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Chain Tilt and Surface Disorder in Lamellar Crystals. A FTIR and SAXS Study of Labeled Long Alkanes

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ABSTRACT: Small-angle X-ray scattering (SAXS) and infrared spectroscopy (IR) are employed in a study of chain tilt and disorder in solution-crystallized long alkanes $C_{198}H_{398}$ and $C_{12}D_{25}C_{192}H_{384}C_{12}HD_{24}$ in extended and once-folded conformations. The as-grown crystals have chains perpendicular to the lamellar surface, but around 90 °C they start tilting relative to the layer normal. The tilt increases gradually to reach 35° just below melting point. The end-labeled alkane allows independent IR probing of molecular disorder at the deuterated surface layer and in the hydrogenous interior of the crystals. The initially small splitting of the CD_2 bending mode doublet and the presence of a singlet component indicated a rough surface in as-grown crystals, with considerable translational disorder. The increase in splitting and decrease in absorbance of the singlet which occur on annealing at progressively higher temperatures showed a steady improvement in translational surface order, concomitant with an increase in chain tilt angle. Thus, it is concluded that the absence of tilt in as-grown crystals is not due to high surface order, as in the case of shorter odd *n*-alkanes, but rather to high nonequilibrium surface disorder with chain ends or folds protruding out of or sunk beneath the surface. It is also concluded that chain tilt only becomes necessary as the crystal surface becomes translationally more ordered and the crystal−amorphous interface sharpens. IR also demonstrated the reversible increase in conformational disorder in the surface layer with increasing temperature and an almost negligible increase in the crystal interior. The gradual change in tilt angle and the existence of noncrystallographic basal planes is interpreted in terms of translational molecular disorder at the surface. The increased central SAXS scatter during the tilting process indicates the creation of voids associated with ridge formation and corrugation of the lamellae.