

## CRYSTAL NUCLEATION IN GLASSY POLY(L-LACTIC ACID)

**René Androsch<sup>a</sup>, Maria Laura Di Lorenzo<sup>b</sup>**

<sup>a</sup> Martin-Luther-University Halle-Wittenberg, 06099 Halle/Saale, Germany, rene.androsch@iw.uni-halle.de

<sup>b</sup> Consiglio Nazionale delle Ricerche, Istituto per i Polimeri, Compositi e Biomateriali, Via Campi Flegrei, 34, 80078 Pozzuoli (NA), Italy

### ABSTRACT

Aging of glassy poly(L-lactic acid) (PLLA) allows formation of crystal nuclei which enhances/accelerates subsequent crystallization at temperatures above the glass transition. The effects of the time and temperature of aging on nuclei formation have quantitatively been probed by analysis of isothermal crystallization at 393 K, using fast scanning chip calorimetry and polarizing optical microscopy. Crystal nuclei begin to form on aging the glass of PLLA at 343 K after about  $10^1$  s. The time of nuclei formation increases exponentially with decreasing temperature, so that aging at 323 K requires a minimum time of  $10^4$  s, and the extrapolated time for generation of nuclei at 295 K is about  $10^8$  s. The aging-controlled increase of the nuclei density in glassy PLLA leads to a distinct decrease of the half-time of crystallization. The half-time of crystallization of nonaged PLLA at 393 K is about 600 s and decreases to less than half of this value due to aging at 343 K for a period of only  $10^3$  s. Nuclei formation on aging the glass of PLLA is connected with a tremendous decrease of the size of spherulites which develop upon subsequent cold-crystallization. The detection of formation of crystal nuclei in glassy PLLA is discussed in the framework of prior analyses of the effect of the crystallization pathway on structure and properties of crystallizable polymers.

**Acknowledgment:** Financial support by the Deutsche Forschungsgemeinschaft (DFG) (Grant AN 212/20) is greatly acknowledged. Abstract is reprinted with permission from *Macromolecules*, Volume 46, 6048–6056. Copyright 2013 ACS.