Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Supplemental Information

## Transformation of Poly(L-lactide) Crystals composed of linear Chains into Crystals composed of Cycles

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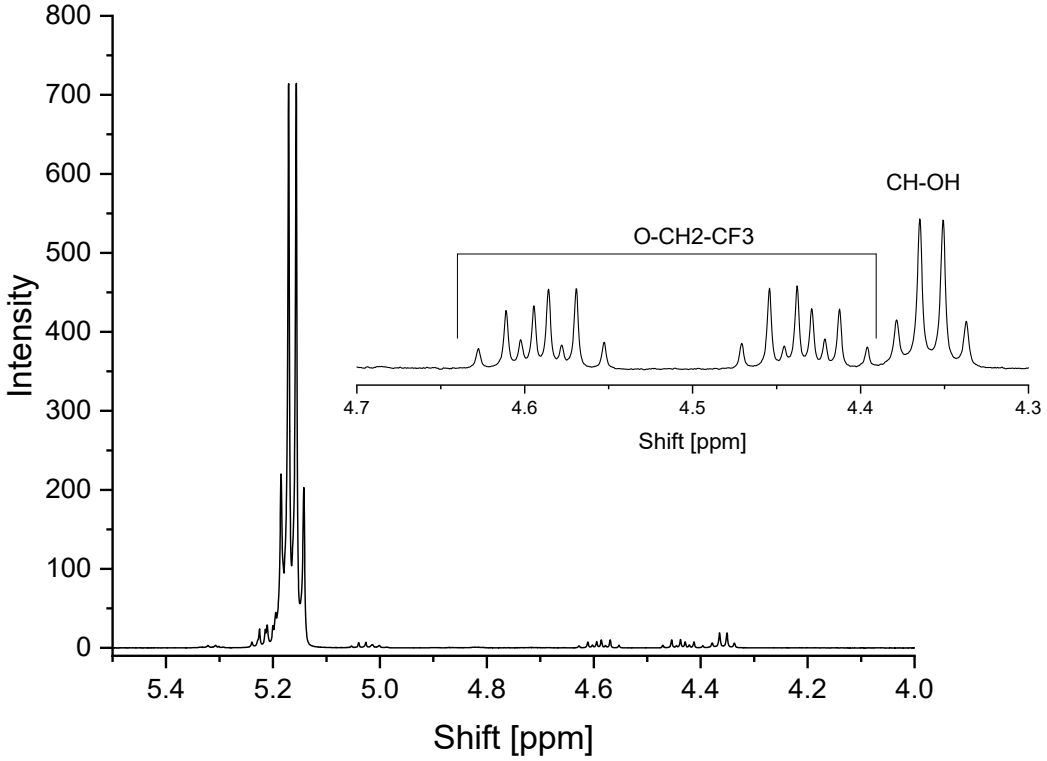



