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| ESRF | **Experiment title:**<br>**In situ studies of gelation process in polyrotaxane solutions** | **Experiment number**:<br>**26-02-383** |
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## Report:

Polyrotaxanes (PR's) is a new class of supramolecules [1] having a necklace-like structure (Figure. 1, **top right**). They contain macrocyclic molecules (rings of the necklace), which are threaded onto a single linear polymer like PEO or PCL. PR's based on cyclodextrine (CD) (Figure 1, **top left**) attract particular attention due to the high number of reactive hydroxyl groups, possibility of the CD to slide along the template chain and biocompatibility. Apart from applications in biology and medicine, such systems can be used to improve solubility or compatibility of the template chain and as enculator in electronical application. Furthermore, PRs can be bridged with a crosslinker and form a "sliding network". Such network in solution forms a "sliding gel" with very high swelling capacity and unusual mechanical properties due to the ability of the crosslinking points to slide along the template chain. At room temperature a solution of PR in DMSO was found to form a physical gel [2] (Figure 1, **bottom**) but the details of the microstructure were not understood. In the present project, we studied *in situ* the gelation kinetics for PR

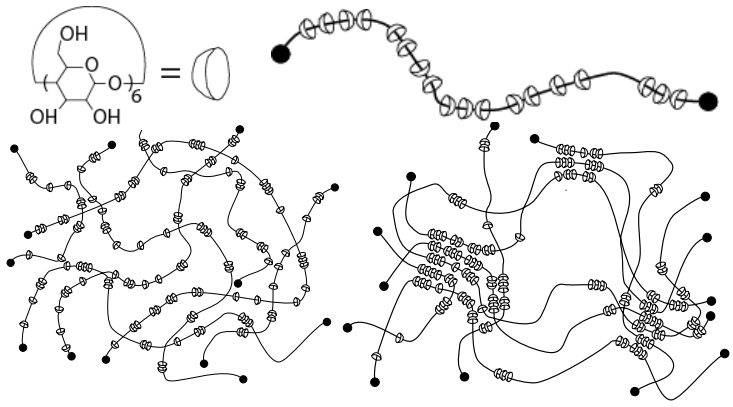


*Fig.1*: Schematic representation of cyclodextrine molecule (**Top left**), PR single chain (**Top right**) and the PR gel just after stopping pre-shear (**Bottom left**) and after self-organized for one day (**Bottom right**)

solutions with PEO as a template chain.

For WAXS measurements solutions of different concentrations and complexation degrees were placed in home-made liquid cell and heated to isotropization point 43°C, then cooled down to the crystallization temperature of 21°C. The observations of the structural changes in the system were followed at this temperature.

Figure 2 (**top**) shows the evolution of the WAXS signal during isothermal crystallization of the sample PR7 at 21°C (the number in the sample title indicates the complexation degree). One can observe the appearance of narrow peaks in the diffractograms. These peaks at 0.21 (120), 0.26 (112/032/13-2), 0.29 (024), 0.30 (22-4) and 0.39 $Å^{-1}$ (124/044) are attributed to the monoclinic crystal phase of PEO [3]. The intensity of the peaks increases with time and reaches a maximum after 100min of crystallization. The positions of the reflexes and the lateral size of the crystals estimated at 640Å do not evolve.

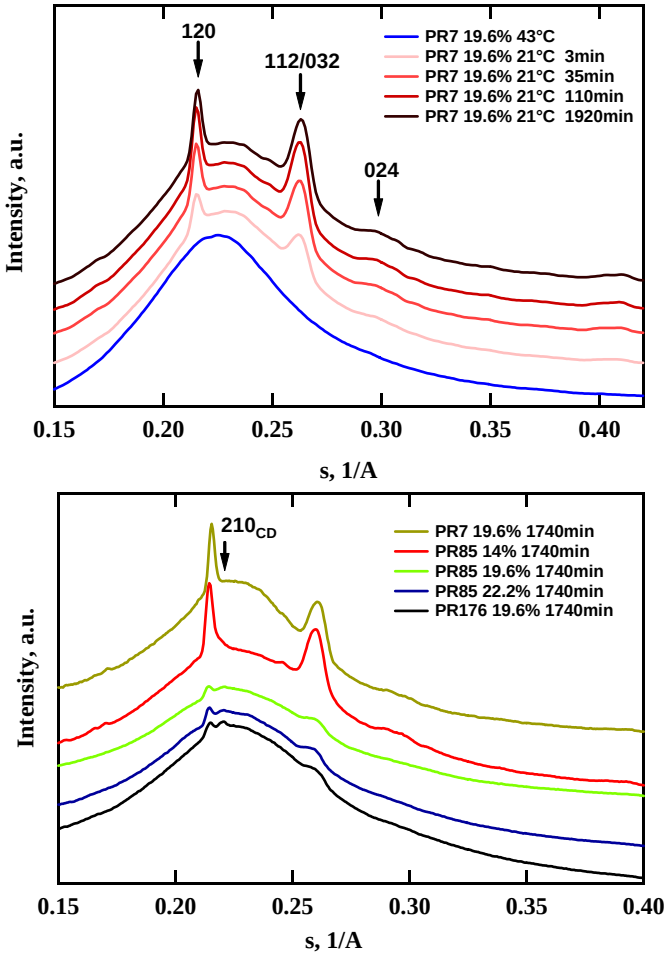


*Fig.2*: WAXS curves corresponding to the crystallization at 21°C of the PR7 (**Top**) and PR85 at different concentration and complexation degree (**Bottom**)

Nevertheless, a well prononced halo in the WAXS profiles is still present even after a long time annealing at 21 °C. Thus, for instance, only 2 % of the naked PEO segments are organized after 32 h. With increase of the complexation degree the intensity of PEO peaks decreases and a weak peak at s=0.22 $Å^{-1}$ corresponding to (210) reflex of the α-CD crystal structure appears (Figure 2, **bottom**). The intensity of this peak increases with the complexation degree while the total crystallinity (which is in this case the sum of the crystallinity of PEO and α-CD) decreases from 0.08 for the $PR_7$ sample to 0.02 for $PR_{176}$. The increase of concentration of PR85 leads to a decrease of crystallinity and realtive content of the PEO crystal phase.

In conclusion, solutions of polyrotaxanes show complex structural behaviour. At 21°C the gelation process takes place due to crystallization of the naked PEO segments. With increase of concentration and complexation degree the crystal phase of α-CD forms, whereas the total crystallinity decreases dramatically. Therefore the variation of the structural parameters of the chain allows to control in a wide range the mechanical properties of the system.

## References:


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