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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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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]: $\epsilon = 1 - \Delta/r$, 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 be

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,
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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:

