EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: "Investigation of the nanostructure development of a PEG-polyacrylate during UV curing"**	**Experiment number**: 26-02-899
Beamline: BM26B	**Date of experiment**: from: October 1st 2018 to: Octorber 4th 2018	**Date of report**: June 24th 2019
Shifts: 6	**Local contact(s)**: Dr. Michela Brunelli	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Daniel Hermida Merino – Dubble/ NWO

Bing Wu* – Dubble/Royal College of Surgeons in Ireland

Report:

As one of the most used soft material, PEG-based polyacrylate material has been used in various industrial applications like biomedical coating and tissue engineering. While UV-curing, due to its simplicity and easy applicability, has been widely used in the industrial production of polyacrylate gels. One of the shortcoming of implementing this radiation-induced radical polymerization is the extensively presented micro-phase-separation in the product. Through using AFM to in-situ study the morphological heterogeneity in gels which were photo-cured from several oligomeric diacrylates, Krzeminski et al. found a rodlike 'microgel' was formed during the initial stage of the curing process. Similar microgel structure has also been observed in DSC.

In our preliminary in-house AFM study, we found a clear phase separation in 50% cured PEG-polyacrylate gel. While the NMR spin diffusion analyses on the similar sample also showed a clear phase separation in the gel with relative low curing degree. Hence, it is important to systematically probe microheterogeneity in a series UV-cured polyacrylates with an in-situ analyses..

Small-angle scattering techniques are well-known for their applications in probing structural heterogeneity on the scale from 10 to 10^4 Å. As shown in Figure 2, from the initial SAXS analyses, two domains are clearly shown in the 50% cured PEG-polyacrylate gel, and with the increasing of the curing degree, the size of the microgel domain increased. Moreover, our past preliminary synchrotron SAXS analyses on systems mixed between diacrylate and monoacrylate with different ratio, also shows a shifting in the size distribution of these microgel structure, which indicates the significant influence of monoacrylate on the formation of microgel structure.

By analysing this UV-curing procedure with synchrotron-based in-situ SAXS-WAXS, one can have a deep understanding on the effect of crosslink density and monoacrylate on the formation of microgel structure during the whole curing procedure

Figure 1 shows examples of this SAXS profile evolution, not all the system will form nanogel during the curing process. For instance, SAXS profiles of PEGDA-250 shows no discernable peak appear at high q range.

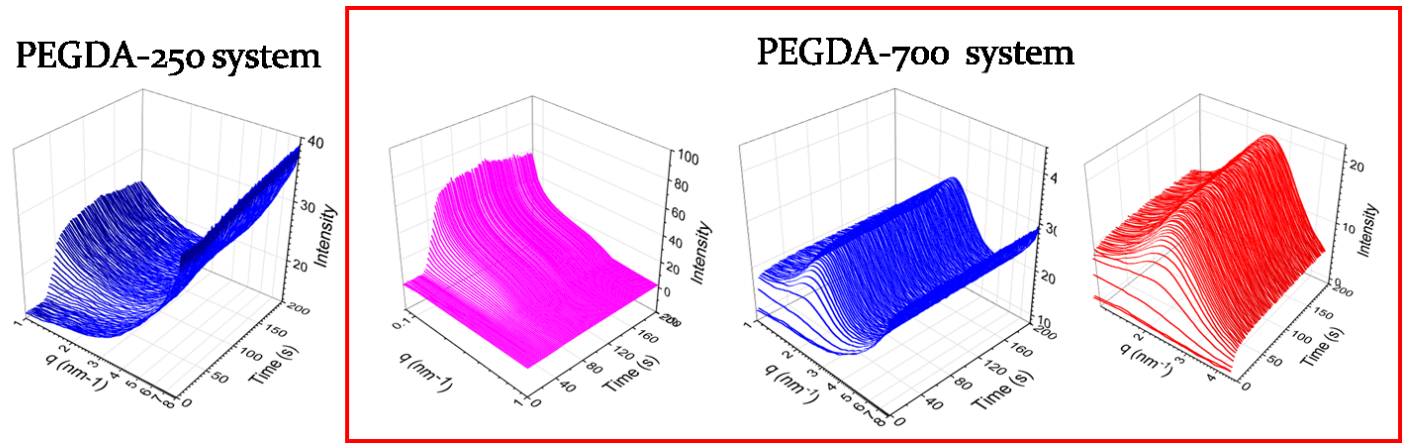

Figure 1. SAXS profile of PEGDA-250 and PEGDA-700 over time..

On the other hand, these profiles with distinguishable peaks can be fitted with a Gaussian function at their high q region, while the fractal dimesion also can be extracted through a simple power law fitting on their low q region.

The fitted parameters for PEGDA-HA system are shown in figure 2. It can be found the nanogel formation undergo a turning point at 30 s for all the composition ratio, and the molar number and size of these nanogels are also affected by the co-polymer portion. The addition of co-polymer into the system (in this case, hexyl acrylate) will increase the polydispersion as well as reduce the overall size of these nanogels, and the kinetic of this gelation process becomes slower.

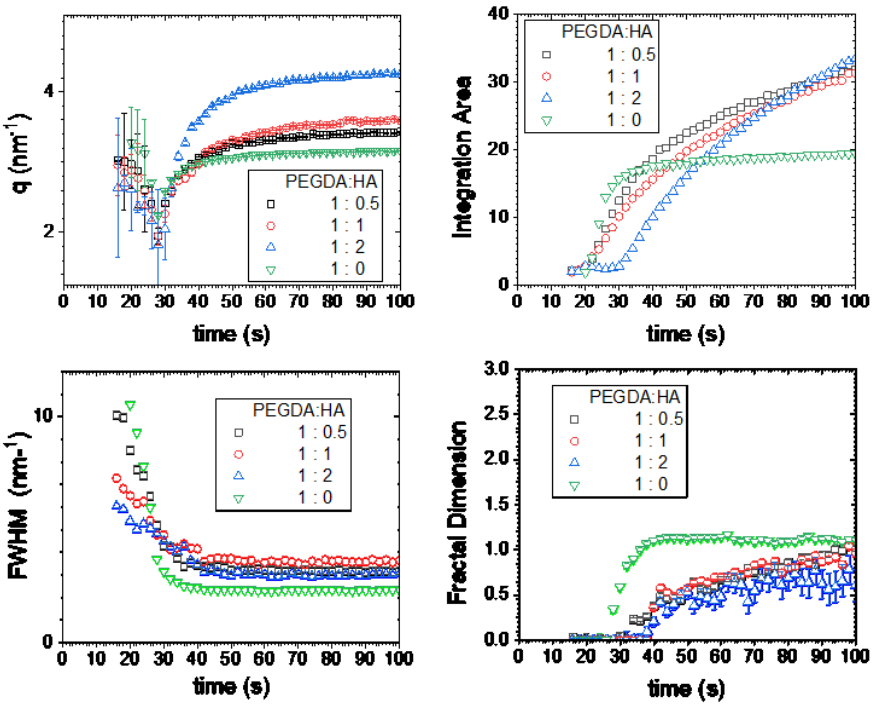

Figure 2: The fitted parameters (peak position, intergartion area, FWHM)for evolution nanogel peak over time, as well as the evolution of fractal dimension from Deybe regime of this system.

The set of experiments promotes the understand of the formation and evolution of nanogel in these acrylates system. and the manuscript is under prepartion.