

**EMERGENCE OF POLYMER PROPERTIES IN POLY-DISPERSE CHAIN
ASSEMBLIES - THE STRUCTURAL DISTINCTION BETWEEN LOW MOLECULAR
WEIGHT LINEAR POLYETHYLENE AND PETROLEUM WAXES REVEALED BY
ELECTRON CRYSTALLOGRAPHY**

D.L. Dorset, ExxonMobil Research and Engineering Company, 1545 Route 22 East, Clinton
Twp., Annandale, NJ 08801

Paraffins and waxes in rectangular layers are often models for polyethylene, given common methylene subcells, as well as the occurrence of sectorized growth for longer paraffins (even those with unfolded chains). Nevertheless, polydisperse oligomer arrays, i. e. narrow distillate cuts of petroleum waxes (e. g. $M_w/M_n = 1.003$), are deformable solids contrasting to the brittleness of more highly disperse (e. g. $M_w/M_n = 1.11$) low molecular weight linear polyethylene. After epitaxial orientation of these materials on organic substrates, it has been possible to determine their 3-D structures by electron crystallography, based on single crystal diffraction patterns. Refined petroleum waxes have a true lamellar structure with an average flat lamellar surface, despite the enhanced concentration of conformational defects and vacancies in this interfacial region (1). Adjacent lamellar layers are therefore laterally shifted to minimize Van der Waals interactions across the end-planes, as is also the case for pure orthorhombic n-paraffins. On the other hand, due to a small fraction of high molecular weight component, linear, unfolded polyethylene cannot form true lamellae (2). When crystallized from the melt, the polymer is essentially 'nematocrystalline', i. e. the chains are randomly distributed along their lengths expressing only the orthorhombic perpendicular polymethylene subcell as the crystalline unit while the chain ends are uncorrelated. Annealed specimens begin to form nascent layers, bringing shorter chain ends in near longitudinal register, but true lamellae do not form because of higher molecular weight chain components that span the layer interfaces as 'molecular reinforcing rods'. Lateral shifts of adjacent layers are thereby prevented so that one chain direction is continuously maintained in the crystal. Similar nematocrystalline behavior is found for Fischer-Tropsch waxes (3) (but not their distillate fractions (4)), as well as some natural plant and insect waxes (5). The bridging effect of a higher molecular weight component, therefore, explains the difference in materials properties.

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