Transitions of Polymers with Precise Oligomethylene Sequences.  
BERNHARD WUNDERLICH, WULIN QIU, University of Tennessee, Knoxville, and ORNL, Oak Ridge — Polyethylene, PE, with precise branches has been analyzed by TMDSC and X-ray diffraction. The branches were methyl, dimethyl, and ethyl groups. Furthermore, atactic poly(octadecyl acrylate) and poly(4,4'-phthalimidobenzoyl-octacosyloxyacarbonyl) were studied. All are compared to LLDPE, of similar branch concentration and linear PE. Compared to LLDPE the precisely structured polymers show much sharper melting. Compared to HDPE lower melting temperatures and heats of fusion were observed, and all have non-orthorhombic structures. In contrast to paraffins of equal length which melt fully reversibly at a similar temperature, the precisely designed polymers melt largely irreversibly with only small amounts of reversing melting which is least for the best-grown crystals. These results have important implications for the description of melting of copolymers. Initial literature: W. Qiu, J. Sworen, M. Pyda, E. Nowak-Pyda, A. Habenschuss, K. B. Wagener, B. Wunderlich, Macromolecules, 39 (2006).

1Supported by NSF, Polymers Program, DMR-0312233, and the Div. of Mat. Sci., BES, DOE at ORNL, managed by UT-Battelle, LLC, for the U.S. Department of Energy, DOE-AC05-00OR22725.