



	Experiment title: Novel Columnar Mesophase with Double Hexagonal Order	Experiment number: 26-02-314
Beamline: BM26B	Date of experiment: from: 24.04 to: 28.04.2006	Date of report: 30.08.2006
Shifts: 9	Local contact(s): Nicolas Vilayphiou Wim Bras	<i>Received at ESRF:</i> <i>Denis Anokhin</i> <i>Raluca Gearba</i> <i>Martin Rosenthal</i>
Names and affiliations of applicants (* indicates experimentalists): D. V. Anokhin^{1*}, R.I. Gearba^{1*}, D.A. Ivanov¹, B. Goderis² ¹ Institut de Chimie des Surfaces et Interfaces, CNRS UPR9069, 15, rue Jean Starcky, BP 2488, 68057 Mulhouse CEDEX, France. ² Catholic University of Leuven, Chemistry Department, Celestijnenlaan 200F, 3001 Heverlee-Leuven, Belgium.		

Report:

Formation of mesomorphic states of different structure and degree of order by polymer chains has received much attention in recent years [1,2]. An interesting family of non-polar flexible macromolecules showing mesomorphic behavior are cyclolinear polyorganosiloxanes (CLPOS) [3,4]. Similar to linear poly(di-*n*-alkylsiloxane)s, CLPOSs are able to form liquid crystalline states with extremely high mesophase stability, for which the temperature window of the mesophase spans up to three hundred degrees, depending on the cycle size, the length and nature of organic side-chains and spacers, the local tacticity in the silsesquioxane fragments and the polymerization degree [4]. The most probable arrangement of the CLPOS in the mesomorphic state is a layer-like packing whereby monomolecular layers are stacked with good long-range order [4]. Within the layer, the cyclohexasiloxane fragments have a strong tendency to lie with their flat sides parallel to the layers. Though some insights about the mesophase structure were obtained from studies of Langmuir films [5,6], a detailed investigation of the layers formation was still missing.

In the frame of the present project, we studied a novel mesophase formed by a cyclolinear polysiloxane, poly[oxy(decamethylcyclohexasiloxane-2.8-diyl)-dimethylsiloxane]s (CLPMSiC). The experimental methods to synthesize the cyclolinear polyorganosiloxane have been given in detail elsewhere [7]. The studied sample of CLPMSiC is characterized by M_w of 40.10^3 g/mol, average degree of polymerization of 80 and intrinsic viscosity of 0.19 dl/g. Oriented samples for X-ray diffraction experiments were obtained by extruding the material in the LC phase with a home-built mini-extruder resulting in 0.7 mm diameter fibers. The measurements were carried out at room temperature (in mesomorphic state) and at -80°C (in crystalline state).

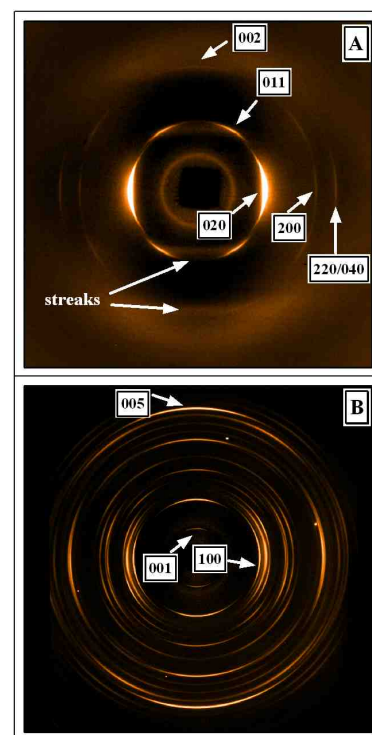


Fig.1 X-ray patterns of CLPMSiC fibers at room temperature (A) and at -80°C (B).

X-ray fiber diffraction measurements show that CLPMSiC can be nicely oriented in the mesophase by extrusion (Fig. 1A). The 2D X-ray pattern measured at 193K corresponding to the crystalline phase is given in Figure 1B. It shows an important number of sharp reflections approximately distributed over five layer lines. The peak positions can be indexed to a triclinic unit cell with parameters $a=8.87$ Å, $b=17.12$ Å, $c=18.92$ Å (fiber repeat), $\alpha=90^\circ$, $\beta=82.2^\circ$ and $\gamma=88.3^\circ$. Note the presence of five diffraction orders in the chain direction. The degree of crystallinity calculated from the diffractogram is very high (0.83), which is typical for the mesophase-assisted crystallization of main-chain LC polymers [8]

