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Report:

Since several decades, inorganic polymers have been attracting increased attention due to their various technological applications. In particular, the siloxanes are widely employed as resins, greases and lubricants. Apart from their practical importance, these polymers are also very interesting from the fundamental point of view. For instance poly(di-*n*-alkysiloxanes) with two to six carbon atoms per side chain form hexagonal columnar mesophases without having any mesogenic moieties in the chemical structure. Linear polydipropylsiloxane (PDPS) is the second member of this family of flexible mesomorphic non-mesogenic poly(di-*n*-alkylsiloxane). PDPS exhibits two crystalline modifications[1,2,3,4,5,6,7,8] and a mesophase for which hexagonal columnar packing of the chains was suggested. The room temperature (RT) crystalline phase of PDPS was firstly described by *Petersen* et al. who identified it as tetragonal with **a**=**b**=9.52Å and **c**=9.4Å. Despite the fact that some preliminary data on the crystalline phases have been previously reported, the detailed structural information lacks. In this work, we studied the structure of the RT crystalline modification and the mesophase of PDPS employing X-ray diffraction on oriented samples [9].

X-ray measurements were performed on BM26 beamline at the European Synchrotron Facility in Grenoble (France) using the energy of 10 KeV. The data were collected in transmission employing 2048x2560 pixels image plates with a pixel size of 98x98 μm^2. The temperature was controlled by a Linkam heating stage operated under a LN_2 flow. The modulus of the scattering vector $\underline{\mathbf{s}}$ ($s = 2\sin q/\lambda$, where q is the Bragg angle and λ - wavelength) was calibrated using three diffraction orders of silver behenate. Fibers with diameter of 0.7 mm were obtained by extruding the material in the liquid crystalline phase with a home-build mini-extruder.

A typical fiber diffraction pattern recorded in the mesophase at 100°C is displayed in Fig.1**.** Two equatorial reflections can be seen in the small-angle region with spacings given by the ratio**:** 1: v3. They can be assigned to the (100) and (110) reflections of a columnar hexagonal mesophase, Col_h.. The wide-angle region of the same diffractogram displays only one broad peak (halo) located at s=0.22 $Å^{-1}$, which is typically attributed to disordered alkyl side-chains. A diffraction pattern of the RT crystalline modification is presented in Fig. 2A. Totally, 34 different reflections distributed over three layers (denoted in Fig. 2A as l=0,±1, ±2) were analyzed. The indexation procedure was started from the equatorial section of the pattern, which fits to a tetragonal

lattice (Fig. 2C) with **a**=**b**=18.96 Å. The **c**-parameter was evaluated from the low-angle near-meridional peak in the first layer indexed as (101). The corresponding lattice parameter is found to be **c**=4.87 Å. Therefore, the PDPS chain conformation is supposed to be close to the planar *cis-trans*, similar to what has been reported for polydiethylsiloxane (PDES), where the chain repeat is 5.02 Å.[10] It should be noted that the full-*trans* zig-zag cannot be realized for linear siloxanes due to a significant difference in the bond angles of O-Si-O and Si-O-Si. The mass density of the RT phase, ?, was evaluated as ? = M_{ru}.Z/ (N_A.$V_{unit\ cell}$), where $V_{unit\ cell} = a^2$.c, M_{ru} is the molecular weight of the repeating unit, Z- the number of chains per unit cell. Assuming that the unit cell accommodates four chains, the density of 0.99 g/cm^3 was found, which is in close agreement with the experimental[9] value of 0.95±0.02g/cm^3.

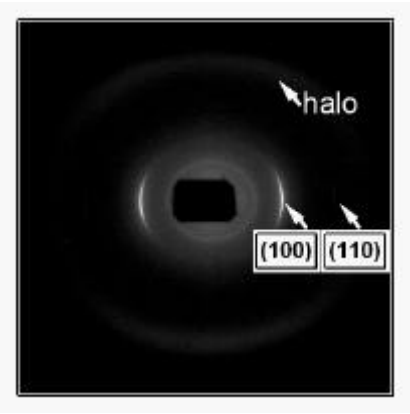

Fig.1. X-ray fiber diffraction pattern recorded in the mesophase at 100°C. The fiber axis is vertical.

Further analysis of the structure in terms of the symmetry group was based on the consideration of the extinction conditions. It was found that only hk0 reflections with h,k=2n, h00 with h=2n, 0k0 with k=2n and 00l with l=2n are present. These extinction conditions imply the presence of glide planes and a two-fold screw axis parallel to (001). However, the extinction conditions given above cannot be simultaneously satisfied by any of the tetragonal symmetry groups. Therefore, we suggested that the group symmetry is lower than tetragonal. Additional arguments supporting this hypothesis came from our studies of single crystals of PDPS. It has been found that PDPS single crystals obtained from dilute solutions do not have a square habit, typical of tetragonal lattices. Moreover, the electron diffraction studies performed on the [hk0] diffraction zone did not show the presence of C4 symmetry. The space group, which allows to construct the unit cell accounting for all systematic absences, is a monoclinic B2/N (N15) with **c** unique.[11] The polymer backbone is conventionally placed parallel to the **c**-axis. The model of the unit cell was firstly built with the help of Materials Studio program (Accelrys, Ltd) and further refined by using Rietveld method. The refinement was performed on a powder diffractogram and satisfactorily reproduced the structure factors of eight most intense Bragg peaks. The refined structure is given in Fig. 3A-C. It can be seen that the planar zig-zags of the chains are oriented parallel to the **a**- direction. The placement of the lateral chains allows understanding such feature of the diffractogram as a very small intensity of (400) and (040) reflexions.

