The Concept of Decoupling of Parts of Macromolecules

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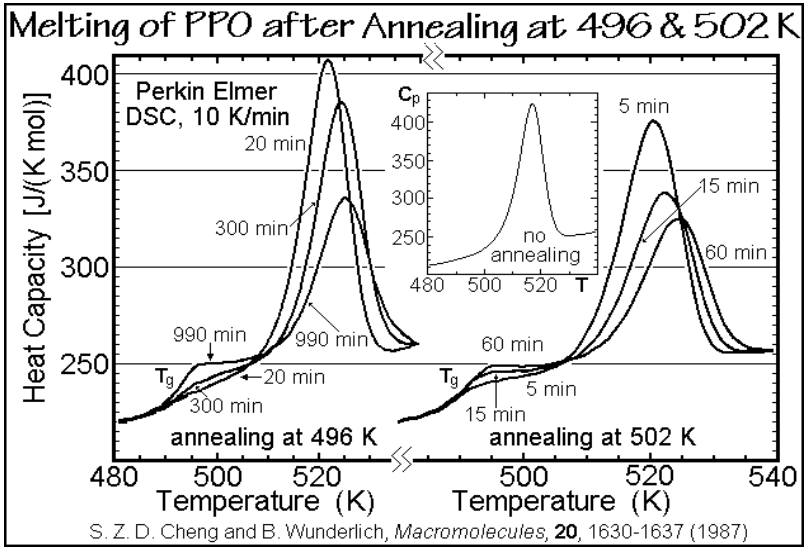
To understand the properties of polymers, the 100 year old equilibrium thermodynamics must now be modified. The picture of small molecules producing large phases with well-defined interfaces has been altered to include macromolecules and nanophases. A macromolecule of many thousand chain-atoms can traverse several nanophases crossing the new, diffuse interfaces. At these interfaces, the molecular parts, being in different phases, decouple and have then different properties. The upper Figure on the right shows the thermal properties of semicrystalline PPO (GE Trademark for an aromatic polyether). The small center shows that a DSC trace of as-produced, about 30%-crystalline PPO shows no the glass transition which was expected at 488 K. The decoupled amorphous phase segments of the molecules are a rigid glass! On annealing below the melting peak, the sample melts as soon as the glass softens. The lower picture illustrates that the decoupled PPO portions have a higher glass transition and hinder the melting.



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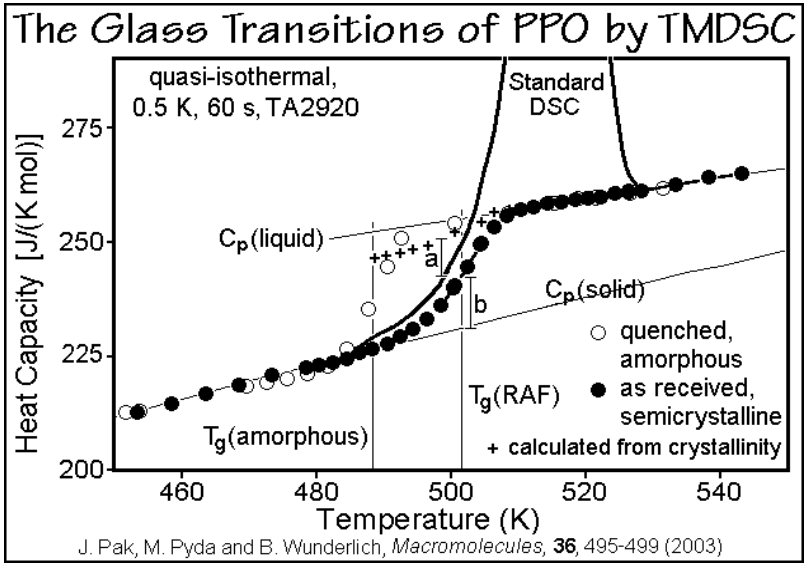

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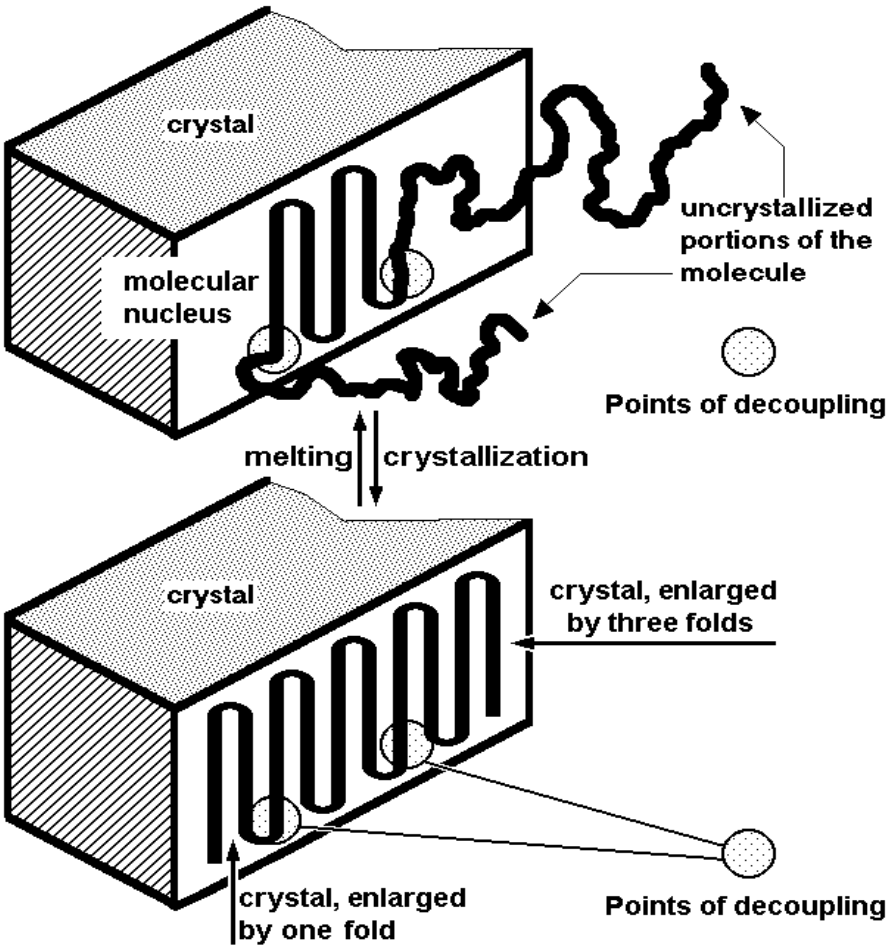
The Intellectual Merit of his research lies in an advance in the understanding of structure and properties of macromolecules, the key materials for the present economy. Instead of treating the large molecule as a single entity, or subdividing it into its constitutional repeating units (CRU), as done in the past, the new coupling concept proposes a variable size of the basic building blocks of the phases, as is illustrated in the right Figure with the schematic for reversible melting on crystal surfaces. Note, reversible melting, detectable on surfaces of many semicrystalline polymers, is not seen for the PPO on the prior bottom Figure due to the glassy nature of the decoupled parts of the molecules. Similarly, the melting temperatures of copolymers may be altered when the melting is decoupled from the mixing after melting, or side-chains are de-coupled from the back-bone of the main chain, as described in the publication on the right.



Reference describing this research:
Bernhard Wunderlich, *J. Polymer Sci.*, *Part B*: *Polym. Phys.*, **42**, 1275–1288 (2004).