Simultaneous Dynamic Kinetic Resolution in Combination with Enzymatic Ring Opening Polymerisation

Jiaxiang Zhou, Wenxin Wang, Kristofer J. Thurecht, Silvia Villarroya, Steven M. Howdle*

School of Chemistry, the University of Nottingham, University Park, Nottingham, NG7 2RD, Great Britain

SUPPORTING INFORMATION:

Analysis of the end group by treatment with oxalyl chloride

The addition of few drops of oxalyl chloride directly in the NMR tube allowed confirmation of the product composition by analysis of the end groups of the polymer. Downfield shifts were observed for neighbouring protons upon addition of oxalyl chloride to terminal hydroxyl functionalities. The signal at 3.65 ppm ($H_b$) shifted to 4.37 ppm ($H'_{b'}$). This signal is due to the methylene carbon next to the oxalyl chloride derivatised chain-end hydroxyl group of the PCL chain. A new signal appears at 2.90 ppm ($H_{d'}$). This signal is due to the methylene carbon next to oxalyl chloride derivatised chain-end carboxyl group, which was not resolved in the original spectra. The signal at 5.90 ppm is due to the methylene carbon bearing the secondary alcohol ($H_a$) from the benzyl alcohol and remains in the same position after treatment with oxalyl chloride.

In all of our reactions, a small amount of adventitious water leads to a competitive initiation by water. The product is PCL homopolymer but is characterized by having a carboxylic acid functionality. Thus, oxalyl chloride treatment can be used to very easily determine the amount of water initiated PCL.
homopolymer present and determine the composition of the final product. Treatment with oxalyl chloride showed a small amount of water initiated PCL homopolymer in the mixture (less than 15\% yield) with the remainder initiated by phenylethanol. Similar results were obtained for both the KR-ROP and DKR-ROP experiments. The percentage of water initiated PCL homopolymer is calculated as the area of the signal at 2.9 ppm divided by that at 4.37 ppm. We made exhaustive efforts to lower the water concentration in the reaction medium to a minimum by drying the enzyme under vacuum and at 35 °C. This drying method effectively removes most of the free and loosely bound water and hence reduces the amount of polymer formed from water initiation.

![Figure S1. Structure of the phenylethanol initiated PCL homopolymer and the water initiated PCL homopolymer before and after addition of oxalyl chloride.](image-url)
Figure S2. $^1$H-NMR spectra of product before and after addition of oxalyl chloride. Downfield shifts were observed upon addition of oxalyl chloride, demonstrating the presence of a low concentration of water initiated PCL homopolymer together with the predominant phenylethanol initiated PCL homopolymer.

Conversion of ε-CL was obtained from the NMR spectrum of an aliquot of the reaction mixture (Figure S-3, $(b+c)/(b+c+c') \times 100\%$). The DP of PCL was calculated by the ratio of the signal intensity at 3.65 ppm, 4.08 ppm and 5.90 ppm (Figure S-3, $(b+c)/2a$).
Figure S3. $^1$H-NMR spectrum of an aliquot of the reaction mixture during DKR-ROP ($t = 12$h).

Chiral GC trace and $^1$H-NMR spectra

Figure S4. Chiral GC trace of the reaction mixture (DKR-ROP, $t = 0$).