature crystal state

Based on the proposed side chain crystallization and the symmetry of a single polymer molecule, it is reasonable to assume that the packing of the main chains of the investigated polymers is orthorhombic or nearly orthorhombic. An attempt was made to calculate the density of the crystals based on this assumption, although it was not possible to refine the type of backbone packing from the X-ray data alone. Each unit cell contains two oxygen atoms, two silicon atoms and two side chains. Thus, in the case of PDDS and PDNS the crystallographic density amounts to 1.13 and 1.19 g cm^{-3}, respectively. The calculated values have been compared with the experimental macroscopic densities of semicrystalline PDDS and PDNS at 20°C, which are 0.924 and 0.929 g cm^{-3}, respectively. The difference with the calculated values might be attributed to the presence of a pronounced fraction of amorphous material at this temperature. X-ray diffraction curves showed that the crystallinity of the two polymers at 20°C was on the order of 40–50%.

In contrast to poly(di-n-alkylsiloxane)s substituted with n-ethyl to n-hexyl side groups, which have been shown to be capable of forming a hexagonal columnar mesophase, PDHepS and PDNS form an isotropic melt when the temperature is raised above the transition observed by d.s.c. In the case of PDOS and PDDS, which showed two transitions in the d.s.c. heating trace, melting occurred at the upper transition.

Diffractograms which were obtained from the isotropic melt (see *Figures 2–5*) consisted of two broad reflections, of which the stronger one was located in the small angle region. A comparable, broad small-angle reflection has been detected for amorphous poly(1-alkylethylene)s[20] and was explained by the existence of some short-range correlation in the positions of the main chains. For poly(1-alkylethylene)s with side chains containing 3 to 17 carbon atoms, it has been shown that the corresponding Bragg distance depended linearly on the number n of carbon atoms in the side chains. Extrapolation to $n = 0$ yielded a value $d_0 = 6.5$ Å which corresponded roughly to the diameter of the main chain. According to these results, the Bragg distance for the small-angle reflection can be taken as a measure for the average distance between the main chains in the amorphous state, which characterizes the average side chain conformation as well.

Similarly, the Bragg distances which are calculated directly from the small-angle reflections of the isotropic poly(di-n-alkylsiloxane)s displayed a linear correlation with n (*Figure 6*). This observation would be consistent with a comb-like conformation in the melt, which is perhaps best described as a tape. The increment per CH_2 group in the side chain amounted to 0.87 Å. This value is three times smaller than the value for an all-*trans* planar zigzag sequence of methylene units. The small increment indicates a disordered *gauche*-saturated conformation of the side chains in the amorphous state. Extrapolation to

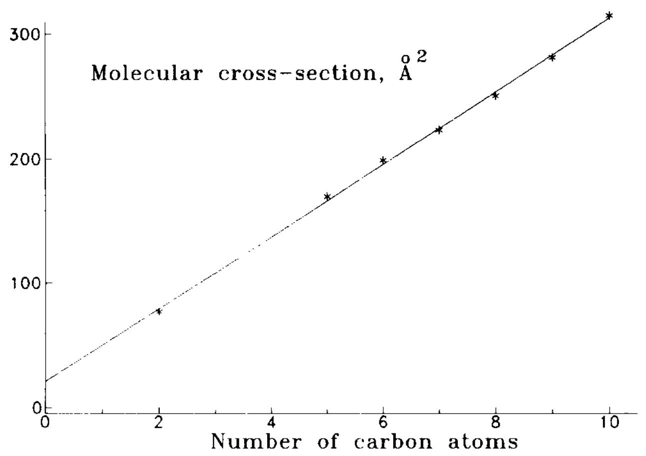

Figure 8 Dependence of the molecular cross-section of the poly(di-n-alkylsiloxane)s on the alkyl side group length in the amorphous state. Details are described in the text

zero side chain length resulted in a d_0 value of 8.3 Å, which is larger than the corresponding values for isotactic poly(1-alkylethylene)s and poly(n-alkylmethyacrylate)s[21], which have been obtained by the same method. To a first approximation, this could be attributed to the high flexibility of the Si–O backbone and the presence of main chain disordering. However, the value of 8.3 Å for the distance between bare $(Si–O)_n$ chains appears to be unreasonably large in comparison with the interchain distance of 4.55 Å displayed by molten PE.

A more consistent picture results, if the polysiloxane chains are assumed to be worm-like with the alkyl side chains forming a time-averaged circular envelope around the Si–O backbone. In this case, we expect to observe a linear relationship between the cylindrical cross-section of the macromolecules and the length of the side chains. The conformationally disordered side chains are assumed to fill the cross-section homogeneously. Assuming that the packing of the scattering objects in the amorphous state is close to hexagonal, the interchain distance d', corresponding to the a-parameter of the hexagonal unit cell, is equal to $2d/\sqrt{3}$. When the molecular cross-section $\pi(d'/2)^2$ was plotted *versus* n, the number of methylene groups per side chain, a linear relation was observed (*Figure 8*). Values for poly(di-n-pentylsiloxane) and for poly(di-n-hexylsiloxane) were added for comparison. Extrapolation to $n=0$ yielded a value of 20.8 Å^2 for the cross-section of the Si–O backbone. This value is comparable with the cross-section of PE in the pseudohexagonal state[22], which is on the order of 20–21 Å^2*. In addition to the small-angle reflection, all investigated polymers displayed a broad reflection with the maximum at ~19° (2Θ). The position of this wide-angle halo corresponded to the spacing of 4.55 Å, which coincides with the interchain distance for liquid paraffins or PE in the melt[22]. For poly(di-n-alkylsiloxane)s, the 4.55 Å spacing can be associated with the average lateral approach distance of the alkane side chains which are in a random conformation.

