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Investigating the Equilibrium Melting Temperature of Polyethylene Using the Non-Linear Hoffman-Weeks Analysis: Effect of Molecular Weight HADI MOHAMMADI, HERVE MARAND, Virginia Tech, Department of Chemistry — The limiting equilibrium melting temperature for infinite molar mass linear polyethylene, T_m^o , has been a point of controversy for about five decades. On one hand, Broadhurst and Flory-Vrij extrapolated melting data for short alkanes to a value of ca. 145°C. On the other hand, Wunderlich proposed a value of 141°C from melting studies of extended-chain PE crystals formed under high pressure. While a difference in T_m^o by 4°C might seem superfluous, it has significant implication for the analysis of the temperature and chain length dependences of crystal growth kinetic data. In this work we estimate the equilibrium melting temperatures, T_m for three linear narrow molecular weight distribution polyethylenes using the non-linear Hoffman-Weeks treatment. The resulting T_m values thus obtained are significantly lower than these predicted by the Flory-Vrij treatment and are within experimental uncertainty indistinguishable from those reported by Wunderlich and Hikosaka et al. Our results also suggest that the constant C_2 in the expression for the undercooling dependence of the initial lamellar thickness ($l_g^* = C_1/\Delta T + C_2$) increases linearly with chain length.

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