**Figure S1** $^{1}$H NMR spectrum (segment) of the starting material PLATFE-25

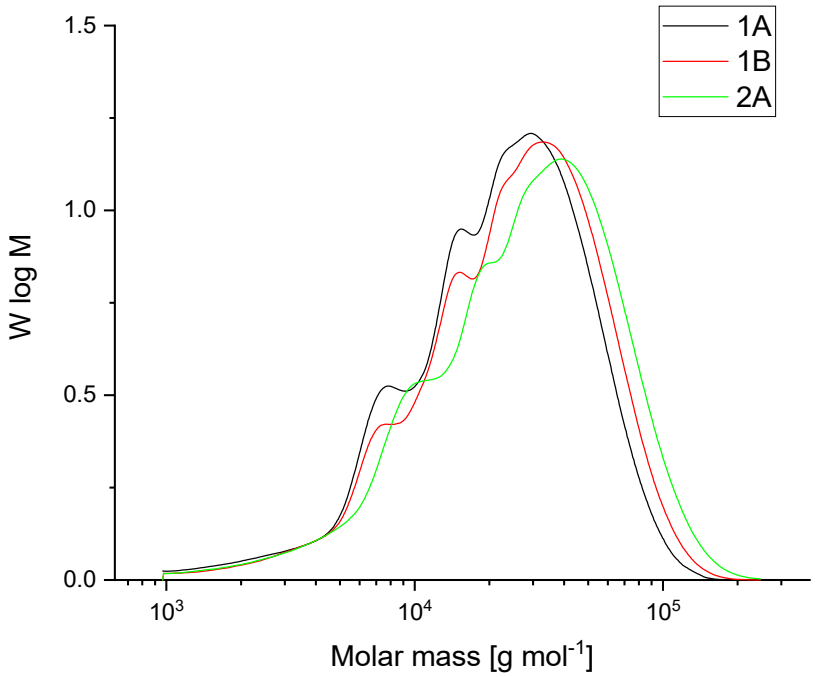



**Figure S2** GPC mass distribution curves of PLAs 1A, 1B, and 2A (Table 1) annealed with $SnOct_2$ at a LA/Cat ratio of 1 000/1

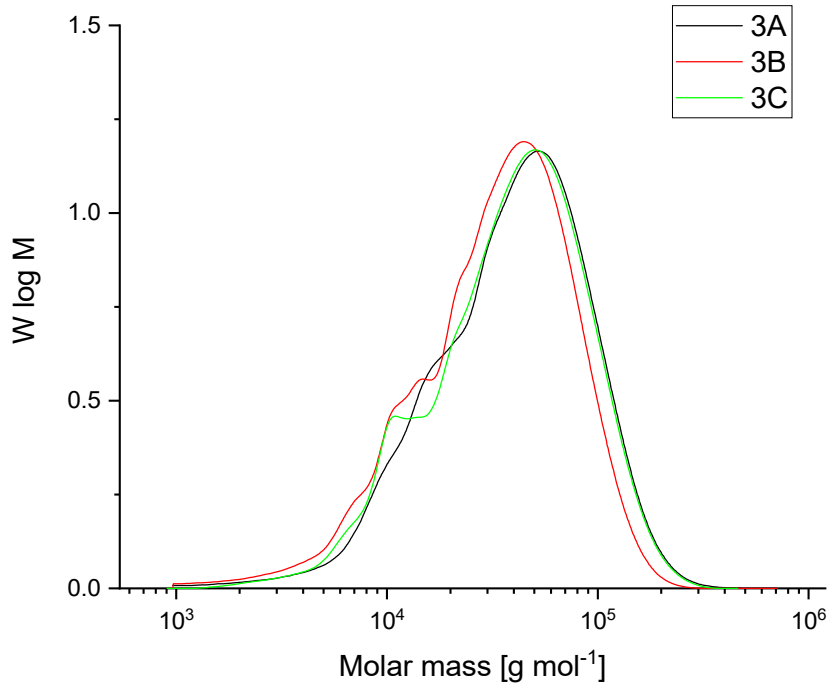



**Figure S3** GPC mass distribution curves of PLAs 3A, 3B, and 3A (Table 1) annealed with $SnOct_2$ at a LA/Cat ratio of 500/1