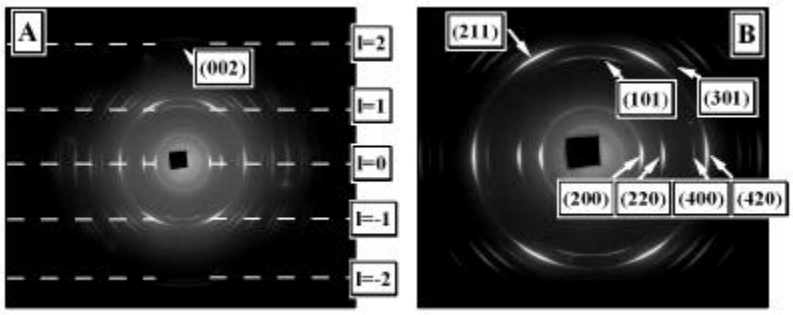

Fig.2. X-ray fiber diffraction pattern corresponding to the RT crystal. The fiber axis is vertical. **A**: wide-angle diffraction pattern showing that the Bragg peaks are grouped in layers with l=0,±1, ±2 indicated by the dotted lines. **B**: X-ray fiber diffraction pattern recorded in the low-angle region.

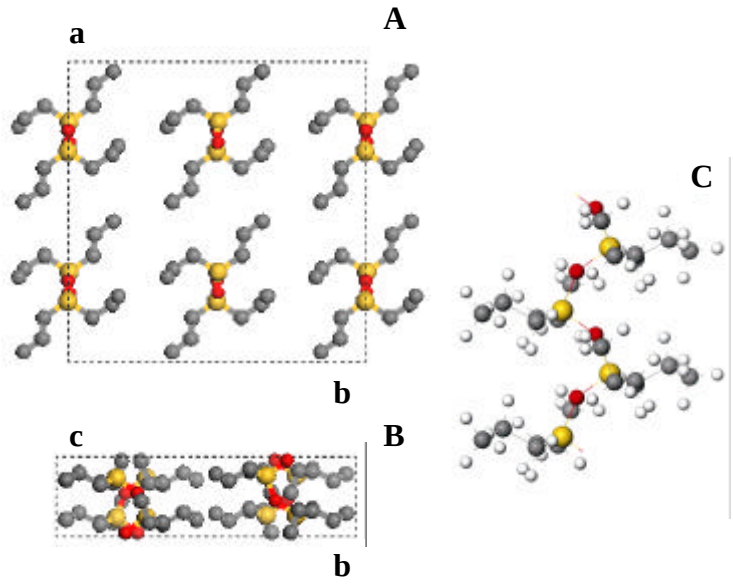

Fig.3. Unit cell of the RT phase of PDPS viewed parallel to the ab (**A)** and ac (**B)** planes, the hydrogen atoms were removed for clarity; **C**: PDPS chain fragment in c*is-trans* conformation.

References:

1. Godovsky Yu. K.; Makarova, N.N.; Papkov V.S.; Kuzmin, N.N. *Makromol.Chem., Rapid Comunn*. **1985**, *6*, 443.
2. Godovsky Yu.K.; Mamaeva, I.V.; Makarova, N.N.; Papkov, V.S.; Kuzmin, N.N. *Makromol.Chem., Rapid Comunn*. **1985**, 6, 797.
3. Shulgin A.I.; Godovsky Yu.K. *Polym. Sci. USSR*, **1987,** *29,* 2845.
4. Godovksy, Yu.K.; Papkov, V. S. *Makromol. Chem., Macromol. Symp*.**1986**, *4*, 71.
5. Shulgin A.I.; Godovsky Yu.K.; Makarova N.N., *Thermochimica Acta*, **1994**, *238*, 337.
6. Out, G.; Turetskii, A.; Moeller, M. *Makromol. Chem., Rapid Commun*. **1995,** *16*, 107.
7. Out, G.; Siffrin,S.; Frey, H.; Oelfin, D.; Koegler, G.; Moeller, M *Polym. Adv. Technol.* **1994**, *5*, 796.
8. Godovsky, Yu.K.; Papkov, V.S.; Magonov, S.N. *Macromolecules*, **2001,** *34*, 976.
9. Gearba et al., in preparation.
10. Inomata, K.; Yamamoto, K. ; Nose, T., *Polymer J.*, **2000**, 12, 1044.
11. International Tables for Crystallography, Kluwer Academic Publishers, 2002, 1st edition, vol. A, p. 199.