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Forty years of confinement! When will RAF be released?¹

PEGGY CEBE, Tufts University

Crystallization of polymers from the melt occurs from a highly entangled state. The crystals and amorphous chains remain in intimate contact throughout the crystallization process, leading to confinement and formation of the rigid amorphous fraction (RAF). Forty years ago, H. Zachmann's group studied mobility of crystalline and non-crystalline regions, and identified rigid non-crystalline fraction using NMR. B. Wunderlich and co-workers recognized the signature of reduced mobility, i.e., confinement, via a heat capacity deficit at the glass transition relaxation. Using modern thermo-analytical methods, such as quasi-isothermal temperature modulated calorimetry, we investigate the vitrification and devitrification of RAF, its relationship to the crystalline fraction, and present methods to distinguish limiting cases of two different lamellar structural models incorporating RAF.

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