

**s5.m3.o1 Crystal Structure and Morphology of Polymers.** B. Lotz, *Institut Charles Sadron, 6, Rue Boussingault, 67083 Strasbourg, France.*

Keywords: electron crystallography, small molecules, organic materials.

Crystalline polymers have highly complex structures and morphologies which stem from the fact that they are "polymolecular": their molecular weight (i.e. chain length) varies considerably for any given sample. The crystal structure rests on the parallel arrangement of extended or helical segments over only short distances (in the tens of nanometers range). The chains then fold back and forth a variable number of times depending on molecular length. The resultant lamellar morphology is best displayed by single crystals grown from solution, but similar lamellae build up three dimensional spherulites produced in bulk crystallization. Thus, two major challenges face polymer crystallographers: to solve the crystal structure (at the unit-cell level), sometimes using very small single crystals (typically down to the pico- or even tens of femtograms range) and to link the crystal structure with the lamellar structure and morphology.

Electron microscopy offers an unusual combination of diffraction and imaging capabilities which is perfectly adapted to the small size of chain-folded polymer crystals. Further, specific preparation and decoration<sup>1</sup> techniques make it possible either to obtain "unnatural" morphologies (by e.g. epitaxial crystallization<sup>2</sup>) or to gain insights into the fold structure. These techniques have helped:

- elucidate the structures of many crystal modifications of polymers, enabling in several cases direct comparison with X-ray fiber diffraction analyses. They have also helped uncover a hitherto unnoticed packing frustration in some structures. Frustration has been confirmed by atomic force microscopy,<sup>3</sup> and leads to highly unusual triangular single crystals.<sup>4</sup>

- uncover the origin of surface stresses in the fold surface of lamellae of polyethylene crystallized from the melt, leading to a spectacular optical "banding" of the spherulites.<sup>5</sup>

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**s5.m3.o2 Electron Crystallography on small organic molecules with high NLO activity.** U. Kolb, G. Nosova\* and I.G. Voigt-Martin, *Institut für Physikalische Chemie, Johannes Gutenberg-Universität, Welderweg 11, 55099 Mainz, Germany, \*Institut of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi pr. 31, 199004 St. Petersburg, Russia.*

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The non-linear optical active compound (E)-1(4 aminophenyl)-3-(4 bromophenyl)-2-propen-1-one (U800) shows a non-linear optical activity up to 800 times urea. The configuration of the molecule in Fig. 1 as well as its dipole  $\mu$  ( $=4.671$  Debye) and hyperpolarisability  $\beta$  ( $7.906 \cdot 10^{-50} \text{ Cm}^3/\text{V}^2$ ) was calculated by semiempirical, quantummechanical methods (MOPAC6.0; PM3)[1].

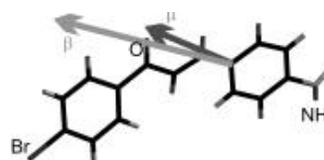


Fig.1: Dipole  $\mu$  and hyperpolarisability  $\beta$  for U800

Approx. 100-200 Å thick crystals were grown from hot ethanol. In diffraction mode three dimensional data sets were measured on a Philips 300 at 100keV by tilting the sample with a rotation-tilt holder around suitable axes (max. tilt angle  $\pm 60^\circ$ ). Determination of the orthorhombic unit cell ( $a=4.351$ ,  $b=1.896$ ,  $c=0.629$  nm) and the non centrosymmetrical space group Fdd2 was performed from 7 zones (tilt around  $b^*$ ) and 6 zones (tilt around  $c^*$ ). The cell parameters were refined using x-ray powder diffraction pattern measured in transmission. Intensities were collected using an Nikon AF-4500 scanner with 2400 dpi resolution and 12 bit grey level.

For simulation methods [2] cell dimensions, space group, the initial model of the molecule (Fig.1) and structure factor amplitudes were used. Packing energy minimisation and simulation of diffraction patterns were performed alternatingly gaining a good R-factor. Based on the obtained atomic coordinates, hyperpolarizability tensors were calculated using quantum mechanical methods and related to the crystal by appropriate coordinate transformation [3]. Separately, a 3D-data set was built up and statistical ab initio methods such as „Maximum Entropy“ [4,5] were used.

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