Experiment Proposal

Experiment number GP2023025

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Experiment title PVA-based Twin-Chain Networks with tuned porosity: structural features and pores investigation

MRF Instrument	**SAXS Xenocs Xeuss**	**Days requested:** 2
Access Route	Direct Access	**Previous GP Number:** No
Science Areas	Chemistry, Cultural Heritage, Materials	**DOI:** -
Sponsored Grant	None	**Sponsor:** -
Grant Title	-	**Grant Number:** -
Start Date	-	**Finish Date:** -
Similar Submission?	-	
Industrial Links	Nikko Chemicals Co. Ltd. Tokyo	

Non-Technical Abstract

Twin-Chain Networks (TC-PNs) are cryogels made of two PVAs, with higher (H-PVA)= and lower (L-PVA) molecular weight, Mw. Phase-separation occurs in the pre-gel sol: L-PVA forms blobs, while H-PVA is mainly in the continuous phase. The study of the fluids/ particulate diffusion mechanism through such matrices is of interest in fields like art restoration, drug delivery and filtration. Gels were analyzed through Confocal Microscopy and SAXS HECUS, but only feature in the 1-100 μm and 1-15 nm could be probed. To this end, we plan to perform FIB-SEM; high-resolution 3D reconstructions will give information about sub-μm pores connectivity. The morphology and structure of gels crosslinks will also be probed: polymer crystallites are expected to be affected by the different porogens. FIB-SEM results will be combined and compared to USAXS/SAXS/WAXS data (proposal contextually submitted).

Publications

ISIS neutron and muon source **IM@IT E-platform:** No

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Sample record sheet

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MRF Instrument **SAXS Xenocs Xeuss** **Days Requested:** 2
Special requirements:

SAMPLE

Material	Polyvinyl Alcohol, Water	Polyvinyl Alcohol, Water	-
Formula	-CH2CH(OH)-	-CH2CH(OH)-	-
Forms	Solid	Liquid	
Volume	cc	15 ml	
Weight	15 g	mg	
Container or substrate	-	-	-
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

Temperature Range	298 - 298 K	298 - 298 K	-
Pressure Range	- mbar	- mbar	-
Magnetic field range	- T	- T	-
Standard equipment	None	None	-
Special equipment	-	-	-

SAFETY

Prep lab needed	No	No	-
Sample Prep Hazards	No	No	-
Special equip. reqs	No	No	-
Sensitivity to air	No	No	-
Sensitivity to vapour	No	No	-
Experiment Hazards	No	No	-
Equipment Hazards	-	-	-
Biological hazards	No	No	-
Radioactive Hazards	No	No	-
Additional Hazards	-	-	-
Additional Details	-	-	-
Sample will be	Removed By User	Removed By User	-

PVA-based Twin-Chain Networks with tuned porosity: structural features and pores investigation

1. Background and Context. Poly(vinyl alcohol) (PVA) is a biocompatible and hydrophilic polymer. Conventional PVA cryogels can be prepared by applying a freeze/thaw process to aqueous PVA solutions; at low temperatures, a water-polymer phase-separation occurs: ice crystals confine the polymer chains in restricted areas and PVA eventually forms crystallites, which act as physical junctions in the network. A new class of PVA cryogels, Twin-Chain Polymer Networks (TC-PNs) was recently formulated by blending two different PVAs, with higher and lower molecular weight, Mw, and hydrolysis degree, HD, (H-PVA and L-PVA, respectively).[1] The pre-gel solutions containing H-PVA and L-PVA (12% w/v) undergo a polymer-polymer phase-separation: L-PVA concentrates in blobs, while H-PVA is mainly localized in the continuous phase. During freezing, H-PVA is physically crosslinked, while L-PVA blobs act mainly as porogens in the final gel structure. After thawing, gels are washed in water to extract unbound polymer (the porogen and unbound H-PVA; residual PVAs: 5% w/v ca.). Washed TC-PN, fig. 1, shows a sponge-like, hierarchical structure which has proven ideal for the cleaning of modern and contemporary paintings: such gels were used to restore unique masterpieces by Pollock and Picasso[1-3], among many others. In addition to art restoration, knowledge about diffusional properties in gels has great relevance in several research fields such as drug delivery, filtration of wastewater, cell growth, adhesion, and entrapment. This research is funded by European Union - PON Research and Innovation 2014-2020, in collaboration with Nikko Chemicals Co. Ltd., Tokyo (raw materials and experiments in Nikko laboratories). Moreover, this research is of interest for, and funded by, European project GREENART (101060941). Both projects focus on green, functional materials for art restoration, such as PVA from sustainable sources.[4]

