The Calorimetry of Nanophases of Macromolecules

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A thermodynamic description of polymeric systems is summarized based on 50 years of gathered experimental information with adiabatic, differential-scanning, and temperature-modulated calorimetry. This experience has led to the description of macro-, micro-, and nano-phases, with macromolecules able to traverse phase boundaries and decouple at surfaces, which gives different parts of the molecule different thermodynamic properties. A typical thermodynamic characterization of a semicystalline polymer is that of a globally metastable system with locally reversible processes. Unique phenomena in polymers include the ability of semicrystalline polymers to undergo cold crystallization and molecular nucleation, possess thermally generated point defects and rigid-amorphous fractions, and to have amorphous, mesophasic, or crystalline macroconformations with glass, with ordering and disordering transitions in all three structures. To describe such multifaceted systems, special combinations of equilibrium and irreversible thermodynamics, as well as statistical and quantum mechanics, are necessary. Only then is it possible to handle violations of phase rules, changes of properties when approaching nanophase dimensions, local reversibility, and enthalpy relaxation. The enthalpy relaxation in polymers originates in the cooperativity of conformational motion, and in the interferences of processes with different time scales. The experiments used to identify the effects of different molecular motions, from typical vibrational time scales of picoseconds to cooperative large-amplitude rearrangements of up to megaseconds, span heating rates of thousands of K/s, with superfast chip calorimeters, to many hours, for slow quasi-isothermal analysis by TMDSC. Selected details of this far-reaching thermal characterization will be presented. More can be found in the 900-page monograph on "Thermal Analysis of Polymeric Materials" (Springer, Berlin, 2005), and the parallel computer course of 3,000 screens of text, graphics, and hypertext (available by download from our ATHAS web site: web.utk.edu/~athas, or from the European Virtual Institute for Thermal Metrology: www.evitherm.org/index.asp, at their home page for thermal analysis and calorimetry).