

On the mechanism and accompanying effects of two-dimensional polymerization in a novel mono-layered monomer crystal

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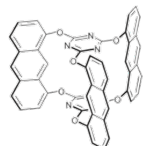
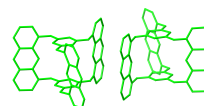


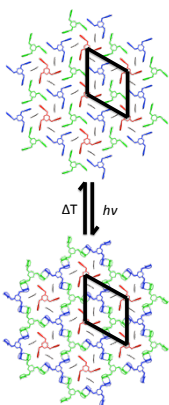
Figure 1: Trifunctional monomer used in this study [2].

Introduction

A recent advance in polymer chemistry is two-dimensional polymerization [1]. This is achieved by pre-organizing trifunctional monomer molecules in a layered arrangement by crystallization. Exposure to intense light triggers a reversible photochemical reaction. New covalent bonds are formed between neighboring monomer molecules and genuine long-ranged ordered two-dimensional polymerization is accomplished. The result of this single-crystal-to-single-crystal transformation is a two-dimensional polymer (2DP) crystal. Single 2DP sheets can be obtained by dry and wet exfoliation [2]. This study aims at unraveling the propagation of two-dimensional polymerization.

Structures

Figure 2: (top) Monomer crystal structure of a single layer viewed along the *c*-axis. Symmetry independent monomer molecules are marked in blue, green and red. The orientationally disordered 2-cyanopyridine solvent molecule is sketched in black. (bottom) Polymer crystal structure of a single layer viewed along the *c*-axis. Symmetry independent polymer moieties are marked in blue and green. The red monomer molecule does not take part in the polymerization reaction.



Monomer crystal
Spacegroup R3
 $a_1 = 19.3425(2) \text{ \AA}$
 $c = 28.8879(4) \text{ \AA}$
 $V = 9359.96(17) \text{ \AA}^3$

$\xrightarrow[\Delta T]{h\nu}$

Polymer crystal
Spacegroup R3
 $a_1 = 19.5041(3) \text{ \AA}$
 $c = 29.1223(7) \text{ \AA}$
 $V = 9594.2(3) \text{ \AA}^3$

Two-dimensional polymerization

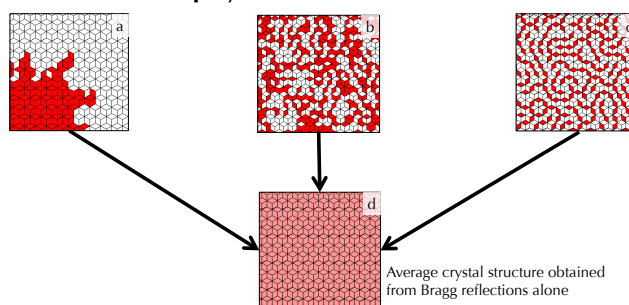


Figure 3: Possible types of two-dimensional polymerization, (a) nucleation-like, (b) random and (c) dimerization-like. All three presented types of polymerization exhibit the same average structure (d) at an identical degree of polymerization. The models vary in the nearest neighbor pair correlation. Bragg reflections are not sensitive to such pair correlations but diffuse X-ray scattering is [3].

Average structure analysis from Bragg scattering

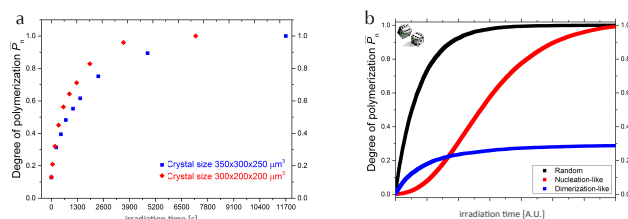


Figure 4: Development of (a) polymerization with irradiation time and (b) Monte Carlo simulations of polymerization from different models of polymerization propagation. The degree of polymerization is derived from the average structure. The random model represented by the black curve and the measured data bear a close resemblance.

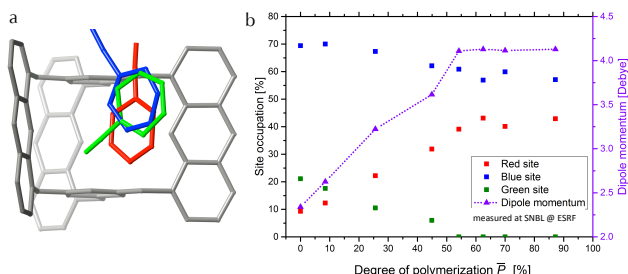


Figure 5: (a) Possible orientations of the disordered 2-cyanopyridine solvent molecule within a layer and (b) their changes with increasing degree of polymerization. The reorientation is a polymerization induced side effect. The change in site occupation of the green site results in a drastic increase of the electric dipole momentum perpendicular to the sheet by 1.9 Debye (b). For comparison, the electric dipole momentum of a single water molecule is 1.85 Debye. Electric dipole momentum is calculated based on the respective site occupations.

Real structure analysis from diffuse X-ray scattering

Deviations from the ideal structure are contained in diffuse scattering [3]. Several diffuse scattering features are found upon polymerization and depolymerization, Figure 6. The 3D- Δ PDF method [4, 5] will be employed to analyze these features to determine the polymerization propagation.

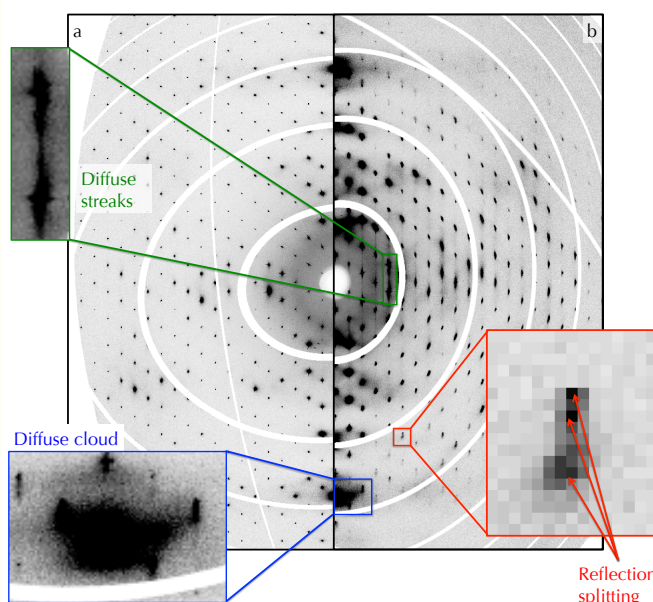


Figure 6: Reciprocal space cut of the 0k layer from (a) a monomer crystal and (b) a ~20% depolymerized polymer crystal. Measured at SNBL @ ESRF with a Pilatus2M detector.

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