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 [1] based on a trifunctional monomer (Fig. 1).

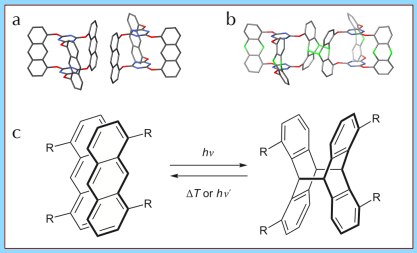

Figure 1: Monomer (a) and reacted polymer (b) with black = C, blue = N, red = O, green = reacted carbons. The dimerization of anthracene (c) is responsible for the polymerization reaction within the crystal.

Following the so-called *single-crystal approach* (Fig. 2), this novel monomer gets crystallized prior to their connection. By irradiation with UV light, genuine two-dimensional polymerization can be achieved within the single crystalline state. Individual sheets with thicknesses of a few atoms and theoretically infinite lateral extent can be obtained through exfoliation by scotch tape or swelling.

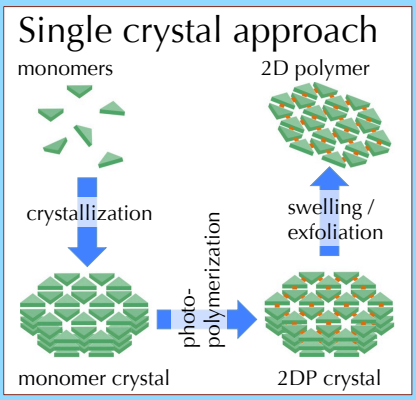

Figure 2: Topological scheme for creating a 2DP using the single crystal approach [2].

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

[1] Kory, M. J., Wörle, M., Weber, T., Payamyar, P., van de Poll, S. W., Dshemuchadse, J., Trapp, N. & Schlüter, D. (2014) *Nature Chem.*, 6(9), 779–784.
[2] Schmidt, G. M. J. (1941) *Pure Appl. Chem.*, *12*, 647– 678 and Wegner, G. (1969) *Naturforsch.*, *24B*, 824– 832.
[3] Simonov, A., Weber, T., & Steurer, W. (2014) *J. Appl. Cryst.*, 47(3), 1146–1152.

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A complete reconstruction of the reciprocal space from Fig. 7 can be viewed on youtube, link provided by QR code.

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).

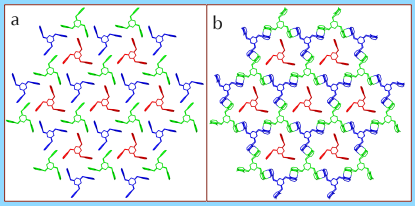

Figure 3: Single sheet viewed along the c-axis in the monomer crystal (a, SG R3 a1 = 19.3599(7) Å, c = 28.8871(14) Å) and polymer crystal (b, SG R3, a1 = 19.5041(3) Å, c= 29.1223(7) Å). Three crystallographic distinct monomers form the sheet. Blue and green ones are forming the interlinked network while red monomers act as a spacer. Solvent molecules omitted for clarity.

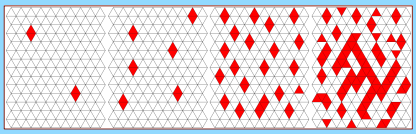

Figure 4: Random like polymerization. Bond formation starts and continues at random locations (**no correlation**).

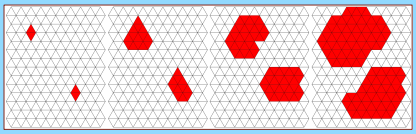

Figure 5: Nucleation like polymerization. Bond formation starts at random locations, while further bonding reactions take place right next to already existing bonds (**positive correlation**).

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 sheet size (Fig. 6).

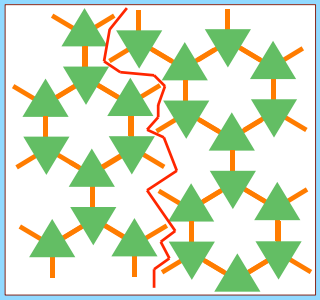

Figure 6: Possible schematic representation of locale distortions during nucleation-like polymerization due to different polymer domain sizes. The two polymer domains are too far apart thus prohibiting further interatomic bonding.

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 [3], written for 3D-ΔPDF 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.

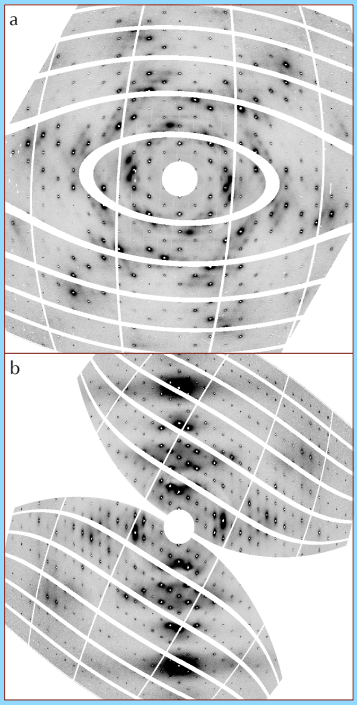

Figure 7: Reciprocal space image reconstruction of the hk0 (a) and 0kl (b) layers of our preliminary Synchrotron measurements at SLS. The grid is a result of the gaps between the detector modules of the Pilatus 6M. Bragg scattering and defective pixels are masked with pure white color. Extensive diffuse scattering streak-like and blob-shaped features can be observed.

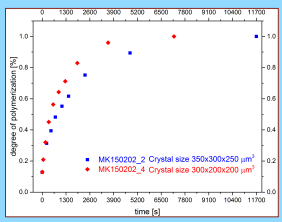

Figure 8: Plot of irradiation times against the overall degree of polymerization. This information was obtained by average structure refinement.