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Laws controlling crystallization and melting in bulk polymers

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When the fundamentals of the structure of semi-crystalline polymers - layer-like crystallites with fold surfaces being embedded in an amorphous matrix - were revealed in the Fifties, considerations about the mechanism of formation started immediately. In the Sixties and Seventies, they became a major field of research and a focus of interest. In the years which followed the approach put forward by Hoffman, Lauritzen and their co-workers [1] gained superiority. The picture envisaged by the treatment - a crystalline lamella with an ordered fold surface and smooth lateral faces, growing layer by layer with a secondary nucleation as rate determining step - is easy to grasp and yields simple relationships. Supercooling below the equilibrium melting point T_f^∞ is the control parameter determining both the thickness d_c and the lateral growth rate of the crystallites G. Experiments carried out during the last decade provided new insights and are now completely changing the understanding. They showed in particular
- that d_c is inversely proportional to the distance to a temperature T_c^∞ distinctly above T_f^∞
- that the activation energy determining G diverges at a temperature T_{zero} clearly below T_f^∞.
Further simple relationships concern
- recrystallization processes: d_c is again inversely proportional to the distance to T_c^∞
- the extension of ordered regions within the lamellar crystallites: it is proportional to d_c. We interpret the observations as indication that the pathway followed in the growth of polymer crystallites includes an intermediate phase of mesomorphic character. A thin layer with mesomorphic inner structure forms between the lateral crystal face and the melt, stabilized by epitaxial forces. The first step in the growth process is an attachment of chain sequences from the melt onto the growth face of the mesomorphic layer. The high mobility of the chains in the layer allows a spontaneous thickening, up to a critical thickness, where the layer solidifies under formation of block-like crystallites. The last step is a perfectioning of the crystallites, leading to a further stabilization. We constructed a thermodynamic scheme dealing with the transitions between melt, mesomorphic layers and lamellar crystallites, assuming for the latter ones that they exist both in an initial 'native' and a final 'stabilized' form. T_c^∞ and T_{zero} are identified with the temperatures T_{mc} and T_{am} of the (hidden) transitions mesomorphic $\rightarrow$ crystalline and amorphous$\rightarrow$ mesomorphic, respectively. Application of the scheme in a quantitative evaluation of small angle X-ray scattering and calorimetric results yields the equilibrium transition temperatures between the various phases, latent heats of transition and surface free energies [2]. [1] J.D Hoffman, G.T Davis, and J.I. Lauritzen. In *Treatise on Solid State Chemistry* Vol.3, N.B.Hannay Ed., page 497. Plenum, 1976. [2] G. Strobl. *Eur.Phys.J.E*, 18:295, 2005.