Electronic Supplementary Material (ESI) for Polymer Chemistry.


**Supporting information**

# Selective degradation in aliphatic block copolyesters by controlling the heterogeneity of the amorphous phase

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## Copolymers before hydrolysis

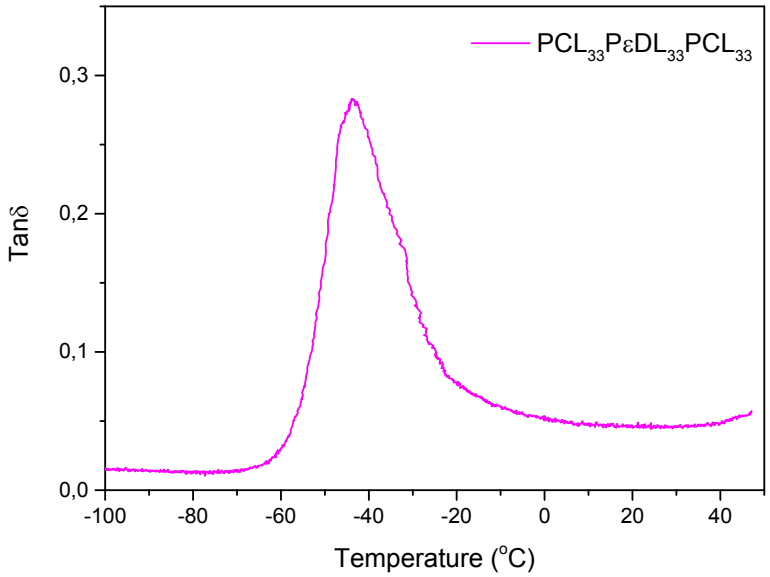
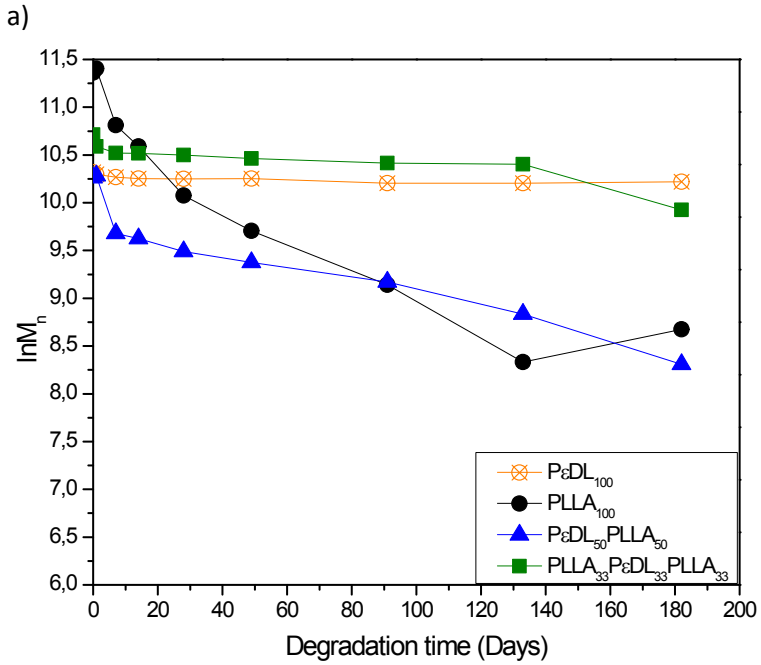



