

Effect of Content and Polarity on the Crystallization of Long-Spaced Aliphatic Polymers with Polar Functional Groups

Stephanie F. Marxsen¹, Manuel Häußler², Stefan Mecking², Rufina G. Alamo¹

¹ FAMU-FSU College of Engineering, Department of Chemical and Biomedical Engineering, 2525 Pottsdamer St, Tallahassee, FL, 32310

² Department of Chemistry, University of Konstanz, Universitätsstraße 10, 78457 Konstanz, Germany

ABSTRACT

We investigate the comparative self-assembly, crystalline structure and morphology, and crystallization kinetics of three sets of bio-sourced, polyethylene-like polymers, including polyesters (PEs), polycarbonates (PCs), and polyacetals (PAs) with aliphatic sequences between precisely placed functional groups (FGs) ranging in length from 18 to 48 methylene (CH₂) groups. We quantify the polarity of each FG in terms of the solubility parameter and demonstrate that melting and crystallization temperatures increase with increasing FG interaction strength (PE > PC > PA) and decrease with increasing FG content. All form lamellar crystals with FGs incorporated in planar layers, evidenced by the presence of layer reflections in the X-ray patterns. PEs and PCs have an isomorphic, polyethylene-like unit cell. In contrast, PAs develop multiple crystalline polymorphic forms depending on the crystallization temperature. Polyethylene-like packing in PEs and PCs is enabled by dipole-dipole interactions between FGs of adjacent chains, which serve to compensate for the enthalpic penalty introduced by the presence of FGs in the crystals. The relatively weaker interactions as well as the drive for gauche bonding in acetal groups lead to a different unit cell in PAs. For the same undercooling and FG content, PEs tend to crystallize faster than PCs, indicating that stronger FG interactions enhance crystallization kinetics. PAs crystallize at lower temperatures than either PCs or PEs, suggesting that the weaker FG interactions in PAs slow crystallization. In general, crystallization rates are normalized when compared at the same undercooling for the same FG type, indicating that FG polarity, rather than content, is the dominant factor controlling crystallization kinetics. Unusual inversions in the crystallization rate at low undercooling with crystallization temperature observed in PEs and PAs will be discussed.

