

**Experiment title:**

A Time-Resolved SAXS/WAXS/DSC Study of the Self-Healing of a Supramolecular Polymer

Experiment number:

SC-4311

Beamline:	Date of experiment: from: 18/7/16 to: 22/7/16	Date of report: 30/1/17
Shifts:	Local contact(s): Daniel Hermida-Merino	<i>Received at ESRF:</i>

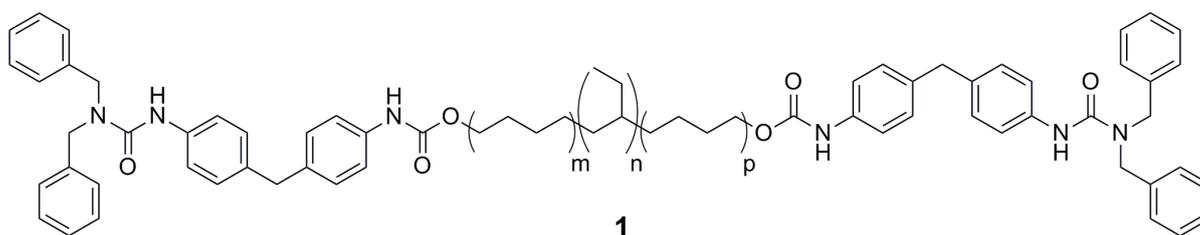
Names and affiliations of applicants (* indicates experimentalists):

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Non-applicant experimentalists: Ben Baker,* Flavien Leroux,* Dept. of Chemistry, University of Reading, Whiteknights, RG6 6AD, UK

Report:

SAXS/WAXS was performed on several thermoreversible supramolecular polymer network. A particular focus was on the supramolecular polyurethane **1** which is related to several polymers previously studied in our group.¹⁻²



A variety of heat/cool and annealing protocols were employed with SAXS and WAXS measurements, in order to correlate to detailed rheological measurements. Representative SAXS data showing peaks from microphase-separated structures is shown in Fig.1.

Materials were prepared by solution casting, quenching and annealing of quenched material, allowing pronounced micro-structural evolution, which leads to rapid increases in modulus as determined by Rheological analysis. Tensile tests showed that the quenched material is soft, weak and ductile (shear modulus ~ 5 MPa, elongation ~ 250 %), but after annealing, at 70 °C for one hour, it becomes stiffer, stronger and more brittle (~ 20 MPa, ~ 20 %). FTIR and NMR analysis, coupled with MDSC and SAXS, were

performed to investigate the network's dynamic structural changes. SAXS results suggest the presence of a lamellar structure in the sample when solution cast at high temperature, or annealed. This is believed to be unique when compared to related supramolecular bisurethane and bisurea polymers, and may be the cause of the observed path dependence. These mechanical properties, which can be switched repeatedly by simple thermal treatments, coupled with its adhesion properties as determined from peel and tack tests, make it an excellent candidate as a recyclable material for adhesives and coatings.

This work is currently being prepared for publication.³

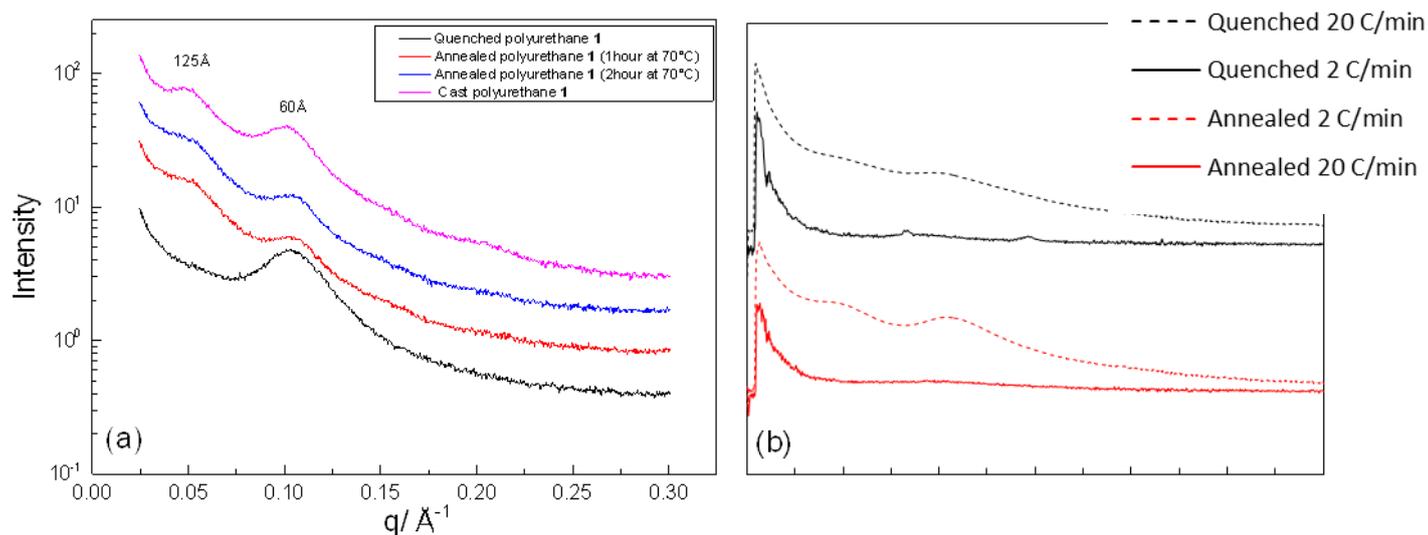


Figure 1. Small angle X-ray scattering (SAXS) of polyurethane **1** with; a) different processing histories, b) different cooling rates with respect to different processing histories.

References

1. Merino, D.H., Slark, A.T., Colquhoun, H.M., Hayes, W., Hamley, I.W. *Polymer Chemistry*, 2010. **1**, 1263-1271.
2. Feula, A.; Tang, X.; Giannakopoulos, I.; Chippindale, A. M.; Hamley, I. W.; Greco, F.; Buckley, C.P.; Siviour, C. R.; Hayes, W. *Chem. Sci.* 2016, **7**, 4291-4300.
3. Tang, X., Feula, A., Baker, B.W., Melia, K., Hamley, I.W., Buckley, C.P., Hayes, W., Siviour, C.R. 2017, *in preparation*