

**Experiment title:**

Self-Organization of Polybases Neutralized with Wedge-Shaped Sulfonic Acid Molecules

Experiment number:

SC-1816

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Shifts: 3	Local contact(s): Sztucki Michael Theyencheri Narayanan	<i>Received at ESRF:</i> <i>Raluca Gearba</i> <i>Denis Anokhin</i> <i>Dimitri Ivanov</i>
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Report:

Supramolecular self-organization is a powerful tool for producing functional materials.¹ During the last decade a concept, based on complexation of polymer chains by low molecular weight amphiphiles via non-covalent interactions such as ionic attraction, coordination interaction, or hydrogen bonding has become a common tool in the construction of nanostructured macromolecular materials.² The polymer chains and the ligands combine to form comb-shaped supramolecules (“complexes”), which in turn self-assemble on a length scale of a few nanometers. Due to the incompatibility between the macromolecule and the non-polar part of the ligand molecules these complexes form microphase-separated morphologies. It is believed that this strategy can be used to manufacture and process non-soluble materials as polyaniline and polypyrrole. To address the concept, in this work we combine the structuring abilities of wedge-shaped sulfonic acids and the ligand acid / polybase complexation to generate a new class of macromolecular materials with an improved processability character given by the presence of liquid crystalline phases. More specifically, poly(vinylpyridines) (P4VP) are neutralized with wedge-shaped sulfonic acids to produce supramolecular cylinders. Depending on the length of the lateral chains attached to the sulfonic acids (8 or 12), the complexes will be denoted in the following as **P4VP(C12-H)_{DN}** and **P4VP(C8-H)_{DN}**, where DN is the degree of neutralization. Only complexes with DN 0.13, 0.25, 0.33, 0.5, 0.8 and 1 have been studied. They were found to exhibit mesophases at high temperatures that are slowly crystallizing upon cooling the material to ambient temperature.

The supramolecular organization of the different complexes has been studied by X-ray diffraction. The measurements were performed on ID2 beamline at the European Synchrotron Facility in Grenoble (France) using the energy of 10 KeV. The data were collected in transmission using a CCD camera. The modulus of the scattering vector \underline{s} ($s = 2\sin\theta/\lambda$, where θ is the Bragg angle and λ - wavelength)

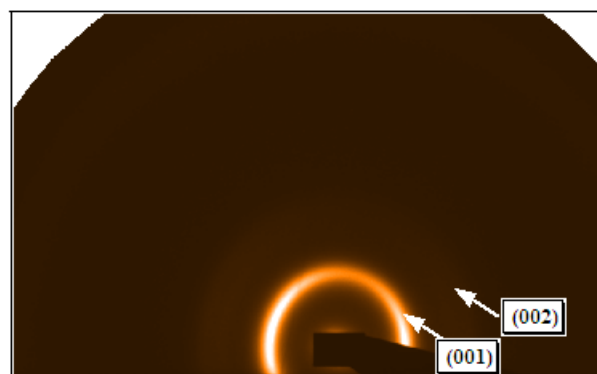


Fig.1. 2D X-ray diffraction pattern of the **P4VP(C12-H)_{0.50}** complex recorded at 25 °C.

was calibrated using several diffraction orders of silver behenate. Fibers with diameter of 0.7 mm were obtained by swelling them into *iso*-butyl acetate and subsequent extrusion using a home-built mini-extruder. Figure 1 presents a 2D X-ray diffraction pattern of an oriented fiber of **P4VP(C12-H)_{0.50}** complex at 25 °C. In the small angle (SAXS) region, a set of two equatorial reflections with s-spacings given by the ratio 1:2 was observed. These reflections can be indexed as the 001 and 002 reflections of a lamellar phase. The wide-angle pattern (not shown here) does not reveal any other features indicating that the studied compound is in a LC state. It was found that all the **P4VP(C12-H)_{DN}** complexes with a degree of neutralization lower than 0.50 form lamellar phases. By contrast, the complexes with a degrees of neutralization higher than 0.80 form a hexagonal columnar (Col_{hd}) phase. A typical 1D X-ray diffraction patterns corresponding to the **P4VP(C12-H)_{0.80}** complex recorded at 25 °C is given in Figure 2. In the SAXS region three peaks with the relative s-spacings given by the ratio 1:√3:2 were found. They can be indexed as 10, 11 and 20 reflections of a Col_{hd} phase with a lattice parameter of 96.9 Å. It was found that the lattice parameter increases with DN. **P4VP(C8-H)_{DN}** complexes exhibit a similar behavior.

The thermotropic behavior of the complexes was further studied with variable temperature X-ray scattering. A typical temperature dependence of the lattice parameter corresponding to the **P4VP(C12-H)_{0.8}** complex is presented on Figure 3. For all the complexes a remarkable decrease of the characteristic distance was observed on heating starting from approximately 50 - 60 °. In this temperature range, the differential scanning calorimetry curves of the complexes with higher DN values reveal an endothermic peak. Therefore, one can speculate that this temperature corresponds to “defreezing” of the side groups. Such thermal behavior of the interlayer distance was observed earlier for columnar mesophases formed by monodendron-jacketed polymers.³

To conclude, all the **P4VP(C8 or C12-H)_{DN}** complexes formed a liquid crystalline lamellar phase at low degrees of substitution, while a hexagonal columnar mesophase was observed at degrees of neutralization of 80 % and higher.

References:

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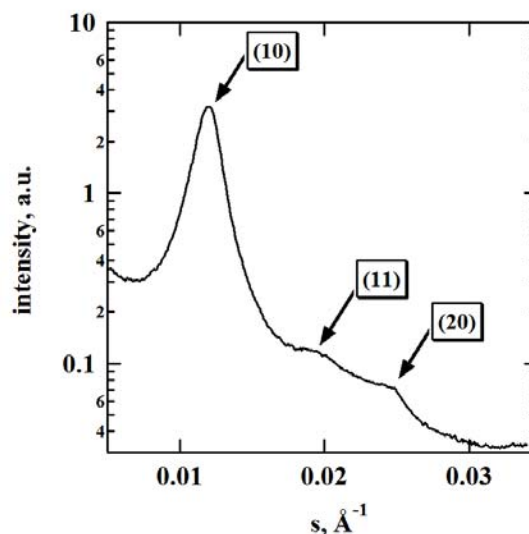


Fig.2. X-ray diffraction pattern of the **P4VP(C12-H)_{0.80}** complex recorded at 25 °C.

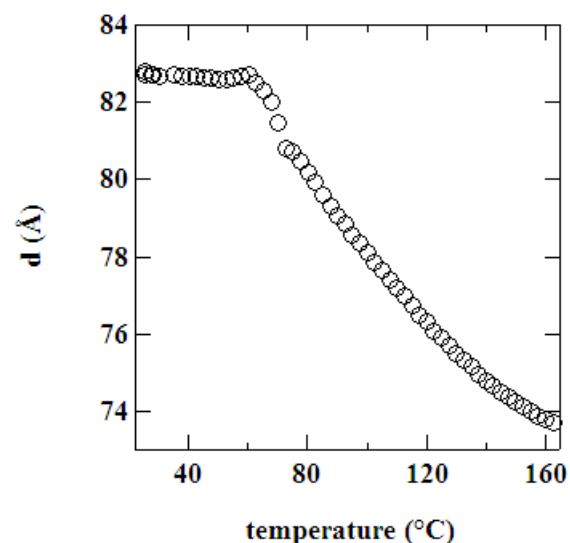


Fig.3. Temperature variation on heating of the characteristic d_{10} distance of the Col_{hd} phase corresponding to the **P4VP(C12-H)_{0.80}** complex.