

FUNCTIONALIZED LACTIC ACID MACROMONOMERS POLYCONDENSATION

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The synthesis of PLA-based macromonomers by direct polycondensation of lactic acid in the presence of HEMA is discussed in this work as a valuable alternative to ROP. In particular, the two processes are compared with respect to the production of three HEMA-LA_n macromonomers, with $n = 2, 4$ and 6 . Detailed kinetic models are developed for both reaction systems, whose parameter values have been found in the literature or estimated by fitting our own experimental data. Through these models, the reaction kinetics (Figure 1) as well as the time evolution of the entire chain length distributions of the products (Figure 2) could be reliably predicted in all cases.

This way, we demonstrated that polycondensation is a valuable alternative to ROP only for macromonomers with average chain length up to 4 and that ROP remains the main route for longer chains when a strict control over the chain length distribution is required. In fact, in the case of polycondensation, a fraction of lactic acid is wasted to form PLA homopolymers. The formation of these byproducts is increasing at increasing values of n , where larger fractions of lactic acid are required. Since the typical size of the macromonomers used for the production of biodegradable polymer nanoparticles aimed at drug delivery is smaller than or equal to 4, polycondensation can be considered an effective production route and a reliable alternative to the more complex and expensive ROP synthesis.

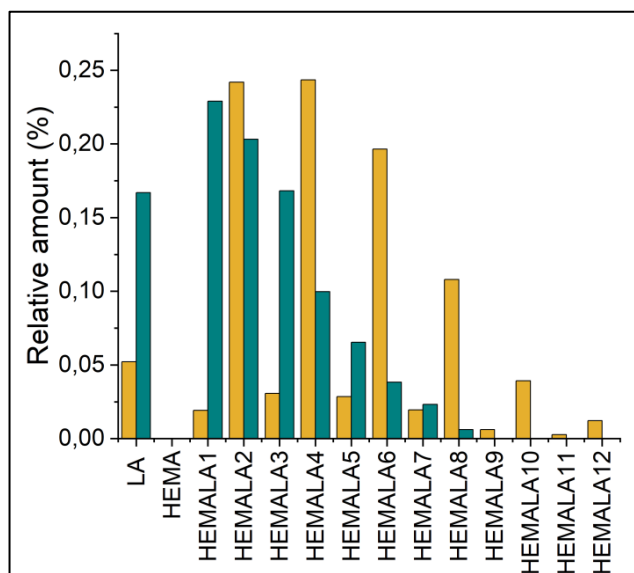


Figure 1 – MWD of HEMA-LA macromonomers produced via ROP (yellow bars) vs. polycondensation (green bars).

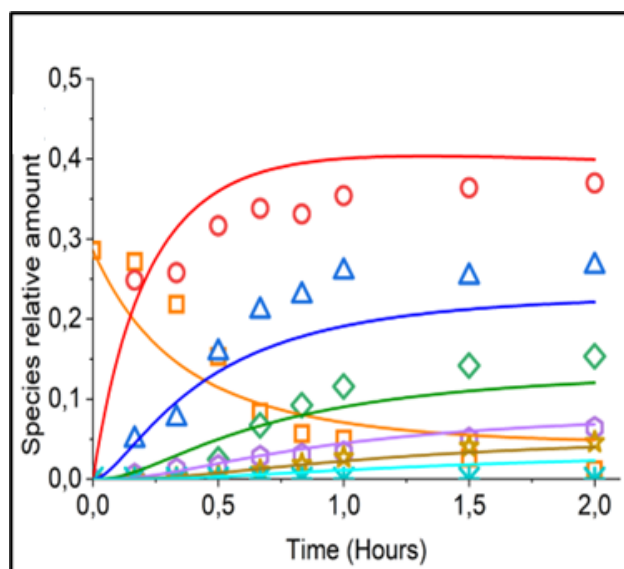


Figure 2 - Relative amount of HEMA-LA_n oligomers vs. time and model prediction. (□) HEMA, (○) HEMA-LA1, (△) HEMA-LA2, (◇) HEMA-LA3, (☆) HEMA-LA4, (☆) HEMA-LA5, (▽) HEMA-LA6.