On Perpendicular and Tilted Chains in Lamellar Crystals

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ABSTRACT

Chain tilt and surface disorder were investigated in end-deuterated long *n*-alkane $C_{12}D_{25}C_{192}H_{384}C_{12}HD_{24}$ crystallized from solution and in *n*-alkane $C_{162}H_{326}$ crystallized from melt. Small-angle X-ray scattering and infrared spectroscopy were employed. Extended-chain crystals of $C_{12}D_{25}C_{192}H_{384}C_{12}HD_{24}$ as-grown from solution have the molecular axis perpendicular to the lamellar surface, but when heated, around 90°C, they start tilting relative to the layer normal. The tilt increases gradually to reach 35° just below the melting point. $C_{162}H_{326}$ crystallized from the melt at small supercoolings has chains tilted at 35° at the outset, as found previously for all melt-crystallized long alkanes and polyethylene. However, for the first time in long alkanes, it is found that when molten $C_{162}H_{326}$ is supercooled to $\Delta T \geq 10$ K, crystals with perpendicular chains form. At still larger ΔT, the chains are once-folded, with a mixed population of tilted and perpendicular chain crystals. The use of Davydov splitting of the CH_2 and CD_2 bending vibration of the end-labelled alkane $C_{12}D_{25}C_{192}H_{384}C_{12}HD_{24}$ allows independent IR probing of molecular disorder at the deuterated surface and in the hydrogenous crystal interior. The initially small CD_2 splitting and the presence of an additional singlet component indicate a rough surface in as-grown crystals, with considerable longitudinal interchain disorder. It is estimated that about 10% of chains are displaced by up to a dozen C-atoms. The increase in splitting and decrease in absorbance of the singlet, which occur on annealing at progressively higher temperatures, are evidence of steady improvement in translational