2. Proposed experiment. Recent experiments have shown that the gels cleaning efficacy is related to the diffusion properties of fluids and particulate within the matrix. Such properties are related to pores size and connectivity/tortuosity, which can be tailored by varying the porogen polymer. Some of the TC-PNs with tailored pores have been already characterized through Confocal Imaging (CLSM) and SAXS (in Kratky geometry, HECUS). However, we could not access pores in the hundreds of nm range, nor we could find structural differences between the samples (all showed the same ξ and similar R, see following section). Therefore, SAXS (Xenocs XEUSS 3.0HR) and FIB-SEM (TESCAN GAIA 3) instruments are requested to investigate TC-PNs containing L-PVAs with different M_w and HD (88%, 80%). SAXS can provide information about phase-separation in the pre-gel sols (polymer chains conformation and aggregates size); as for the hydrogels, SAXS will give access to mesh-sizes in the 1-120 nm range and inhomogeneities up to the micron scale in the Ultra-SAXS (U-SAXS) mode. According to preliminary experiments, SAXS profiles obtained through XEUSS 3.0 system are expected to show the presence of two different mesh-sizes (around 10 and 100 nm, respectively) and two different surface fractal dimensions. The scattering curves will be fitted according to an extended model, proposed by Hudson et al.[5] Information about sub-micron pores and connectivity will be retrieved also from the high-resolution 3D reconstructions of FIB-SEM. Image analysis will be performed with Matlab/ImageJ. TC-PNs micron-scale pores differ sensibly among the investigated systems (see following section), crystallinity and mechanical properties are almost the same. Therefore, additional WAXS experiments, combined with FIB-SEM imaging, will provide details about crystallites clusters size and morphology: crystallites structure alterations are expected if different porogen chains are included in the crosslinks. FIB-SEM requires freeze-dried gels, therefore sample pores size will be compared qualitatively according to the expected shrinkage. Nonetheless, the high-resolution imaging will give structural detailed information, that cannot be easily accessed with other techniques.

3. Summary of previous experimental proposals or characterisation. We recently investigated the structure of TC-PNs containing three L-PVAs (L-1, L-2, L-3), differing in their Mw, but with the same HD ($M_{wL-1} < M_{wL-2} < M_{wL-3}$, HD = 88%). The different Mw affected the morphology of the polymer-polymer phase separation and, consequently, the gels porosity at the micron-scale (pores

size between 2 and 30 µm, see CLSM images in fig. 1 B-G). Nonetheless, other gel properties such as the crystallinity (related to crosslinks, measured through Differential Scanning Calorimetry, DSC) and mechanical elasticity (investigated through linear rheology) remained almost unchanged. Nanoscale features of the gels were investigated through SAXS HECUS (fig.1H). Using a fitting model[5] that includes a contribution from the polymer network held by fixed polymer junctions (PVA crystallites) and a second contribution from polymer chains in solution, we extracted from fits one mesh size (ξ) and chain radius of gyration (R). We found that while R is smallest for the sample with lower Mw (L-1), ξ does not vary significantly between samples (ξ ≈ 5 nm).