**Figure SS.** Tanδ as a function of temperature of $PCL_{33}P\varepsilon DL_{33}PCL_{33}$ prior to hydrolysis.

## Molar mass changes under hydrolysis



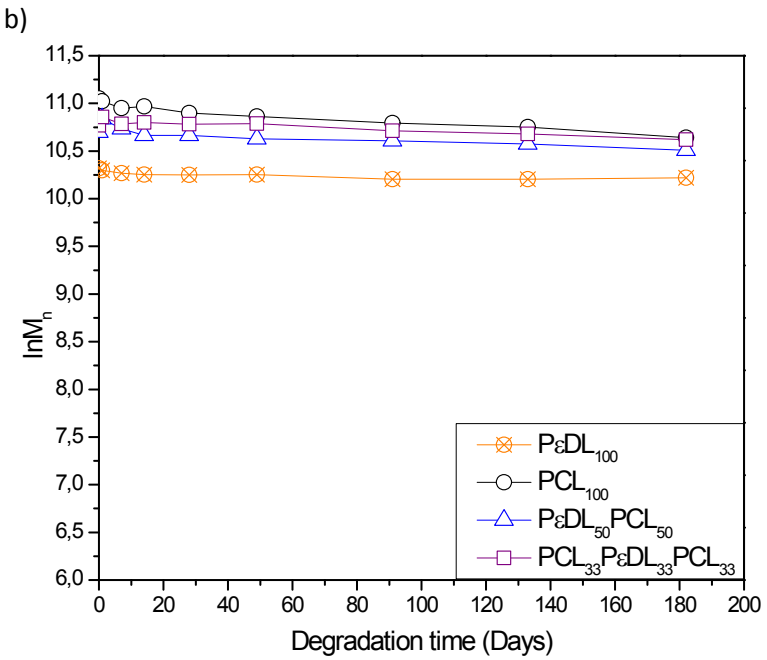
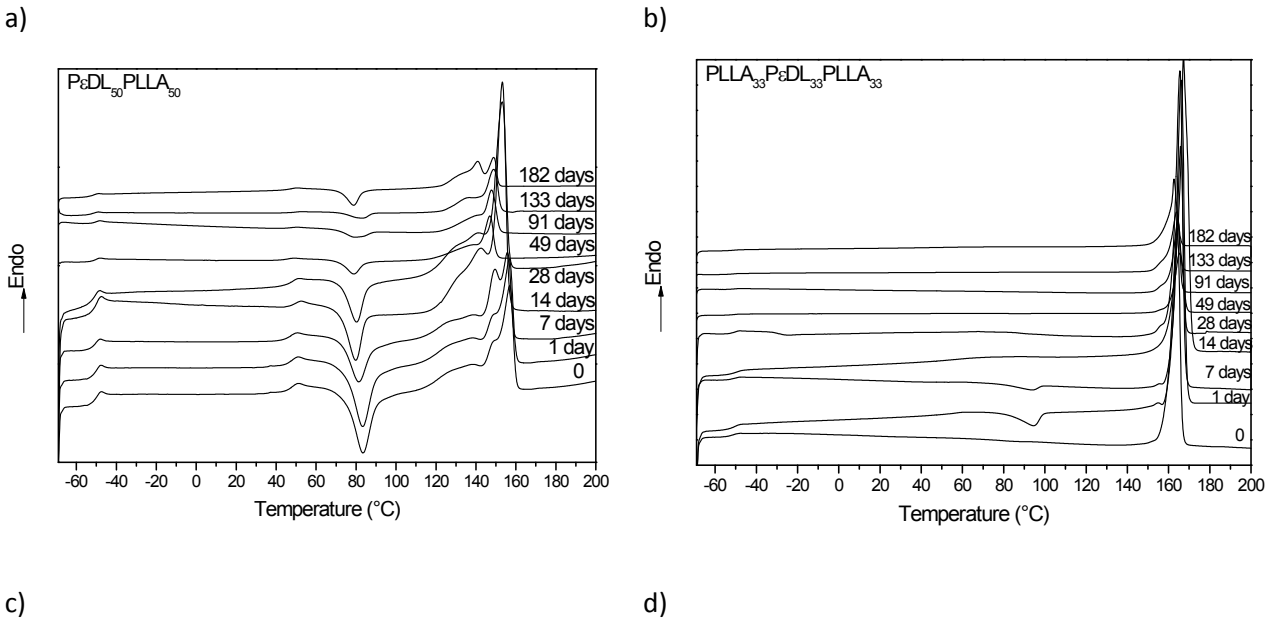



**Figure S1.** Logarithmic number-average molar mass of a) PLLA and PεDL homo-, di-, and tri-block copolymers; b) PCL and PεDL homo-, di-, and tri-block copolymers under hydrolysis in water at 37 °C.

