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Reversible Processes Between the Glass and Melting Transition of Poly(oxyethylene)[1] WUNDERLICH BERNHARD, WULIN QIU — Heat capacity, C_p, of poly(oxyethylene), POE, with molar mass from 1,500 to 900,000, was analyzed by quasi-isothermal, temperature-modulated DSC. The oligomers form extended-chain crystals which melt fully irreversibly and permit direct measurement of the thermodynamic C_p. The POE with higher mass yield folded-chain crystals and indicate locally reversible melting. The reversing, apparent C_p depends on mass, as well as on the amplitude of modulation. Its maximum in the melting range increases with molar mass, but decreases at larger amplitudes of temperature modulation. After separation from the apparent C_p, the thermodynamic C_p depends on the melting temperature and increases beyond the calculated, vibrational C_p, from the ATHAS Data Bank. Molar masses of 8,000 to 20,000 have almost the same C_p, but deviate initially at higher temperature. These quantitative observations permit a more detailed discussion of the origin of the thermodynamic C_p and the locally reversible melting of the metastable POE.

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