Stage-wise Pre-assembly in Melt Prior to Liquid Crystals

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We investigate two unusual phenomena in self-assembly of anisotropic molecules from isotropic (Iso) melt: a heat-capacity (C_p) maximum, and spontaneous formation of the recently discovered chiral liquid phase in achiral compounds (Iso*). Based on experiments on newly synthesised non-chiral monomers, dimers and polymers, we construct a thermodynamic theory that shows why many liquid crystals (LC) and some crystals form in two stages, i.e. (i) continuous equilibrium growth of nano-clusters in the melt through strong intermolecular core-core interactions, causing the C_p-maximum, followed by (ii) establishment of chiral long-range order (LRO) through a second-order Iso-Iso* transition and/or a first-order phase transition to a phase with positional LRO (Iso-LC, Iso*-LC, Iso*-crystal or Iso-crystal). The first process (i) is equivalent to cluster formation in solutions, known as "supramolecular polymerization", where the lack of inter-cluster interaction rules out the establishment of LRO. Furthermore, we argue that separation into a broad and a sharp transition is universal in condensed matter where strong interactions by themselves cannot lead to LRO, either because the clusters are 1D or due to strong frustration. Clusters must first grow to critical size when, at T_c, the weak interactions reach ~$k_B T_c$ per cluster, prompting LRO formation. A situation similar to that in LCs is seen in spin ordering in magnetic crystals, but only near 0 K.

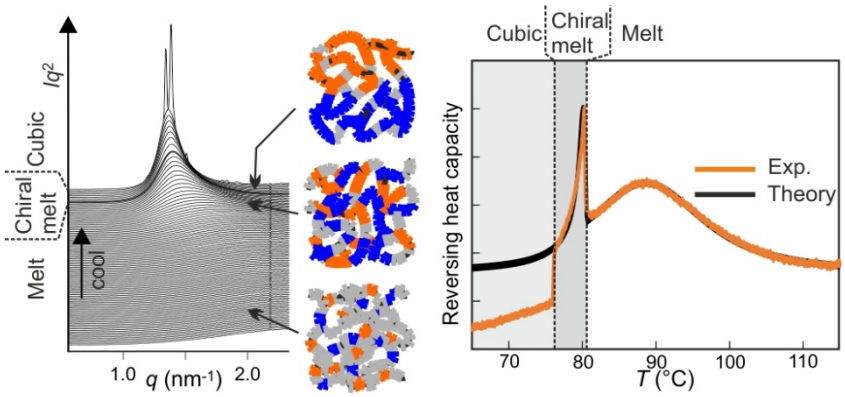

Figure 1. Pre-assembly of polycatenar compounds in the melt on cooling leads to increase in the correlation length (SAXS, left) and eventually the establishment of long range order. The pre-assembly is accompanied by a C_p-hump in the melt (right), which contains the majority of the enthalpy of self-assembly. This is followed by a 2nd order transition to chiral melt, before the 1st order transition to cubic or other LCs on cooling.

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