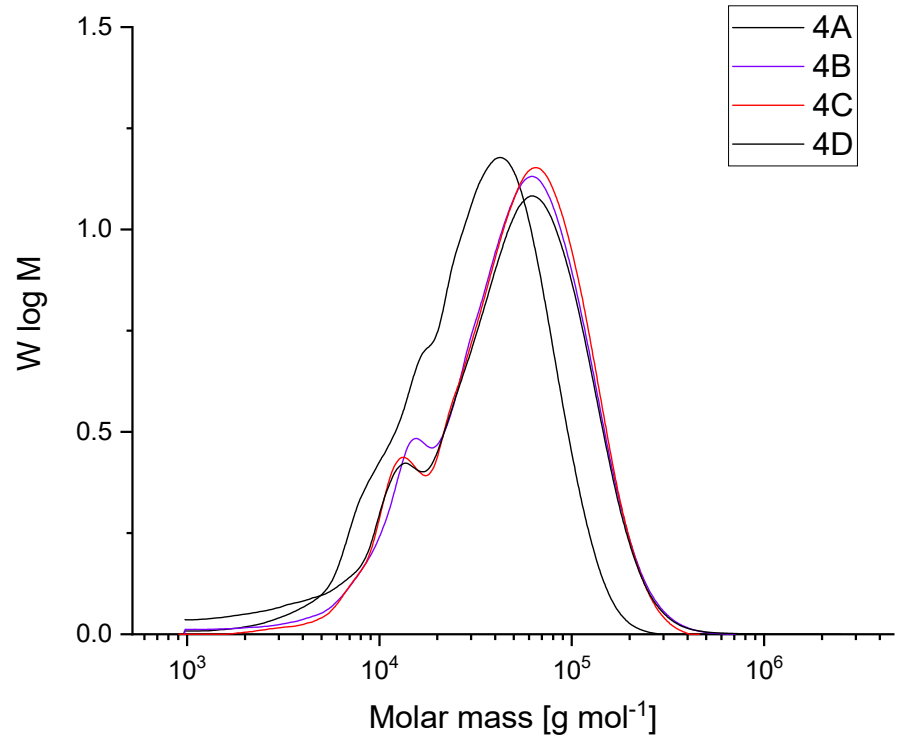



**Figure S4** GPC mass distribution curves of PLAs 4A-D (Table 1) annealed with $SnOct_2$ at a LA/Cat ratio of 250/1

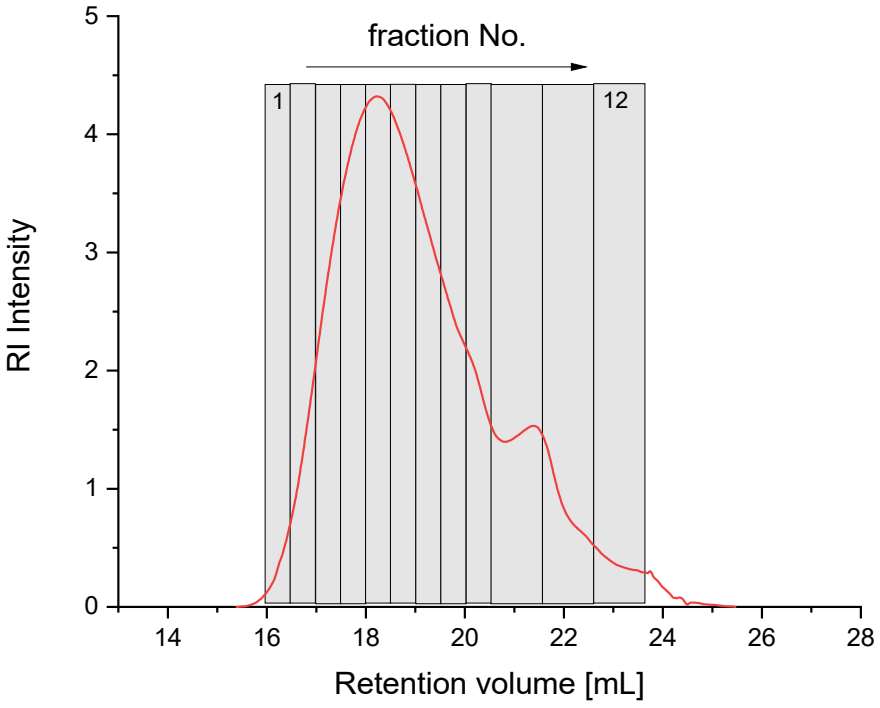



**Figure S5** GPC elution curve of the PLA prepared with $SnOct_2$ at 160 °C/28 days with indication of the fractionation.

