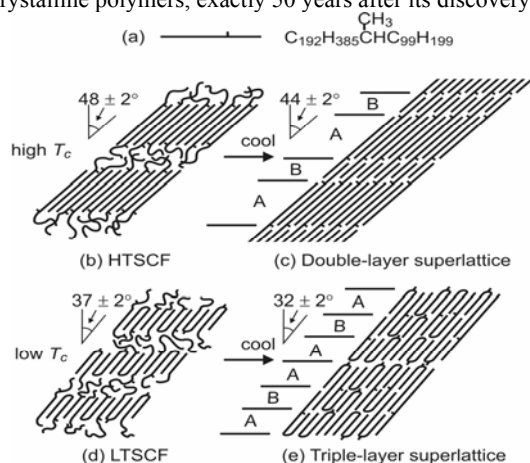


MS12 O1

Semicrystalline Nanostructures in Crystalline and Semicrystalline Ultralong Alkanes Xiangbing Zeng, Fangning Xie, Goran Ungar, *Department of Engineering Materials, University of Sheffield, Sheffield, U.K.*
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Keywords: SAXS, Superlattice, Polymers

Lamellar structure and its formation from melt has been studied in ultra-long monodisperse alkanes using real-time versions of small-angle neutron and X-ray (SANS and SAXS) and low-frequency-shift Raman scattering. Pure and binary linear unlabeled and deuterium end-labeled alkanes were examined, as well as an asymmetrically methyl-branched alkane, $C_{192}H_{385}CH(CH_3)C_{99}H_{199}$. It was possible to study the structure and the transformation of the initial transient Non-Integer Folded (NIF) form into a variety of secondary phases, whose formation depends on temperature [1,2]. These secondary phases include the extended-chain form and two mixed folded-extended forms: the double-layer and the triple-layer superlattice. The semicrystalline form, which features in pure alkanes as the transient NIF, becomes a stable high-temperature form in either binary mixtures of linear alkanes [3] or in pure branched alkanes. The rich layer polymorphism in the asymmetrically branched alkane was found to be due to the anchoring of the methyl branch at the crystal surface. Two semicrystalline and two superlattice forms were found [4] - see Figure. The exceptionally high chain tilt angle (46°) was caused by the inability of surface overcrowding to be alleviated by chain folding. The study provides new insights into the complex problem of chain folding in crystalline polymers, exactly 50 years after its discovery.



Schematic drawing of the different lamellar structures found in the asymmetrically branched alkane $C_{192}H_{385}CH(CH_3)-C_{99}H_{199}$. (a) The molecule, (b) high- T_c semi-crystalline form, (c) double-layer superlattice, (d) low- T_c semi-crystalline form, (e) triple-layer superlattice.

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MS12 O2

The fat bloom mechanism of chocolate clarified from X-ray powder diffraction data. Jan van Mechelen, Rene Peschar, Henk Schenk, *Laboratory for Crystallography, University of Amsterdam, Amsterdam, The Netherlands.*
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Triacylglycerols (TAGs) play a dominant role in the properties of consumer products that contain fats and oils. Both TAGs and mixtures of TAGs show polymorphism that depends on the crystallization temperature (T_c) and the immediate thermal history of the material. With an increase of temperature, or much slower in course of time under isothermal conditions, phase transition processes take place in which the less stable phases melt and higher-melting phases crystallize. In this way, all lower melting phases (γ , α and β') change into the metastable β_2 . The latter, however, in its turn eventually changes into the highest melting (β_1) phase [1]. Polymorphic phase transitions are generally unwanted in consumer products. Chocolate, for example, contains cocoa butter that with the common industrial tempering process usually is crystallized in the β_2 phase, better known as β -V. The inevitable $\beta_2 \rightarrow \beta_1$ transition in cocoa butter, commonly referred to as the β -V \rightarrow β -VI transition, is a well-known, though not appreciated, phenomenon to the manufacturers and consumers as this transition brings forth fat bloom on the chocolate [2]. It has been hypothesized that this and other polymorphic phase transition processes involve (re-)packing of the long fatty-acid acyl chains and/or layers. To establish the precise mechanism of such phase transition processes, crystal structure models are indispensable. In a previous paper we presented a crystal structure model of the β_2 -polymorph of SOS and the (similar) β -V polymorph of Ivory Coast cocoa butter [3]. More recently, we also solved crystal structures of the β_1 -polymorph of several monounsaturated TAGs and the (similar) β -VI polymorph of cocoa butter [4]. The experience gained with the structure determination and refinement of the β_1 -polymorphs has incited us to re-analyze the initial β_2 structure determination. This has led to new insight in the β_2 conformation and a novel β_2 structure model has been obtained for symmetric mono unsaturated TAGs. Furthermore, we solved the β_2 -polymorph crystal structures of the asymmetric 1-palmitoyl-2-oleoyl-3-stearoylglycerol (POS) and 1-stearoyl-2-oleoyl-3-arachidoylglycerol (SOA) [5,6]. To our knowledge, the latter two are novel polymorphs whose existence has not been reported before in literature. The novel β_2 structure model will be discussed in relation to the previously published β_2 -SOS model and the model of the β_1 polymorphs. All the models were obtained using direct-space search techniques (FOX, [7]) and high resolution laboratory and synchrotron powder diffraction data.

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