

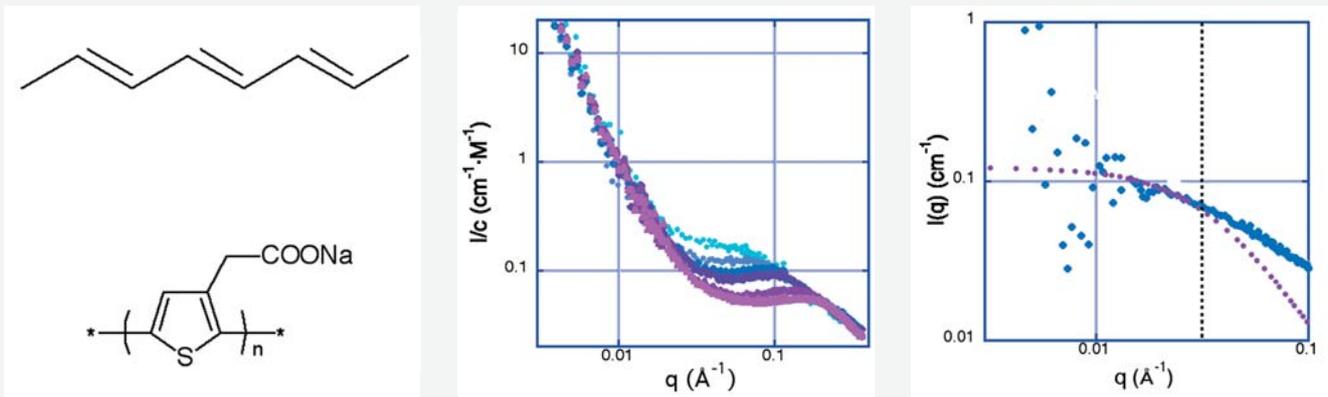
[C1. P. Vallat] Molecular structure of conjugated polyelectrolytes

Conjugated polyelectrolytes are a new class of polyelectrolytes. Their backbone consists of an alternation of simple and double (and/or triple) bonds. Thanks to this conjugation, π -electrons are delocalized along the backbone. Therefore, the polarizability of these chains is strongly enhanced and can even modify the structure of the solutions.

We study aqueous solutions of a specific conjugated polyelectrolyte: poly(3-thiophene acetic acid)(P3TAA). This macroion is prepared at different degrees of ionization. In a first step, our aim is to study the behavior of these chains in solution when they are completely ionized (with sodium as a counter-ion: P3TNaA) and compare it to the case of saturated polyelectrolytes. While the polyelectrolyte character of the chains can not always overcome the strong polarizability of rigid conjugated polyelectrolytes, the flexible chains of P3TNaA are soluble on a molecular level. It also appears that the behavior of this polyelectrolyte is that of a hydrophilic flexible saturated polyelectrolyte apart from a stronger tendency to self-aggregate (stronger upturns at low q values). However, the heterogeneities are in small quantities and the scaling laws predicted for flexible polyelectrolytes also apply here.

When salt (monovalent cation) is added to the solutions, upturns remain unchanged. Moreover, when the signal of the heterogeneities is subtracted, it appears at high enough ionic strength that the chains behave as neutral polymers with a correlation length ξ_c of 40Å (i.e. $I(q)=1/(1+q^2\xi_c^2)$). This highlights two important facts. **First**, the fact they do not vanish shows heterogeneities are not a polyelectrolyte effect: they differ from what observed for polyions at low ionic strength, or with divalent cations. They exist prior to the polyelectrolyte state, i.e. in the neutral state (degree of ionization zero). **Second**, the fact that they do not increase shows an absence of macroscopic aggregation, even without electrostatic repulsion and in spite of the strong polarizability linked to conjugation. We believe this is due, in this particular example, to the flexibility of the backbone.

[Collaboration : P. Vallat, J.-M. Catala, F. Schosseler, M. Rawiso, Institut Charles Sadron, Strasbourg and LLB]



Left: general scheme of conjugated polymer (top) and molecular structure of P3TNaA (bottom)

Middle: effect of concentration c of salt-free aqueous solutions of P3TNaA; $c=0.08$ (top) to $1 \text{ mol}\cdot\text{L}^{-1}$ (down)

Right: effect of addition of salt on solutions of P3TNaA solutions – upturn subtracted (full diamonds). Comparison with Lorentzian fit (empty diamonds).

[C2. S. Desvergne] Two polymers made of the same segments which do not mix because of their different architecture

We have mixed deuterated polystyrene linear chains with branched polystyrene chains (“polymacromonomers”), allowing the localisation of the two species by SANS. Deuterated and non deuterated segments can be considered as equivalent here. In spite of this, SANS shows that the linear chains interpenetrate weakly with the branched ones. For the most compact branched architectures, the mixture remains very inhomogeneous at the 10 nm scale, as the result of a kind of depletion, and also in agreement with mean field theory (H. Fredrickson). Our observation can be related with the coexistence of chains of different branching rate in real.

[Collaboration : S. Desvergne (thesis), F. Boué, J. P. Cotton, A. Brûlet, LL; Y. Gnanou, V. Herroque, LCPO Bordeaux]

Blue : linear chains

Red : branched chains