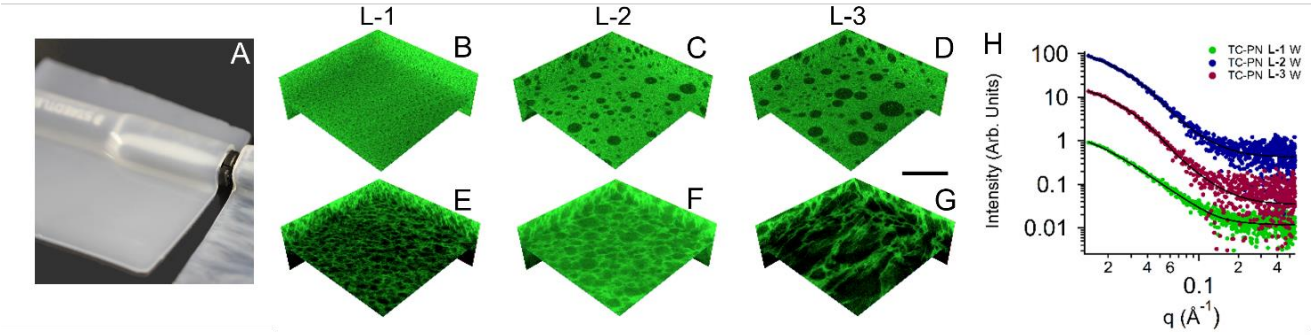

Figure 1. A) TC-PN gel. B-G) Confocal images of sols and gels, with H-PVA labeled in green; B) L-1, C) L-2 D) L-3 pre-gel sol; E) L-1, F) L-2 G) L-3 gels; Scalebar: 50 µm. H) SAXS curves and fitting of L-1, L-2 and L-3 gels.

4. Justification of experimental proposals request. Sols and gels morphology in the µm-range can be easily accessed by CLSM, but the structure in the 1-120nm range is not characterized. The combination of U-/SAXS/WAXS and FIB-SEM measurements would help to get a more complete picture of gels nanostructure, from pores size and connectivity to crosslinks morphology. Moreover, U-/SAXS of the pre-gel sol would give information about the morphology of phase separation, *i.e.* the template of the final gels structure. The measurements plan is the following (see also Table 1):

- **SAXS/WAXS**: measurements of TC-PN pre-gel solutions (SAXS only) and networks(SAXS + WAXS). Systems contain H-PVA + L-PVA of different Mw and HD (L-1, L-2, L-3 with HD=88% and LL-1, LL-2, LL-3 with HD=80%); a system of pure H-PVA will be used for comparison. Q range: from about $2x10^{-5}$ $Å^{-1}$ to about 3 $Å^{-1}$. High Resolution Mode. Sample-to-Detector (SD) distances: 1800, 400, 80 mm plus a fourth scan in U-SAXS mode.

- **FIB-SEM imaging of TC-PN networks**: the 7 gels (including neat H-PVA), stained and fixed in epoxy resin, will be mounted in a stub for the auto-slice and view procedure. Data will be collected on at least a 5*5*5 µm micron cube. Images will be collected at an electron acceleration voltage of 2 kV, recording data with the mid angle or in-chamber BSE detector. The image resolution will be set to optimize the resolution and signal to noise ratio. We plan to achieve a slice thickness (along Z) of 10 nm and a resolution on each slice of at least 3 nm.

U-/SAXS/WAXS experiments will require 10800 s + 3600 s + 2400 s + 600 s (in USAXS mode and at SD 1800, 400 and 80 mm respectively) per sample. Thus, we request 2 days for SAXS (Xenocs XEUSS 3.0) measurements. As for FIB-SEM setting and measurements, we request 2.5 days of machine time.

Table 1. Measurements plan for TC-PN systems characterization.

Technique	USAXS/SAXS (3 days)	WAXS (0.5 days)	FIB-SEM (2.5 days)
Samples	TC-PN sol and gels (14 samples)	TC-PN gels (7 samples)	TC-PN gels (7 samples)

References

1) Mastrangelo, R. et al., *PNAS* **2020**, *117*, 7011.
2) Bonelli, N. et al., *JCIS* **2019**, *536*, 339.
3) Pensabene Buemi, L. et al. *Herit. Sci.* **2020**, *8*, 77.
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5) Hudson, S. D. et al., *J. Chem. Phys.* **2009**, *130*, 034903
6) Shibayama, M. et al., J. Chem. Phys. 1992, 97, 6829.