Intriguing structural features of a novel two-dimensional polymer (2DP)

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Introduction

Traditional one-dimensional polymers (1DP) as used in plastics or rubber are made from bifunctional structure units (monomers), which can be connected to other bifunctional monomers via linear covalent bonding. This linear bonding results in one-dimensional long-range ordered polymers. The synthesis of a sheet-like polymer was achieved in 2014 \cite{1} based on a trifunctional monomer (Fig. 1).

Possible future applications depend on sheet size and perfection and may include surface coating, molecular sieves, catalytic surfaces or macro scale anisotropic materials.

The Problem

Single crystal structure refinement already revealed the monomer (Fig. 3a), polymer (Fig. 3b) and partially-polymerized average structure. The question of interest is how the polymerization propagates within the crystal. There are two possible extreme scenarios, either completely random (Fig. 4) or continuous growth from a distinctive point (nucleation, Fig. 5).

The exact nature of the propagation is of interest because it can lead i.e. to local distortions in the crystal lattice which may prohibit further polymerization reactions and thus reducing the overall degree of polymerization. This information was obtained by average structure refinement.

The Solution

For various good reasons, diffuse X-ray scattering is usually neglected during data reduction. However, it is sensitive to the local atomic arrangement and their correlations, which can not be resolved by standardized methods. Recent developments in X-ray sources, detectors and software finally allow us to record data sets of diffuse scattering for quantitative analysis. Using Synchrotron measurements and the Yell program \cite{3}, written for 3D-APDF refinement, we will follow and quantify the changes in the real structure of an individual single crystal during polymerization. By relating the real structure with irradiation times, we will be able to determine the type of polymerization.

Possible future applications are depend on sheet size and perfection and may include surface coating, molecular sieves, catalytic surfaces or macro scale anisotropic materials.