Conformational Heat Capacity of Liquid Poly(vinyl methyl ether) in the Absence and Presence of Water

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The conformational heat capacity of amorphous poly(vinyl methyl ether), PVME, without and with water have been evaluated from a fit of experimental data to a one-dimensional Ising-like model for two discrete states, characterized by parameters linked to stiffness, cooperativity, and degeneracy. For PVME-water system additional changes in the conformational heat capacity arise from the interactions of the PVME chains with water. The liquid heat capacities at constant pressure, C_p, of amorphous PVME, without and with water have been computed as the sum of vibrational, external, and conformational contributions. The vibrational contribution was calculated as the heat capacity arising from group and skeletal vibrations. The external contribution was estimated from experimental data of the thermal expansivity and compressibility in the liquid state. The experimental liquid C_p agrees with these calculations to better than ±3%. The calculated liquid C_p was employed in the thermal analysis of the apparent C_p in the region of the devitrification, melting, demixing, remixing, vitrification and crystallization within the PVME-water system.