## Thermal properties of the materials under hydrolysis




c)

d)

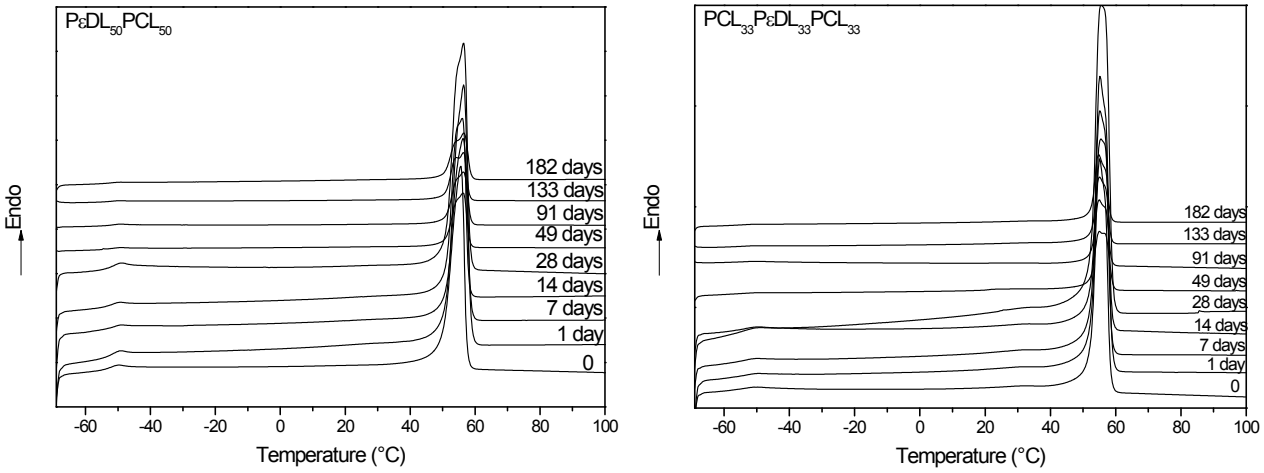
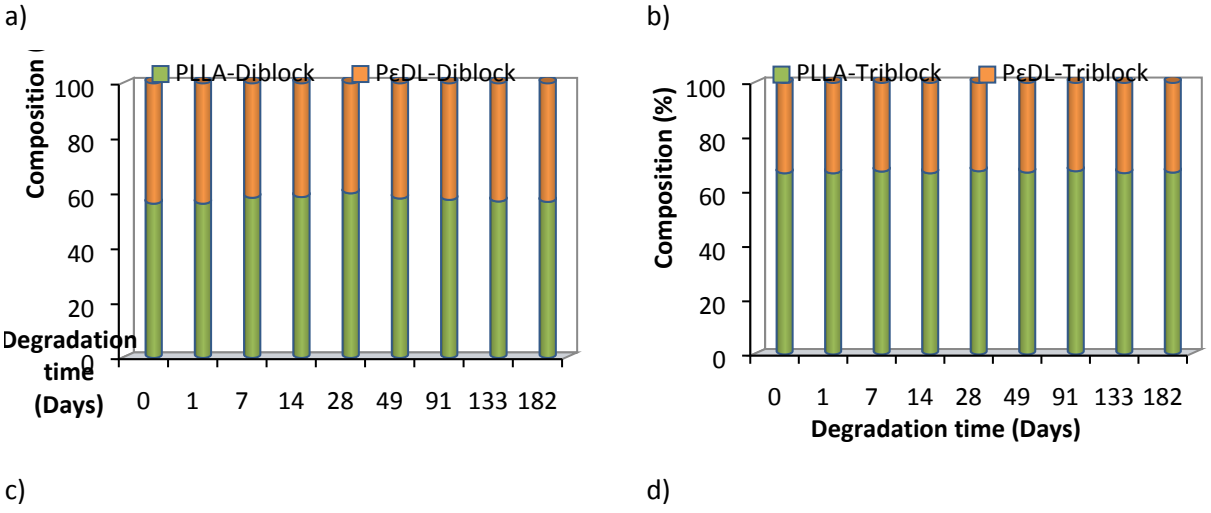



