Structural correlation between the columnar mesophase and the melt in poly(di-n-alkylsiloxanes)

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SUMMARY:

Phase transitions of poly(dialkylsiloxanes) substituted with propyl and butyl groups are reported based on X-ray diffractometry. The structure in the mesophase and in the melt of polymers with 2 to 10 carbon atoms in each side chain is compared. Both phases display a linear dependence of the molecular cross-section on the length of the alkyl group demonstrating their structural similarity. By means of differential scanning calorimetry it is shown that the temperature range of the mesophase remains practically unchanged in width as well as in absolute temperature for dibutyl up to dihexyl substituted polysiloxanes.

Introduction

The melting behaviour of symmetrically substituted poly(di-n-alkylsiloxanes) has attracted considerable scientific attention because of the feasibility of mesophase formation despite the absence of classical mesogenic groups. This behaviour has been reported for poly(diethylsiloxane) (PDES)\(^1\)\(^2\), poly(dipropylsiloxane) (PDPS)\(^2\)\(^3\), poly(dibutylsiloxane) (PDBS)\(^4\), poly(dipentylsiloxane) (PDPeS)\(^5\) and poly(dihexylsiloxane) (PDHS)\(^5\) as well as for a number of poly(di-n-alkylsilylene)s\(^6\) and polyorganophosphazenes\(^7\)\(^8\).

The origin of the mesomorphic state in these organic-inorganic hybrid polymers is not entirely clarified. For poly(di-n-alkylsiloxanes) it has been observed\(^2\) that beyond a side group length of 6 carbon atoms, mesophase formation is impeded and melting occurs directly from the crystal phase\(^5\)\(^9\). Similar behaviour has been reported for poly(di-n-alkoxyphosphazene)\(^)\(^7\)\(^8\). In contrast, the denser substituted poly(di-n-alkylsilylene)s show mesophase formation even with side groups containing 14 carbon atoms\(^6\). It has been suggested that if the contribution of the side groups to the total melting entropy becomes too large, the columnar mesophase becomes unstable\(^2\). In this light, it is of interest to investigate the structural differences between the columnar mesophase and the melt, particularly with respect to the influence of the side group length.

This paper presents structural data obtained by wide-angle X-ray diffraction on PDPS and PDBS in the bulk state. In addition, a comparison is made of the structure of the columnar mesophase and of the melt formed by a series of poly(di-n-alkylsiloxane)s with side groups containing 2 to 10 carbon atoms.

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Experimental part

Materials: All poly(di-n-alkylsiloxane)s have been prepared by means of anionic or cationic ring opening polymerization of hexa-n-alkylocyclotrisiloxanes in the bulk state using caesium hydroxide or trifluoromethanesulfonic acid as an initiator. Details have been described elsewhere.\(^5\)

Wide-angle X-ray diffractograms of the bulk polymers were recorded at different temperatures using a Guinier-Simon camera with monochromatic Cu-K\(_\alpha\) radiation and a circular film as described before.\(^5\)

Differential scanning calorimetry: A Perkin-Elmer DSC-7 equipped with PE-7700 computer and TAS-7 software was used to monitor the thermal transitions of the bulk samples at a scan rate of 5 K/min. Cyclohexane, gallium and indium were used as calibration standards. The onset of the recorded endotherm upon heating was taken as the transition temperature.

Results and discussion

The influence of the side group length on the melting behaviour of poly(di-n-alkylsiloxane)s is shown in Fig. 1.\(^3,9\) All polymers but the heptyl- and nonyl-substituted homologues form two crystalline phases. In addition, columnar mesophase formation is displayed by poly(di-n-alkylsiloxane)s substituted with ethyl to hexyl groups. Beyond a side group length of 6 carbon-atoms, direct melting occurs of the crystal phase into the isotropic melt.

\[
\begin{align*}
\text{Temperature in K} & \quad \text{Number of carbon atoms per side group} \\
700 & \quad 2 \\
600 & \quad 3 \\
500 & \quad 4 \\
400 & \quad 5 \\
300 & \quad 6 \\
200 & \quad 7 \\
100 & \quad 8 \\
0 & \quad 9 \\
\end{align*}
\]

Fig. 1. Influence of the side group length on the melting behavior of poly(di-n-alkylsiloxane)s

Fig. 2 depicts diffractograms of the different phases formed by PDPS. The strong reflections in the diffractograms recorded at 20 °C are consistent with the structural data described before, which suggested packing of the polysiloxane main chains in a tetragonal unit cell with an \(a\) parameter of 9.52 Å. At −80 °C, the diffractogram displays a large number of reflections which pointed to a well developed three dimensional crystalline structure. Comparison with the diffractogram recorded at 20 °C reveals a superposition of reflections of the tetragonal crystal modification and a number of other reflections at Bragg spacings of 10.21, 8.35 and 6.10 Å. Hence, the low-temperature crystal phase might be composed of two crystalline modifications,
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Fig. 2. Temperature-dependent wide-angle X-ray diffractograms of poly(dipropylsiloxane) hereafter called C1 (tetragonal) and C2. This resembles the behaviour of PDES, which is known to form a monoclinic and tetragonal crystal modification. The number of reflections in the PDPS diffractogram at -80°C is not sufficient to define the C2 phase, but in view of the similarity between PDPS and PDES it seems plausible that the C2 phase of PDPS is monoclinic as well. The three main reflections can then be assigned with Miller indices 110, 100 and 010 of the monoclinic unit cell.