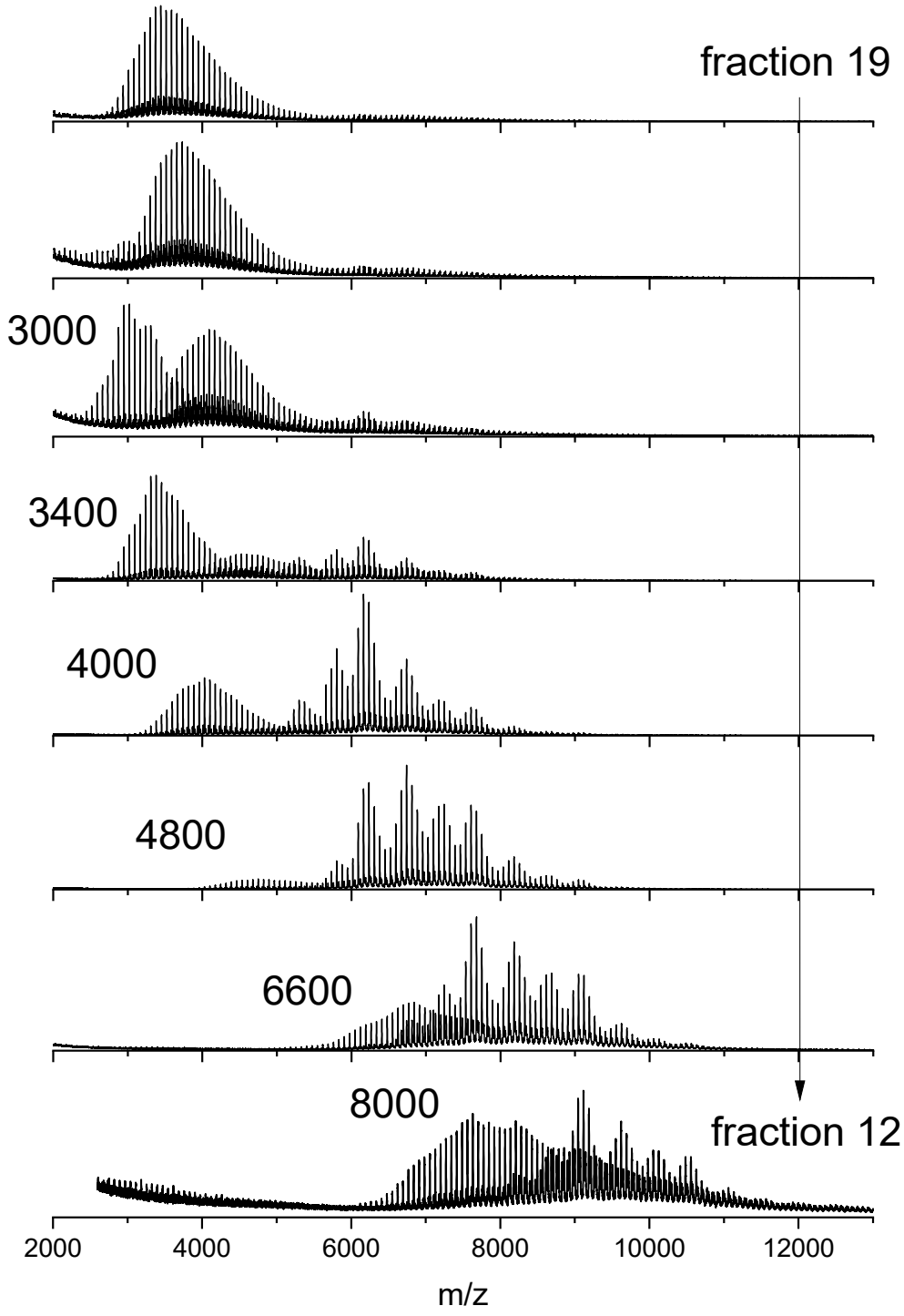



**Figure S6** MALDI TOF mass spectra of fractionated PLA-TFE annealed with $SnOct_2$ at 160°C for 42 days (LA/Cat = 250/1), fractions 12-19 showing MALDI mass spectra with single peak resolution