**Figure S2.** 2nd heating scan DSC thermograms of the of a) $P\varepsilon DL_{50}PLLA_{50}$, b) $PLLA_{33}P\varepsilon DL_{33}PLLA_{33}$, c) $P\varepsilon DL_{50}PCL_{50}$ and d) $PCL_{33}P\varepsilon DL_{33}PCL_{33}$ after different hydrolysis times in water at 37 °C as determined by DSC analysis.

## Compositional changes of the copolymers under hydrolysis




c)

d)

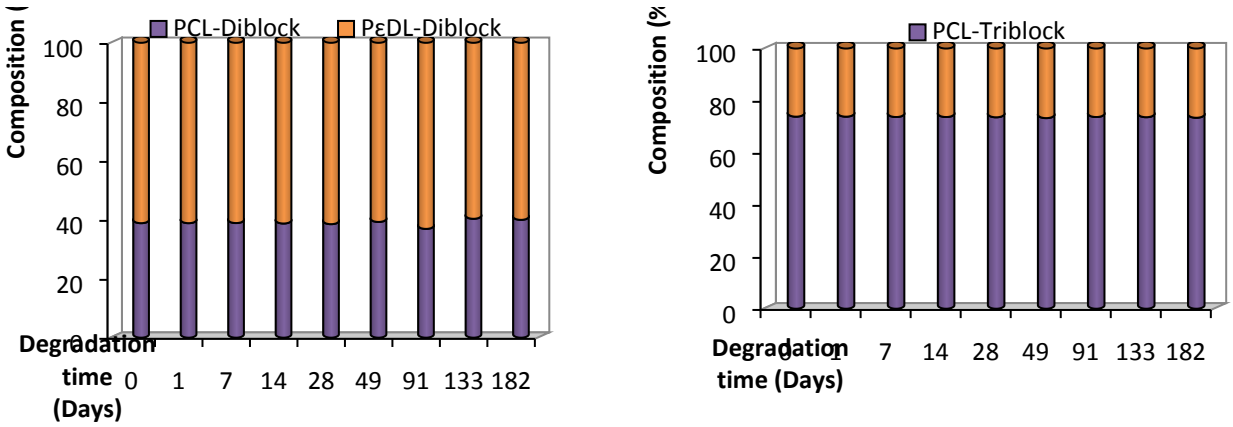



**Figure S3.** Composition of a) $P\varepsilon DL_{50}PLLA_{50}$ diblock, b) $PLLA_{33}P\varepsilon DL_{33}PLLA_{33}$ triblock, c) $P\varepsilon DL_{50}PCL_{50}$ diblock, and d) $PCL_{33}P\varepsilon DL_{33}PCL_{33}$ triblock after different hydrolysis times in water at 37 $^{o}$C as determined by $^{1}$H NMR by comparing the peaks of the comonomers in the respective composition.

