Experimental report

06/09/2022

Proposal:	**9-11-2078**	**Council:**	4/2021

Title: Structural characterization of contractile materials based on electrochemically responsive [c2]daisy chain rotaxanes

Research area: Chemistry

This proposal is a new proposal

Main proposer:	**Damien DATTLER**
Experimental team:	Sylvain PREVOST Christian CARMONA VARGAS Damien DATTLER
Local contacts:	Sylvain PREVOST

Samples: electroactive [c2]daisy chain rotaxane
electroactive [c2]daisy chain rotaxane polymer

Instrument	Requested days	Allocated days	From	To
D11	2	2	03/09/2021	05/09/2021

Abstract:

Switchable functional molecules capable of producing mechanical work constitute an active focus in nanotechnologies as they can be a source of components for molecular-based devices and materials. In particular, the dynamic nature of mechanically interlocked molecules allows their components to undergo relative internal movements which can be exploited in translation and circumrotation. Over the last few years, our group has demonstrated the possible integration of nano-machines resulting in the formation of responsive materials such as polymer chains, gels or films that can behave as artificial muscles. Within the framework of a FET-OPEN H2020 European project, our current research focuses now on the generation of biomimetic artificial muscles based on electrochemically responsive [c2]daisy chain rotxane polymers for soft robotics. In th current proposal, SANS will be used to investigate the structural changes during the extension and contraction events of our supramolecular polymers as a function of external parameters. Correlations are expected between these environmental changes at the molecular level and the resulting macroscopic properties.

Structural characterization of contractile materials based on electrochemically responsive [c2]daisy chain rotaxanes

Experiment number:

9-11-2078

Beamline

D11

Date of experiment

From 03/09/2021 *to* 05/09/2021

Days

2

Local contact(s):

Sylvain PREVOST

Names and affiliations of applicants (* indicates main proposer)

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We previously reported the structural characterization of pH sensitive bistable [c2] daisy chain rotaxanes gels crosslinked by Small-Angle Neutron Scattering (SANS) revealing that the macroscopic response of the gel results from the synchronized actuation of the mechanical bond at the molecular level.[1] With the present experiments, we aimed to study an electro active [c2] daisy chain polyurea and to investigate its behaviour in solution.

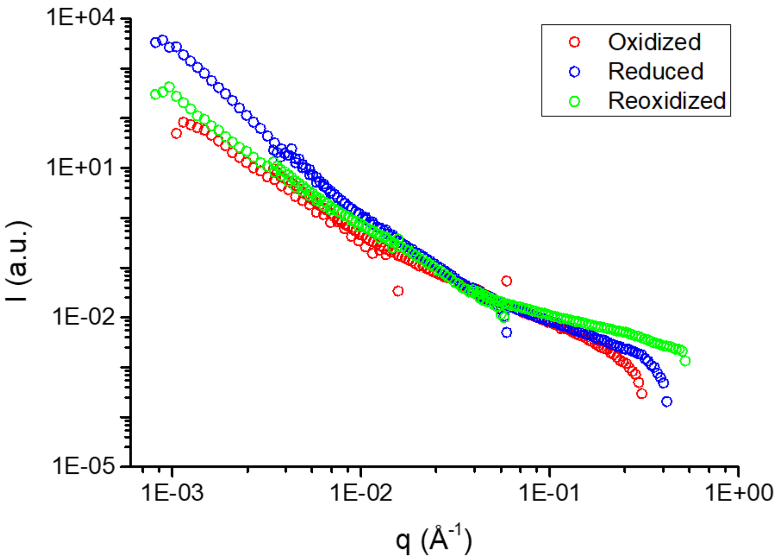

Figure 1 : . Superimposition of the SANS spectra of a 0.5% (m/v) solution of polyurea **Ext** in DMSO-d_6 in its initial oxidized state (empty orange circles), **Cont** (reduced state, empty blue circles) and **Ext** after reduction (reoxidized, empty green circles).

The study started by determining the optimal conditions for the concentration of the polymer in solution. The results showed that the concentration c=0.5% (m/v) represents the best compromise between signal intensity and aggregation in deuterated dimethyl sulfoxide. We then carried out the characterisation of the polyurea in its extended (oxidized) and contracted (reduced) state. The curves are displayed in Figure 1 and the data obtained for extended polymer and the contracted polymer indicate that the systems possess different organisations.

Large values of *q* give information on the local structure of the objects. In this region, we observe a continuous and non-reversible change in the curves along the molecular actuations. This behaviour is not in agreement with what we expected, nevertheless, we need further experiments to confirm and explain such behaviour. The curves are rather smooth, indicating that we do not a have a free polymer but a self-assemble of polymer chains in solution, however, further studies and complementary experiments are required to determine the supramolecular global structure of the polymer.

Additionally, in the mid-q range a slope with a decay $q^{-5/3}$ is observed for all the three curves, which indicates that polymer chains are solvated in a good solvent. At low values of q, slopes with a decay q^{-3} for extended polymer and q^{-4} for contracted polymer were observed for the scattered intensities, indicating the presence of large assemblies. For extended polymer, such assemblies present rough interfaces, while for contracted polymer, smooth larger aggregates are expected. Once the system is contracted, the rigidity increases, giving a better tendency to form bundles of chains, what could explain the aggregates in such state. Hydrogen bonding between the urea units, as well as π-π stacking of the MDI aromatic units can contribute to the formation of well organised and compact bundles of chains in the contracted state. Importantly, this $q^{-3} \rightarrow q^{-4}$ transition is reversible as it can be observed in the curve for the reoxidized system (green empty circles).

To conclude, we used SANS to elucidate the structural changes taking place in different oxidative state of an electro active [c2] daisy chain. The analyses showed very important structural changes in the whole measurement scale but above all they demonstrate the reversible behaviour of the system at the polymer scale. The results obtained are a first example studying the behaviour of reversible electroactive polymer in solution by SANS. Further studies could be undertaken by modulating the redox potentials but also the chain length of the polymer, and SANS will be once more be essential to determine the structure-property relationship of these system.

References

1. Goujon A, Lang T, Mariani G, et al. Bistable [c 2] Daisy Chain Rotaxanes as Reversible Muscle-like Actuators in Mechanically Active Gels. *J Am Chem Soc*. 2017;139(42):14825-14828.