X-ray pattern recorded in the mesophase at room temperature (Figure 1A) displays three equatorial reflections located at 8.40, 4.76 and 4.18 Å with relative spacings given by the ratio: 1: $\sqrt{3}$: 2. This fact allows identifying ordering of the chain axes on a 2D hexagonal lattice (Figure 2B). However, in addition to equatorial peaks the pattern shows sharp strong off-meridional peaks with a spacing 8.04 Å that are located on the first layer line. X-ray patterns of the mesophase of a typical linear polysiloxane, poly(di-ethyl siloxane), have not shown such a feature. In our case, the first small-angle equatorial peaks together with the off-meridional peaks form a characteristic six-spot pattern having an almost hexagonal symmetry. Typically, the presence of sharp off-meridional peaks in the X-ray fiber diffractograms indicates that the sample is in the crystalline state, whereby the atom positions can be described by three dimensional order in three dimensions. This is however not the case of the CLPMSiC sample at room temperature, which exhibits characteristic features of a liquid crystal. It is important to note that the structure of the sample at room temperature is very different from that at low temperature (crystalline phase), as can be seen from X-ray diffraction patterns. For example, the described off-meridional peaks are absent in the X-ray pattern of the crystal (Fig. 1B). Therefore one can directly rule out the possibility that these unusual features of the mesophase X-ray pattern are due to incomplete melting of the low-temperature crystal. Moreover, X-ray diffraction experiments performed as a function of temperature show that the observed mesophase pattern disappears at the isotropization point, as is expected for a thermotropic LC.

It was found that an orthorhombic unit cell with parameters $a=9.66$, $b=16.72$ and $c=9.1$ Å (fiber repeat) can account for all the observed reflections. Thus, the mentioned off-meridional peak acquires the index of 011. The other weaker off-meridional peaks on the first and second layer lines are indexed to 031 (4.76 Å) and 022 (4.05 Å). Taking into account these indices, it becomes clear that the quasi-hexagonal pattern formed by 020 and 011 reflexes corresponds to 2D ordering of the structure in the (100) plane. Thus the mesophase is probably composed of layers of chains oriented parallel to the **bc** plane with the interlayer distance of 8.4 Å given by the first equatorial peak 020. Inspection of Miller indices for all the observed reflexes shows that there are no correlations between different layers along the **a**-direction because there are no (hkl) peaks with all three indices different from zero. Therefore the mesophase structure has a double 2D hexagonal and quasi-hexagonal ordering occurring simultaneously in the **ab** and **bc** planes. The origin of the double hexagonal arrangement can be explained by molecular structure of the CLPMSiC chain (Fig. 2A). The CLPMSiC macromolecule can be then viewed as a necklace in which bulky organosiloxane cycles pack on a hexagonal lattice in the **bc** plane (Fig. 2C). According to the proposed orthorhombic lattice it means that the chains in each **bc** plane are shifted by $b/2$ and $c/2$ with respect to their neighbors. The different **bc** layers can freely slide along the chain axis, which will eliminate spatial correlations between the layers (Fig. 2D). During sliding of the layers the spheres of the organosiloxane cycles can move along the grooves of the neighboring layer while maintaining hexagonal packing of the chain axes in the **ab** plane (Fig. 2A).

In conclusion, cyclolinear polysiloxane was found to form a novel mesophase which is characterized by hexagonal and quasi-hexagonal order in two mutually orthogonal planes, i.e. besides hexagonal packing of the chain axes there is also a hexagonal ordering in the plane parallel to the chain direction.

References:

1. Auriemma, F.; De Rosa, C.; Corradini, P. *Adv Polym Sci* **2005**, 181, 1.

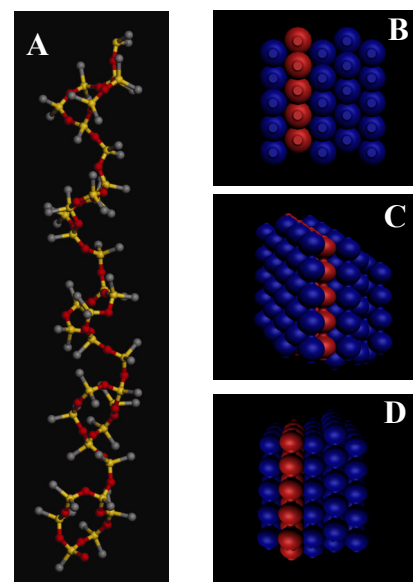


Fig.2 View of the chain in the mesophase (A); model of CLPMSiC mesophase: **ab**-projection (B), **bc**-projection (C), **ac**-projection (D). One layer is colored in red.

2. Ungar G.; Zeng X.B. *Soft Matter* **2005**, 1 (2), 95.
3. Godovsky, Y. K.; Papkov, V.S. *Adv Polym Sci* **1989**,88,129.
4. Godovsky, Y. K.; Makarova, N. N. In: *Self-Order and Form in Polymeric Materials*; Keller, A.; Warner, M.; Windle, A. H.; Editors; London: Chapman & Hall, **1995**. pp 43-55.
5. Jensen, T. R.; Kjaer, K.; Brezesinski, G.; Ruiz-Garcia, J.; Möhwald, H.; Makarova, N. N.; Godovsky, Y. K.; *Macromolecules*; **2003**,36,7236.
6. Godovsky, Y. K.; Brezesinski, G.; Möhwald, H.; Jensen, T. R.; Kjaer, K.; Makarova, N. N. *Macromolecules*; **2004**,37,4872.
7. Makarova, N. N.; Godovsky, Y. K. *Progr Polym Sci*; **1997**,22,1001.
8. Gearba, R. I.; Anokhin, D. V.; Bondar, A. I.; Godovsky, Y. K.; Papkov, V. S.; Makarova, N. N.; Magonov, S. N.; Bras, W.; Koch, M. H. J.; Masin F.; Goderis B.; Ivanov, D. A. *Macromolecules*; **2006**,39,988.