At 100°C, i.e. above the second phase transition observed by DSC, the diffraction pattern changes considerably. A strong small-angle reflection at $d = 11,1$ Å appears, which was accompanied by a very weak but discernible reflection at $d' = d \sqrt{3}$ demonstrating a nearly hexagonal packing of the siloxane main chains in the mesophase. Additionally, a broad amorphous halo is observed with its maximum intensity at approximately 4.55 Å ($2\theta$).

At 240°C, PDPS is in the melt and the diffractogram displays only one reflection corresponding to $d = 9.95$ Å together with the broad halo mentioned above. The intense low-angle reflections is remarkably sharp and resembles the small-angle reflection in the mesophase. Hence, the molecular packing in the amorphous phase of PDPS is comparable to that in the columnar mesophase with additional long-range distortions. The appearance of a small-angle reflection in the amorphous state of poly(di-n-alkylsiloxane)s has been observed before and was explained by the existence of some short-range correlation between the main chain positions. The broad halo was correlated to the average lateral approach distance between the disordered alkyl side groups.

So far, we did not obtain fibre diagrams from poly(dipropylsiloxane) to confirm which diffraction is located equatorial and which one is on the meridian. Consistent fibre patterns have, however, been obtained by means of drawn gel blends for the higher homologues, i.e. poly(dipentylsiloxane) and poly(dihexylsiloxane).

Fig. 3 depicts diffractograms of bulk PDPS recorded at different temperatures. Similar to PDES and PDPS, the diffractogram pertaining to the low-temperature crystal phase displays a large number of reflections hinting at a well ordered crystal structure. The mesophase diffractogram at -3°C resembles that of mesomorphic
PDPS, with the interchain reflection \( d \) located at slightly smaller angles due to the increase in the length of the side groups. Nearly hexagonal packing of the main chains can be deduced from the presence of a weak but sharp reflection at \( d' = d/\sqrt{3} \).

Fig. 4 shows a plot of the interchain distance in the columnar mesophase and the melt as a function of the side group length. The interchain distance in the mesophase was calculated as the \( a \) parameter of the hexagonal unit cell according to \( a = 2d/\sqrt{3} \), where \( d \) represents the Bragg distance of the intense small-angle reflection. The linear dependence suggests a similar structure for all mesomorphic polymers, which can approximately be described as a two-dimensional packing of cylinders. The effective diameter \( a \) of these cylinders increase linearly with an increment of 1.26 Å upon addition of one methylene unit into each side group. This value is lower than expected for a planar all-\( \text{trans} \) zigzag side group conformation (2.54 Å), suggesting a rather high degree of side group disorder like it has been observed before by means of solid-state \( ^{13}\text{C} \) NMR \(^{14}\). Extrapolation to zero side group length yields \( a_0 = 7.2 \) Å as the average diameter of the unsubstituted polysiloxane chain in the columnar mesophase.
The dependence of the interchain distance in the amorphous phase on side group length is also depicted in Fig. 4. Because of the absence of a regular structure, the calculation of the interchain distance from the experimentally observed reflection is not straightforward\(^5\). However, it is reasonable to assume a distorted hexagonal arrangement of the polymer chain segments in the isotropic melt. For bundles of parallelly oriented chain molecules, the interchain distance is obtained by multiplication of the Bragg spacing derived from the position of the principal amorphous reflection by a factor of 1.11\(^5\). In the case of random orientation, this factor equals 1.25. For amorphous poly(di-\(n\)-alkylsiloxane) an intermediate value of 1.16 was chosen, assuming that the amorphous polymers are packed in a distorted hexagonal columnar lattice.

From Fig. 4 it appears that the interchain distance in the amorphous phase did not show a linear correlation with the side group length. In a recent paper we proposed that the physical appearance of amorphous poly(di-\(n\)-alkylsiloxane) can be described as flexible cylinders with cross-sections of uniform density\(^6\). In line with this suggestion, a linear correlation was observed between the cross-section and the alkyl side group length. In the present work, the same method has been applied to the columnar mesophase.

![Fig. 5. Influence of the side group length on the molecular cross-section of poly(di-\(n\)-alkylsiloxane) in the hexagonal columnar mesophase (□) and in the melt (△)](image)

Fig. 5 shows the dependence of the molecular cross-section on the alkyl side group length for the amorphous phase and the columnar mesophase. Both phases display a linear correlation with a similar intercept but with a slightly higher increment value for the amorphous phase, which can be explained by the deviation from hexagonal ordering of the polymer chains in the melt. Extrapolation to zero side group length yields a theoretical value for the cross-section of the bare siloxane main chain of 20–22 Å\(^2\) for both the columnar phase and the melt. This similarity is in line with results of solid-state MAS \(^{29}\)Si NMR measurements, which suggested a comparable conformational state for both phases\(^4,5,14\).