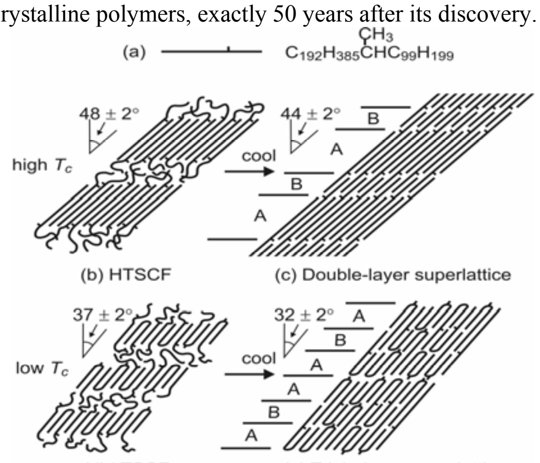
MS12 O1

Complex Layered Nanostructures in Crystalline and Semicrystalline Ultralong Alkanes Xiangbing Zeng, Fangning Xie, Goran Ungar; *Department of Engineering Materials, University of Sheffield, Sheffield, U.K.* Email: g.ungar@shef.ac.uk

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 $C_{192}H_{385}CH(CH_3)\text{-}C_{99}H_{199}$. (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 Crystallogrphy, University of Amsterdam, Amsterdam, The Netherlands.* E-mail: janvm@science.uva.nl

Keywords: ß-polymorph, fat bloom, high-resolution X-ray powder diffraction.

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 (Tc) 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 → 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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MS12 O3

Molecular Packing in Solid Solutions: Paraffin Waxes vs. Cholesteryl Esters. Douglas L. Dorset, CSR, ExxonMobil Research and Engineering Co., 1545 Route 22 East, Annandale, New Jersey 08801 USA.
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Keywords: chain polydispersity, structure determination, molecular packing

Polydispersity of linear polymethylene chains is universally employed by synthetic (waxes, polymers) and natural (waxes, lipids) substances to control materials properties. The stability of solid solutions depends on a molecular homeomorphism criterion described by Kitaigorodskii [1]: $\varepsilon = 1 - \Delta/r$, where Δ and r are, respectively, non-overlap and overlap volumes of solid solution components. Beyond a sharp limiting value for ε, a miscibility gap is reached and then true eutectic behavior, with characteristic crystal structures described in a recent monograph [2]. It is, however, not easy to describe the crystal structures of solid solutions simply. For strictly linear molecules, viz: the n-paraffins, two types of structures are possible. One is a so-called 'nematocrystalline' array, where, because of a very long chain component, true lamellar assemblies cannot be formed. These give relatively brittle materials and are characteristic of some low molecular weight polyethylenes as well as synthetic Fischer-Tropsch waxes. Lamellar waxes are formed from chain arrays within a relatively narrow molecular weight distribution. There is an average packing of chain lengths within a lamella and a distribution of conformational defects at its surface, which is also, on average, rather flat. Such materials are soft and pliable. Evidence is found for a distribution of localized crystal structures which, on average, do not correspond to the lowest energy polymorphs of the pure components. When the chain length difference (Δ) is just great enough to reach a miscibility gap, there is an undefined diffusion mechanism over time that leads to a succession of separated superlattice layers, similar to alloys. The same superlattice remains part of eutectic structures but is epitaxially joined to nearly pure component domains. Strict linear molecule structures can be distinguished from linear chain derivatives where a portion of the molecule is tethered within the unit cell, a simple example being the polydisperse linear chain alcohols [3]. Unlike the n-paraffins where, on average, continuous Vegard's law-like behavior is observed, the increase of lamellar thickness is step-like over the concentration range of two components. Crystal structures of cholesteryl ester solid solutions [2] reveal that average chain substitution in the unit cell can be observed only in the case of monolayer I arrays and only when the chains differ by one methylene unit. With a greater chain difference or for the bilayer polymorph, there are preferential packing sites for the different chain lengths within the average unit cell. How these packing motifs might change for different molar ratios has not been determined. The only generalization that can me made so far for all solid solutions is that Nature Abhors a Vacuum, even at a molecular level.

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MS12 O4

Synthesis, characterization and phase transitions in the long-chain n-alkylammonium halides and metal-halides. Gert J Kruger[a], Charmaine van Blerk[a], David G Billing[b], Andreas Lemmerer[b] and Melanie Rademeyer[c], [a]*Department of Chemistry, University of Johannesburg, Johannesburg,* [b] *Department of Chemistry, University of the Witwatersrand, Johannesburg,* [c] *Department of Chemistry, University of KwaZulu-Natal, Pietermaritzburg, South Africa*. E-mail: gjkruger@uj.ac.za

Keywords: crystal and molecular structure, single-crystal X-ray analysis, polymethylene chain.

The structures and properties of crystals of organic molecules containing the polymethylene chain provide a fascinating glimpse into polymorphism and the packing forces that operate between molecules in the solid state. If these substances are modified by the addition of functional groups with structure-directing properties at the ends of the polymethylene chains, additional information about packing can be obtained. A study of the structural properties of primary *n*-alkylammonium halides and their metal halides enabled us to evaluate the relative importance of intermolecular forces of the two types as the polar ends of the layers form strong hydrogen-bonded networks that dominate the packing on crystallization. In recent years we have systematically studied the crystal chemistry of the alkyl ammonium and diammonium salts $\{C_nH_{2n+1}NH_3X$ and $(NH_3C_nH_{2n}NH_3)X_2\}$ and the organic–inorganic perovskite-type hybrids $\{(C_nH_{2n+1}NH_3)_2MX_4\}$. We will illustrate the synthesis, trends in the crystal chemistry, and the investigative methods used, in the study of the chlorides, bromides and iodides. Two factors influence their molecular packing in a crystal lattice – the forces between the end groups in a layer and the van der Waals interactions between the alkyl chains in a layer. Both forces contribute to the lattice energy, and their relative strengths determine the crystal structure. Most of these long-chain compounds exhibit polymorphism because of their conformational flexibility and the weak intermolecular forces directing the packing. The typical interdigitated and tilted packing is illustrated by the packing in the *n*-octadecylammonium iodide crystals: