Microfluidic Control of Nanoscale Stereocomplexation in Poly(lactic acid)

Lorenzo Lombardi[1], Massimo Christian D'Alterio[2], Rocco Di Girolamo[2], Claudio De Rosa[2], and Pier Luca Maffettone[1]
[1]Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Naples, Italy
[2]Department of Chemical Sciences, University of Naples Federico II, Naples, Italy

ABSTRACT

Poly(lactic acid) (PLA) is one of the most promising bio-based polymers for sustainable materials engineering, owing to its renewable origin, biodegradability and broad range of applications. A particularly attractive feature of PLA is its ability to form stereocomplex (SC) crystals through the association of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) chains. Compared with conventional PLA homocrystals, stereocomplex crystals exhibit tighter molecular packing and enhanced thermal stability, providing a route toward improved performance. However, conventional bulk processing methods offer limited control over nucleation, crystal purity and spatial localization of the stereocomplex phase.

Here, we introduce a continuous microfluidic approach for the controlled formation of PLA stereocomplexes under well-defined non-equilibrium conditions. Enantiomerically pure PLLA and PDLA solutions are brought into contact within a Y-junction microfluidic device, where transport, mixing and residence time can be precisely controlled. The lower solubility and greater thermodynamic stability of the stereocomplex phase in the selected solvent promote selective SC crystallization while suppressing competing homochiral crystallization.

The microfluidic platform makes it possible to directly connect flow conditions and mass-transfer timescales with stereocomplex formation. Increasing residence time systematically increases the stereocomplex fraction, while device geometry and operating conditions provide additional control over crystallization kinetics and productivity. X-ray scattering and differential scanning calorimetry are used to quantify crystalline structure, stereocomplex content and thermal properties. Importantly, the optical accessibility of the device enables direct observation of the interaction region by optical and polarized-light microscopy, providing a unique experimental window on stereocomplex nucleation and growth.

These results demonstrate how microfluidic processing can be exploited as a tool for directing molecular organization and crystallization at the microscale and nanoscale. Beyond PLA, the approach illustrates a broader strategy in which confined flows and controlled mass transport are used to manipulate polymer self-organization under continuous processing conditions. This provides both a platform for investigating crystallization kinetics and a potential route toward scalable manufacturing of high-performance, fully bio-based materials.