Two-stage crystallization of poly(ε-caprolactone) studied by Fast Scanning Calorimetry

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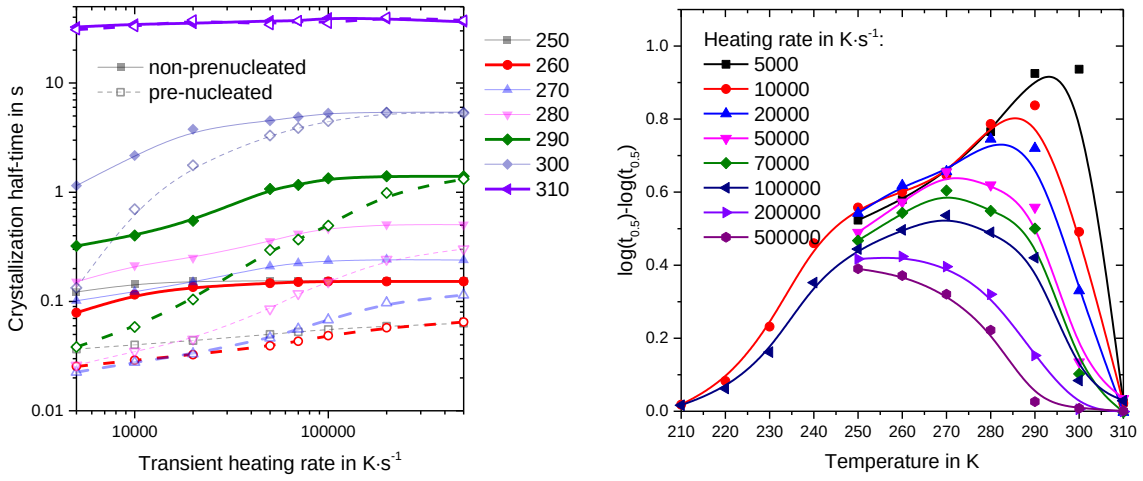
The efficiency of pre-formed homogeneous crystal nuclei for overall crystallization at different temperatures was studied over a wide range of crystallization temperatures in poly(ε-caprolactone). Tammann's two-stage crystal nuclei development method was used implying formation of nuclei at large undercooling close to the glass transition temperature and following their isothermal growth (development) at higher temperatures. Fast scanning calorimeter devices allowed us to achieve deep supercooling to the glass transition temperature by sufficiently high cooling rates required to prevent homogeneous nuclei formation on cooling. In order to understand the influence of heating in between pre-nucleation and final crystallization stages, the transient heating rate was varied in the range of maximum possible (500,000 K/s) down to 5,000 K/s, where the first signs of crystallization on heating occurs. Slow heating allows nuclei formed in the previous stage to grow on the way to the crystallization temperature. In addition, further nuclei may be formed in the course of the heating process. Even fastest transient heating doesn't prevent the further growth of pre-nucleated clusters at higher temperatures up to 290 K – 80 K above their formation. This supports the representation that broad distribution of cluster size is formed at pre-nucleation stage, so that some of them are still overcritical at relatively high temperatures. Neither pre-nucleation nor formation of additional nuclei in slow heating (though fast enough to avoid growth of crystals in the sample prior to reaching the crystallization temperature) are effective for crystallization above 310 K.



a b

Figure 1 a) The crystallization half-time at different prehistory and b) the difference between crystallization half-times of thermally pre-nucleated and not pre-nucleated samples. Different heating rates corresponds to the transient heating in between nucleation and development stages.