

Thermodynamic Characteristics and Physico-Chemical Properties of Polymethacrylic Acid and its Blends with Water

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In a vacuum adiabatic calorimeter the heat capacity C_p of air-dried polymethacrylic acid (PMAA) containing 2.5 mass% H_2O was measured over the range 6 to 320 K with an uncertainty of 0.3%. The heat capacity of anhydrous PMAA was calculated with regard for an additive contribution of C_p of water. The thermodynamic characteristics (enthalpy, entropy, Gibbs function) of PMAA were estimated between $T=0$ K and 320 K. A relaxation transition of an endothermic character that can be classified as gamma-transition was seen on a C_p vs. T plot of air-dried PMAA. Its mean temperature was 300.6 K. In a bomb calorimeter the standard enthalpy of PMAA [$H_c(s, 298.15) = -1975.9 \pm 6.3$ kJ/mol] was determined and from this value the standard enthalpy of its formation in a solid state was found to be $H_f(s, 298.15) = -455.7 \pm 6.3$ kJ/mol. The enthalpy of polymerization of MAA (l) (-40.6 ± 6.3 kJ/mol) was evaluated too. Beta- and alpha-transition in PMAA samples (1.7 and 2.5 mass% H_2O) were recorded by differential thermal analysis in range 80-550 K. The transition temperatures in anhydrous PMAA ($T_{\beta}=341$ K; $T_g=444.5$ K) were determined by the extrapolation towards the zero content of water. The solubility limit of “free” water phase in PMAA was determined by calorimetry method from the fusion enthalpy of this phase, it was equal to 40.6 ± 0.7 mass% H_2O .