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| Experiment title: Influence of pressure on hydrogen bonded polymers; polyamides and biopolymers | Experiment number: SC1279 |
| Beamline: ID02 | Date of experiment: from: 10 th Sept 2003 to: 14 th Sept 2003 |
| Shifts: 12 | Local contact(s): Peter Boesecke |
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Report:

Copolyamides, based on 1,12-dodecanedicarboxylic acid and different ratios of 1,2-ethylenediamine and piperazine, i.e. PA-(2.14-co-pip.14), as well as the corresponding homopolymers PA-2.14 and PA-pip.14, were studied by SAXS and WAXS. Up to a pip mol ratio of 0.62, the 2.14 and pip.14 units co-crystallize in a common crystal lattice, slightly deviating from the structure of homopolyamide 2.14. The hydrogen bonds obviously tolerate significant amounts of comonomer before the crystal structure is changed significantly. For pip mol percentages of 0.90 and higher, both repeating units co-crystallize in a slightly distorted PA_{pip.14} crystal structure. For pip mol percentages of 0.70 and 0.82, however, the X-ray patterns show peaks that stem from both the PA-2.14- and the PA-pip.14-like crystalline structure, indicating that the two structures coexist in this composition range. Since the intersheet distance practically remains unaffected upon incorporation of the piperazine rings, it is concluded that these rings are oriented parallel to the hydrogen-bonded sheets. Furthermore, from the composition-dependency of the experimentally determined lattice spacings, keeping in mind that the intersheet distance is constant, it is concluded that the hydrogen-bonded sheets are shifted parallel to one another.

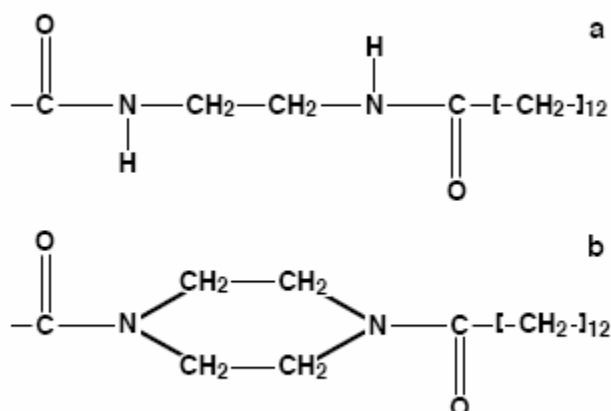


Figure 1: Chemical structure of (a) 1,2-EDA- and (b) piperazine-based repeating units.

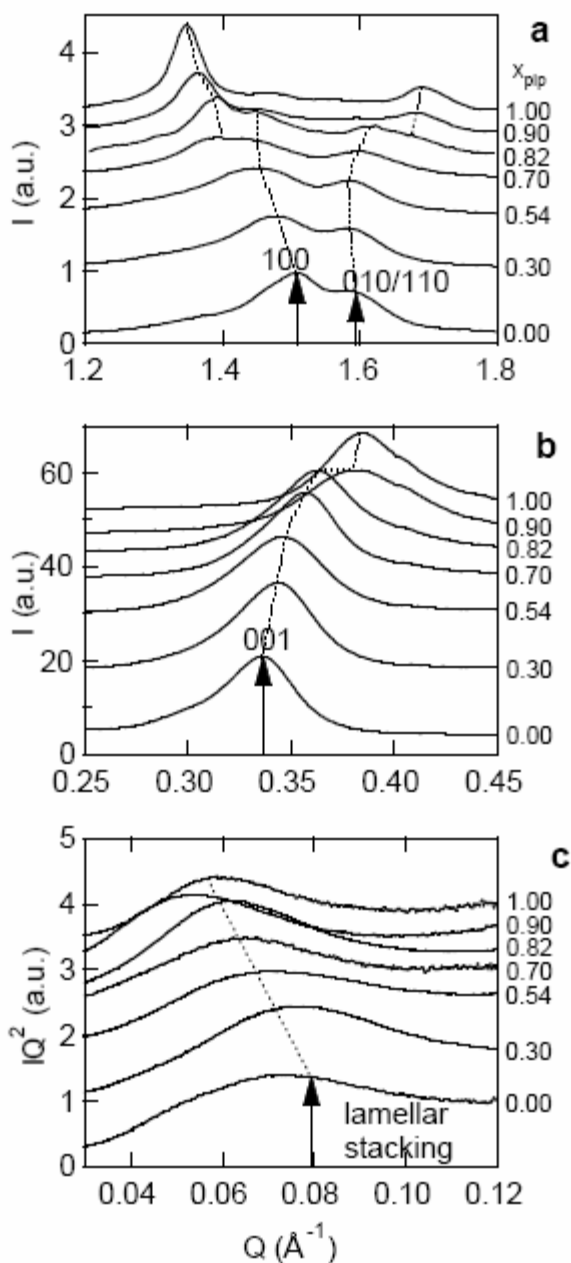


Figure 2: Examples for the X-ray diffraction from the SAXS/WAXD station of ID2 on copolyamides with the indicated molar fraction x_{pip} of piperazine-based amide units. The indices of the crystalline reflections are indicated for the PA-2.14 homopolymer ($x_{\text{pip}} = 0$). The vertical offset of all graphs is proportional to x_{pip} . (a) 100 and 010/110 reflections, (b) 001 reflection, (c) Lorentz-corrected diffraction intensity due to lamellar stacking. The dotted lines describe the general trend of the different peak positions and serve as a guide to the eye.

The detailed paper on this work has been accepted for publication,

Cocrystallisation in Piperazine-Based Polyamide Copolymers: Small- and Wide-Angle X-Ray Diffraction Studies; Sven Hoffmann, Bert Vanhaecht, Jan Devroede, Wim Bras, Cor E. Koning, Sanjay Rastogi; *Macromolecules* 2004 (ma048456e) in press, galley proof awaited.