

*Two-dimensional polymers: from monomer to polymer crystals and back*Gregor Hofer¹, Florian Grieder¹, Martin Kroeger², A. Dieter Schlueter³, Thomas Weber¹¹X-Ray Platform D-MATL, D-MATL, ETH Zürich, Zürich, Switzerland, ²Computational Polymer Physics, D-MATL, ETH Zürich, Zürich, Switzerland, ³Institute for Polymer Chemistry, D-MATL, ETH Zürich, Zürich, Switzerland
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Recently, polymer chemists applied the well-known concept of single-crystalline photo-dimerization to create two-dimensional (2D) networks in the single-crystalline state. They are called 2D polymers [1]. To achieve this, the monomer is crystallized in a layered arrangement and the obtained crystals are photo-irradiated. This causes covalent bonds to form between adjacent monomer molecules, resulting in a single crystal of 2D-polymer sheet stacks. Heat treatment reverses the bond formation and the original monomer crystal is recovered. Polymerization and depolymerization can be suspended at any time by removing the crystals from the triggering source, allowing for detailed ex-situ structural investigations of any intermediate state. This provides valuable insights into the structural changes associated with these rather complex conversions.

The focus of this study is on the 2D polymer developed by Kory et al. [2] which is currently under technical production. Because of the foreseen importance of this novel 2D material, our aim is to understand the fundamental properties of 2D polymerization and depolymerization in detail by single-crystal total X-ray scattering. We address this by analyzing monomer, intermediate and polymer structures of these isosymmetrical, but non-isostructural phase transformations. Experiments were carried out at synchrotron and in-house sources, where we collected data sets from several single-crystals at different temperatures. The Bragg scattering shows a discontinuity and a strong hysteresis effect in the length of the crystal axes during both polymerization and depolymerization (see Figure). Complex structural changes are observed, which result from an interplay between molecular shifts and distortions, and also from the orientation dynamics of the incorporated solvent molecules. The polymerization reaction kinetics, which was also monitored by single-crystal X-ray diffraction, shows a smooth development and delivers insights about possible real structure propagation models.

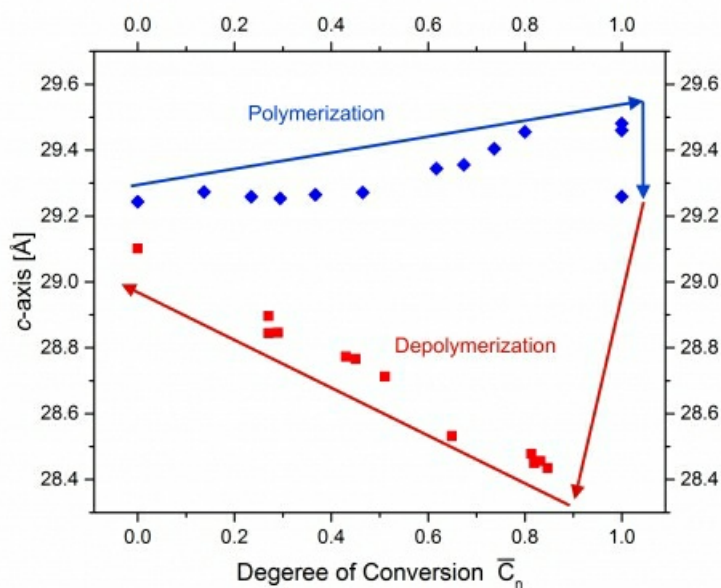
Combined results from the average structure and from simulations indicate random polymerization propagation, but this awaits proof by ongoing investigations of the diffuse scattering via the 3D- Δ PDF method [3]. The diffuse scattering shows several features, such as maxima at systematic extinct lattice positions that appear upon the first step of conversion, are most intense at 50% conversion and gradually fade thereafter. Upon depolymerization, we observe additional streaking along c^* centered on the Bragg peaks which supports our findings that polymerization and depolymerization proceed in structural different fashions.

Figure: Development of the c-axis upon polymerization and depolymerization.

[1] Payamyar, P., et al. (2016). Chem Commun. 52, 18–34.

[2] Kory, M. J., et al. (2014). Nat. Chem. 6, 779–784.

[3] Welberry, T. R. & Weber, T. (2016). Crystallogr. Rev. 22, 2–78.



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