

## UNFOLDING OF ULTRA-LONG ALKANES BY X-RAY DIFFRACTION

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Due to the connectivity along the polymer chain, polymer crystals are unique in that the whole crystal is directly influenced by a change in the packing density at the surface, e.g. it has been known for some years that the stem length of chain-folded polyethylene crystals affects the lattice parameters of the crystalline unit cell. The supposition is that the presence of chain folds at the surface causes an expansion in the lattice cell perpendicular to the chain axis and that the effect increases as the distance between the surfaces decreases. This implies that the crystal thickness might influence the "bulk" free enthalpy which has wide ranging implications for our understanding and interpretation of polymer crystallisation and melting. Previous studies of surface effects have used whole polymers and are therefore affected by significant differences in the folding behaviour of individual chains and by possibly significant differences between different crystals.

In this work, we examine how the stem length, fold density and temperature influence the lattice parameters of a sequence of long *n*-alkanes (from C<sub>102</sub>H<sub>206</sub> upto C<sub>296</sub>H<sub>594</sub>), which serve as model systems for polyethylene. Due to their uniformity of length, long alkanes crystallize with an integer number of folds per molecule, so as to reject the chain ends to the crystal surface while maximising the crystallinity. The *n*-alkanes in this study can be produced with up to two folds per molecule, depending on the crystallisation conditions and chain lengths, allowing us to work with samples with similar stem lengths, but a range of different fold densities.

Changes in the crystalline structure during heating were monitored by wide-angle X-ray diffraction. Measurements show that there is a decrease in the lattice parameters at a certain temperature, for a once-folded crystal as the crystal unfolds. This is not observed on heating an extended chain crystal. Just prior to this occurring, there is a strong increase in the peak width, providing a wide-angle signature of the increase in crystal disorder that occurs prior to unfolding. For an initially twice folded crystal, two unfolding events can be followed during heating, with their lattice contractions, as the crystal first transforms to the once folded, and then to the extended state before finally melting. These results show, unequivocally for the first time, the contraction of the crystal lattice that occurs as a polymer crystal transforms to a more stable form, with possible far reaching implications for our interpretation of the relationship between crystal thickness, melting temperature and fold surface energy. In addition, the extent of disorder present in the samples, as a function of temperature is examined.

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