Both PDOS and PDDS were observed to form an intermediate state between the melt and the low temperature crystal phase (*Figure 1*). X-ray diffractograms deriving from this phase are depicted in *Figures 3* and *5*. Three characteristic features could be observed:

1. The number of diffraction peaks was less than in the low temperature state and the two broad reflections deriving from the amorphous melt became rather pronounced.
2. The low-angle reflection corresponding to the interchain distance between the siloxane main chains was shifted to wider angles. The decrease in the Bragg distance amounted to 1.2 Å for PDDS and 1.8 Å for PDOS, respectively.
3. Instead of the reflections corresponding to 4.15 and 3.75 Å, a single peak appeared with the maximum at 4.25–4.35 Å.

The first observation hinted at a significant decrease in the ordering of the crystal phase and the onset of partial melting. The shrinkage of the interbackbone distance, i.e. the distance spanned by the alkyl side chains, might be explained by the presence of *gauche* defects within the side groups. The third observation might give some information concerning the particular structure of the intermediate state. The reflections with $d=4.15$ Å and $d=3.75$ Å have been assigned above to the packing of the alkyl side chains in a paraffinic orthorhombic unit cell. The transformation into a single reflection at 4.25–4.35 Å at the transition into the intermediate state might be explained by a pseudohexagonal arrangement of the side chains. This interpretation would be consistent with the observed shrinkage of the interbackbone distance and with the behaviour of pure n-paraffins. It is well known that n-alkanes with an odd number of carbon atoms of $7<n<41$ exhibit a disordering transition from the three-dimensionally ordered state into the so-called rotator phase[23]. Within this phase, the chains possess high rotational mobility and are arranged hexagonally with an interchain distance of 4.25 Å in the (*ab*) plane. The rotator phase is not found for the even number n-alkanes[24]. Hexagonal packing of the side chains has been described in the literature for comb-shaped poly(n-alkylarylate)s, poly(n-alkylmethacrylate)s and poly(alkylvinylether)s as well as for n-alkylsubstituted polyesters[25]. In the latter case, the hexagonal phase was formed after a different crystallization procedure and has been shown to exist at temperatures as low as −196°C. Similar structures with hexagonal or monoclinic packing of the side chains have also been proposed for poly[bis-(2,2,3,3-tetrafluoropropoxy)phosphazene][26].

Contrary to pure paraffins, the intermediate state in poly(di-n-alkylsiloxane)s has been detected in the case of even numbers of side chain carbon atoms. This might be explained by the fixation of the n-alkyl side chains at the Si–O backbone, by which the number of carbon atoms which effectively determine the melting behaviour is equal to $n-1$.

It must be pointed out that no strict evidence of a two-dimensional hexagonal arrangement of the side chains in the intermediate state can be given, as we could not observe any other reflections in the wide-angle region in the diffractograms of PDOS and PDDS. In view of the rather low intensity of the 4.25 Å reflection and its relatively large halfwidth, pseudohexagonal ordering of

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* We suggest that deviations from a linear d *versus* n dependence which have been observed for poly(n-alkylethylene)s and poly(n-alkylmethacrylate)s with long side chains ($n>16$)[21] can be attributed to a gradual transition from a disordered comb structure to a worm-like averaged shape

the side chains cannot be assumed to persist over large distances.

CONCLUSIONS

Symmetrically substituted poly(di-n-alkylsiloxane)s with n-alkyl side groups containing 7 to 10 carbon atoms have been studied in the bulk state by temperature dependent X-ray measurements. In contrast to poly(di-n-alkylsiloxane)s with side chains containing two to six carbon atoms, no hexagonal columnar mesophase has been detected for the homologues substituted with longer side chains. Furthermore, the low temperature crystalline state of the investigated polymers appeared to be less ordered than in the case of poly(di-n-alkylsiloxane)s with shorter side chains. In all cases, an intense low-angle diffraction peak has been recorded. The spacing corresponding to this low-angle reflection exhibited a linear dependence on the length of the side chains, and has been assigned to scattering at intermolecular planes. At low temperatures, it is proposed that the packing of the polysiloxane chains is orthorhombic, with planar all-*trans* side chains oriented normal to the main chain. With respect to the packing of the side chains, a paraffinic orthorhombic unit cell has been suggested based on the X-ray data. The thermal behaviour of the investigated polymers hinted at the occurrence of an odd–even effect. Whereas PDHepS and PDNS melted in one step, a state of intermediate order was observed in the case of PDOS and PDDS, for which a pseudohexagonal packing of the side chains is proposed.

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