Experimental Test of Tammann's Nuclei Development Approach in Crystallization of Macromolecules

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A first attempt to probe the size distribution of homogeneously formed crystal nuclei in polymers was realized employing Tammann's two-stage crystal nuclei development method and fast scanning calorimetry [1]. A transfer heating rate of 500 000 $K \cdot s^{-1}$ prevents nuclei growth on heating in poly(ε-caprolactone) (PCL). Data collected in a wide range of crystallization temperatures allow, in combination with a theoretical model based on classical nucleation theory, for an estimate of the nuclei size distribution and the growth rate. The employed temperature profile was adapted from Tammann's two-stage crystal nuclei development method implying formation of nuclei at large undercooling (low temperatures) and following their isothermal growth at higher temperatures. Fast scanning calorimetry allowed us to reach the deep supercooling of the melt at 100 000 $K \cdot s^{-1}$ avoiding homogeneous nuclei formation and heterogeneous nuclei growth. Then crystal nuclei were allowed to form isothermally at the temperature corresponding to the maximum of the steady-state nucleation rate for homogeneous nucleation (210 K for PCL, T_g = 209 K), where both the effect of heterogeneous nucleation and the growth rate are low. The presence of these crystal nuclei and its effect on crystallization were probed by heating the sample to higher temperatures and observation of the overall crystallization process, determining the crystallization half-time. The transfer heating rates up to 500 000 $K \cdot s^{-1}$ were applied in order to minimize growth on heating. A theoretical explanation of the observations was developed. The study focuses on early stages of nucleation and growth and is therefore widely independent of specific features of polymer crystallization.

[1] E. Zhuravlev, J.W.P. Schmelzer, A.S. Abyzov, V.M. Fokin, R. Androsch, C. Schick, Experimental test of Tammann's nuclei development approach in crystallization of macromolecules,
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