## $^{1}$H NMR of the copolymers

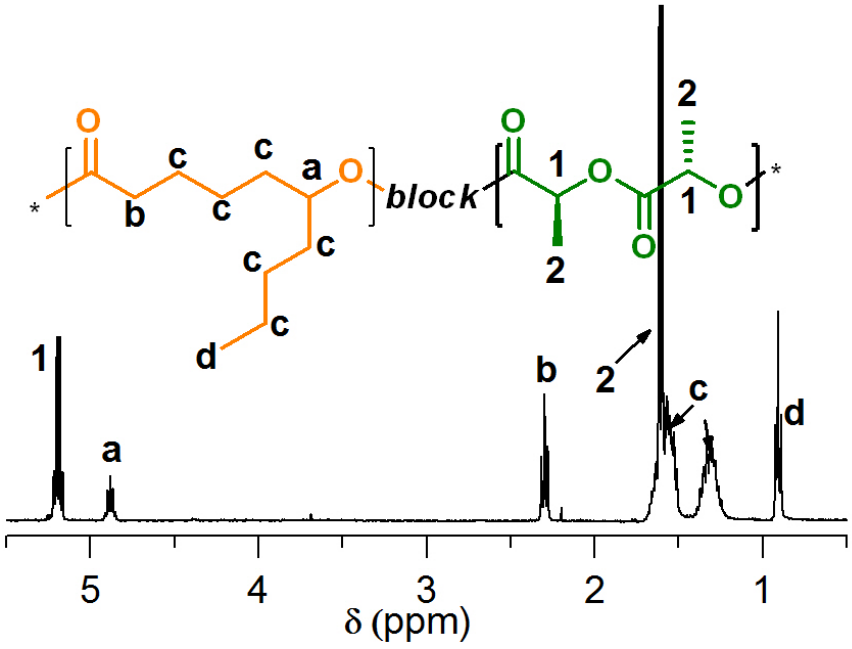



**Figure S4.** $^{1}$H NMR spectra of the block-copolymer of ε-Decalactone and L-Lactide

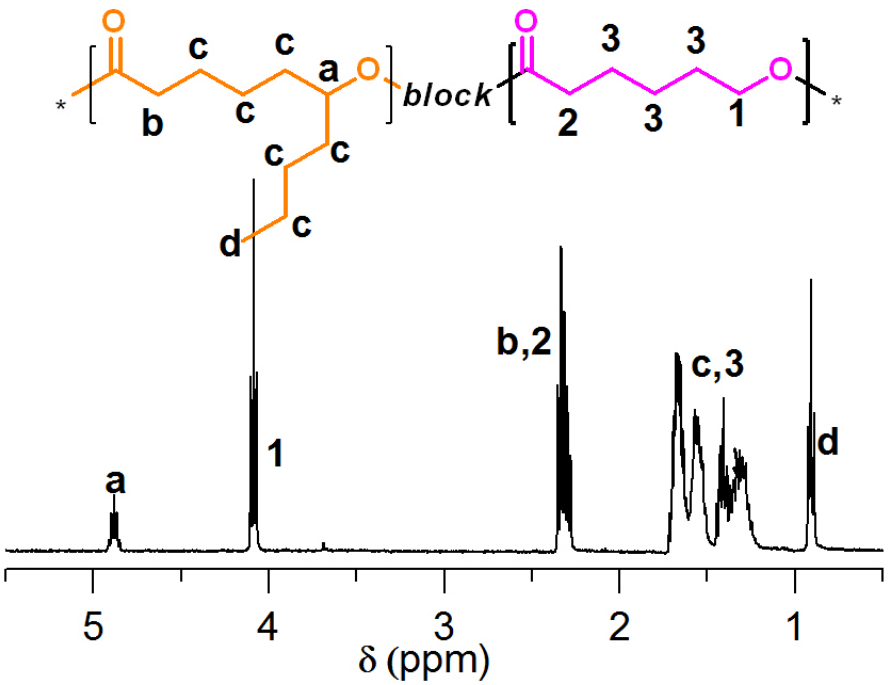



**Figure S5.** $^{1}$H NMR spectra of the block-copolymer of ε-Decalactone and ε-Caprolactone