

**Experiment title:**

3DXRD photo-crystallographic studies of long-time bulk photodimerisation reaction in multigrain solids

Experiment number:

MI 900

Beamline:

ID09B

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18

Local contact(s):

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Report:

Aim of proposal No MI 900 was the determination of the photo-conversion statistics of photo-active molecular crystals upon grain size, optical penetration depth and illumination time. The system investigated was the [2+2] photodimerisation of 2-benzyl-5-benzylidene-cyclopentanone (BBCP). For the studies we applied the techniques of 3D-XRD and the graindex approach as been developed by ID11 and RISO National lab to our photo-crystallographic research.

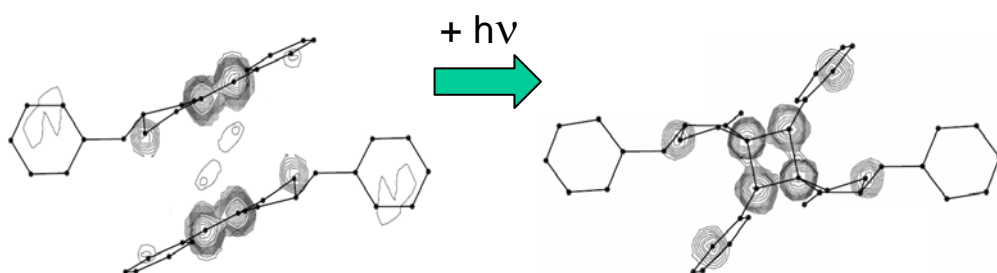


Figure 1: Molecular switch of BBCP from the monomer to the dimer state.

Figure 1 summarises the structural features of the photo-switching process of BBCP from the reactant to the product state as been derived from the crystallographic data (monomer: $R1 = 0.0426$ (11722 unique Bragg reflections), $wR2 = 0.1242$, $GooF = 1.842$, ca. 45000 reflections in total, dimer: $R1 = 0.0495$ (9834 unique Bragg reflections), $wR2 = 0.1394$, $GooF = 1.675$, spatial resolution: $d = 0.6 \text{ \AA}$). The x-ray diffraction patterns were analyzed by the use of the software package SHELXTL.

By applying the two-phase model, the photo-transformation kinetics within the various BBCP grains could be studied. Their sizes ranged from 5 μm to 14 μm . Figure 2 shows the transformation kinetics of one grain.

Within a transformation time of about 30 min, a 10 μm thick BBCP crystal transformed totally from the monomer / reactant to the dimer product state / phase.

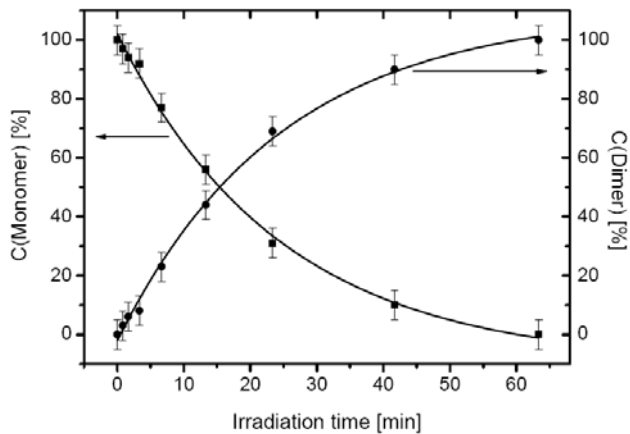


Figure 2: Photo-transformation kinetics of one grain.

For polycrystalline samples, the indexing programs GRAINDEX [2], GrainSpotter [7] and ImageD11 [8] have been applied. After the structure refinement, the R1 values varied between 3.2% and 3.7% for the various grains.

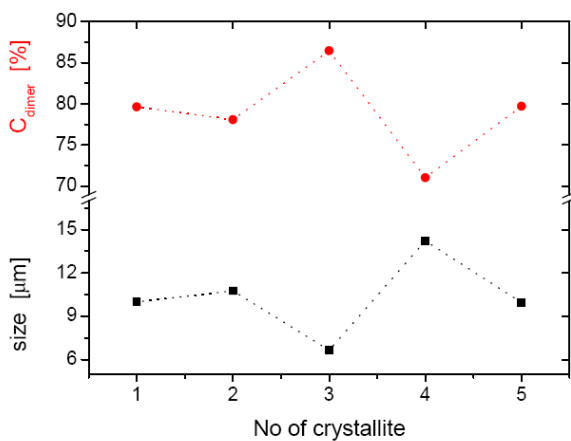


Figure 3: Relation between grain size and photo-conversion ratio in BBCP polycrystals.

Figure 3 emphasises the relation between grain size and photo-conversion ratio for 5 selected crystals. From the refined photo-conversion rate c_{dimer} , by applying monoexponential kinetic laws, the size of the transformed grain could be deduced.

References

- [1] J. Davaasambu, et al., *J. Am. Chem. Soc.*, submitted (2009).