Experimental report

30/03/2022

Proposal: **9-11-2004** **Council:** 4/2020

Title: Structural characterization of photoactive polymeric gels crosslinkedwith rotary molecular motors

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Alexis PERROT**

Experimental team: Alexis PERROT
Damien DATTLER

Local contacts: Sylvain PREVOST

Samples: PDMS
NaPSS
PS
P3HT
PEG20000
PEG10000
LCN

Instrument	Requested days	Allocated days	From	To
D11	3	2	19/03/2021	21/03/2021

Abstract:

The last two decades have seen the exponential rise of the development of smart materials sensitive to their external environment, as a consequence of the changes of the local physicochemical properties of their molecular components. Our team developed a molecular motor, which can continuously produce a torque under constant input of UV light, that can be used as a crosslinking agent in polymeric networks. We reported the formation of gels of poly(ethylene glycol) that can contract over time under UV light, as a consequence of the braiding of the macromolecules caused by the unidirectional rotation of molecular motors. Our current research focuses now on the exploration of the impact of the polymeric backbone on the contraction of the gel, by varying the persistence length and the contour length of the macromolecules. Therefore, SANS will be used to explore the change in the conformation of the macromolecules upon contraction of the material, in order to establish the structure-property relationship of our systems.

Structural characterization of photoactive polymeric gels crosslinked with rotary molecular motors

Experiment number:

9-11-2004

Beamline

D11

Date of experiment

From 19/03/2021 *to* 21/03/2021

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 poly(ethylene glycol) (PEG) gels cross-linked with light-driven molecular motors by Small-Angle Neutron Scattering (SANS) and Small-Angle X-Ray Scattering (SAXS) at different stages of their contraction under UV irradiation. [1] With the present experiments, we aimed to expand our understanding of these systems by characterizing gels formed from PEG with different average molecular weights $\overline{M_w}$ formed at their respective overlap concentrations c*. We also analysed gels formed with poly(dimethylsiloxane) (PDMS) to observe the influence of the chemical nature of the network strands both in the dry and swollen states.

Concerning the PEG gels crosslinked with molecular motors, we observe the overall same trend as we observed in our initial systems (Figure 1). In the low-q range, we observed an evolution of the intensity scaling with q^{-4} or q^{-3}, indicating the presence of aggregates at this length scale. In the mid-q range, the signal scales with $q^{-5/3}$, characteristic of a real polymer chain swollen in a good solvent. Finally, the evolution scaling with q^{-1} in the high-q range indicates the rod-like behaviour of the chain when probed at a length scale smaller than its persistence length.

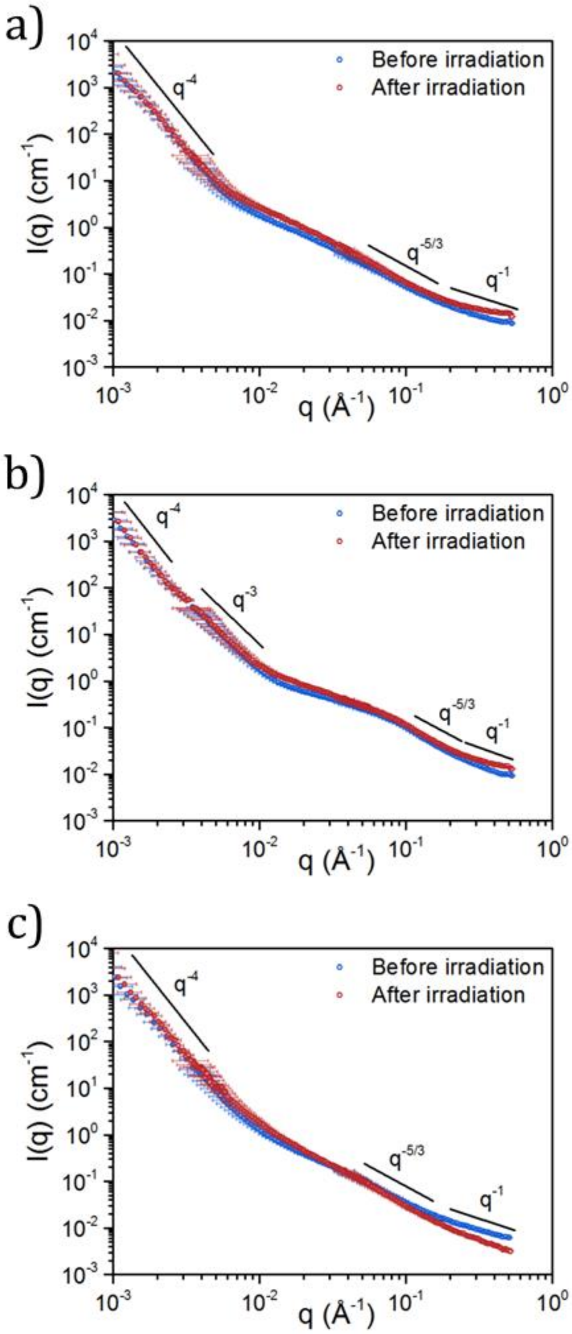

Figure 1. SANS spectra of gels formed from PEG of **a.** 3 000 g mol^{-1}, **b.** 6 000 g mol^{-1} and **c.** 10 000 g mol^{-1}. The gels were formed at their respective c* in DMF, swollen in water, and irradiated with UV light (λ = 365 nm) at 80 mW cm^{-2} for 1 h.

We determined the persistence length l_p of PEG in our gels by measuring the scattering vector q* at which the transition $q^{-5/3}$ – q^{-1} occurs, which is linked to l_p by the formula:

$$l_p = \frac{1.91}{q^*}$$

For our three systems, the values of l_p range between 0.7 nm and 1.1 nm, which is in accordance with the value we previously reported. [1]

The correlation length of the mesh ξ can be determined by a Lorentzian fit of the data of the mid-q range of the spectra, according to this formula:

$$I(q) = \frac{I_0}{1 + q^2\,\xi^2}$$

In all three cases, ξ increases after irradiation, as we observed in our initial systems. [1] However, it is important to notice that the relative increase is higher when the network strands are longer. ξ was multiplied by 1.05 with PEG at 3 000 g mol^{-1}, 1.16 with PEG at 6 000 g mol^{-1}, and 1.44 with PEG at 10 000 g mol^{-1}. At the macroscopic scale, we observed that gels formed with PEG at higher molecular weights contracted to a higher extent. Consequently, SANS analysis was critical to correlate the macroscopic contractile behaviour of our materials to the microscopic structural changes of the network.

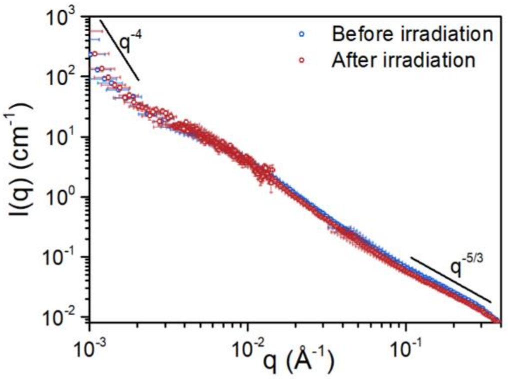

Figure 2. SANS spectra of PDMS gels crosslinked with molecular motors. The gels were crosslinked in dichloromethane, swollen in THF, and irradiated under UV light (λ = 365 nm) 80 mW cm^{-2} for 1 h.

We investigated for the first time PDMS gels crosslinked with molecular motors (Figure 2). The evolution of the signal intensity as a function of the scattering vector is similar to the one observed for gels based on PEG. Importantly, we also observed an increase in ξ after irradiation, which is 1.32 times higher after 1 h under UV light. Therefore, SANS analysis was essential to demonstrate that the structural changes occurring during the braiding of the polymer strands by molecular motors is independent from the chemical nature of the strands themselves.

To conclude, we used SANS to correlate the structural changes taking place under UV irradiation to the macroscopic shape change of our materials. This analysis was conducted for the first time at the respective c* of gels formed from PEG having different molecular weights, and evidenced the higher increase in mesh size when longer polymer chains are used. We also studied PDMS-based gels and observed that the mesh size also increases in that case, indicating that the chemical structure of the strand does not significantly alter the mechanism of contraction of our materials. Consequently, our further investigations will focus in the implementation of other types of polymers in such photoactive systems, and SANS will be once more be essential to determine the structure-property relationship of these gels.

References

[1] G. Mariani, J.-R. Colard-Itté, E. Moulin, N. Giuseppone and E. Buhler, “Structural properties of contractile gels based on light-driven molecular motors: a small-angle neutron and X-ray study,” *Soft Matter,* pp. 4008-4023, 2020.