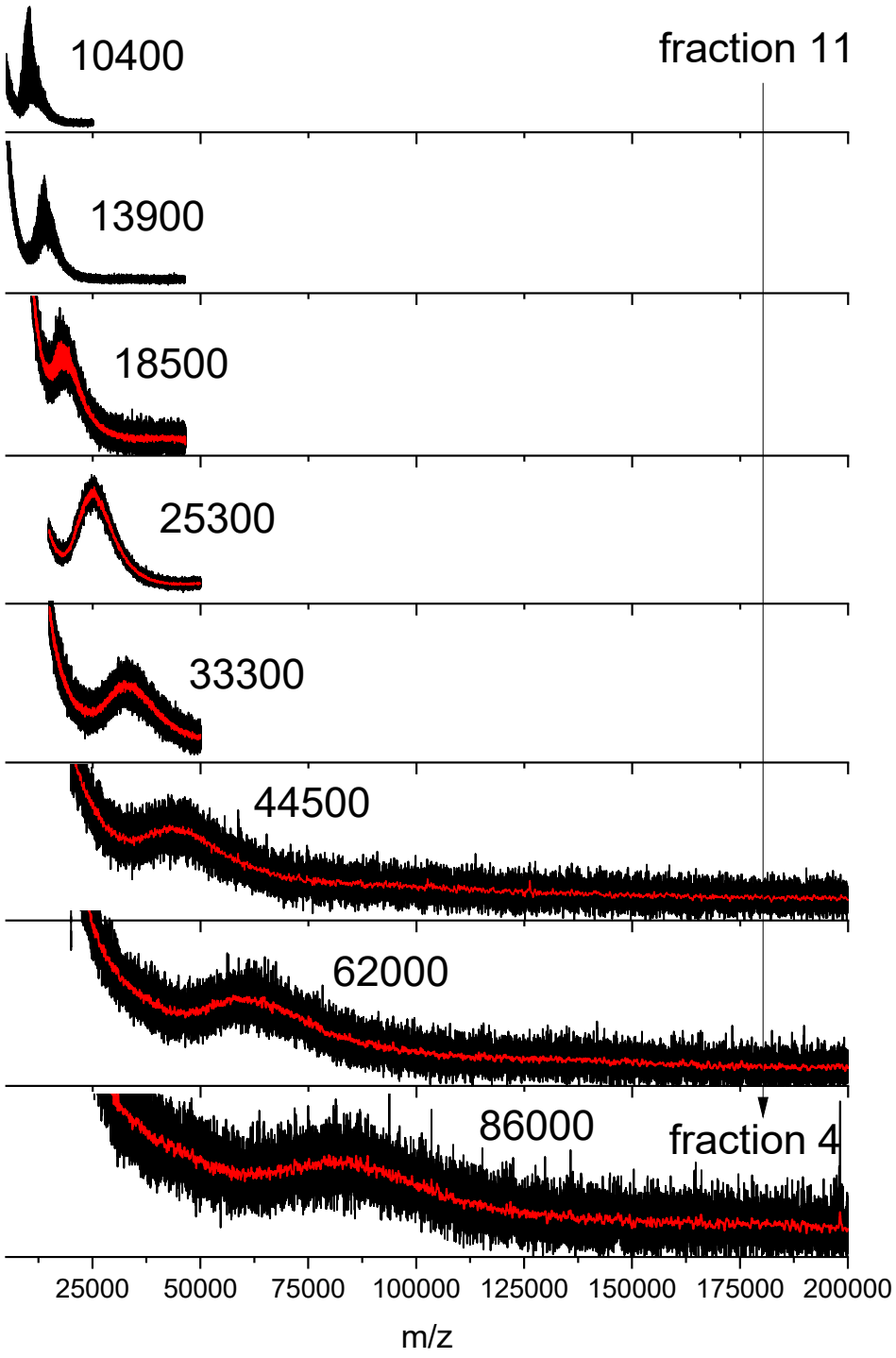



**Figure S7** MALDI TOF mass spectra of fractionated PLA-TFE annealed with $SnOct_2$ at 160°C for 42 d (LA/Cat = 250/1), fractions 11-4 with non-resolved mass spectra, red line indicates FFT smoothing (Origin2021, OriginLab, USA) for $M_p$ determination

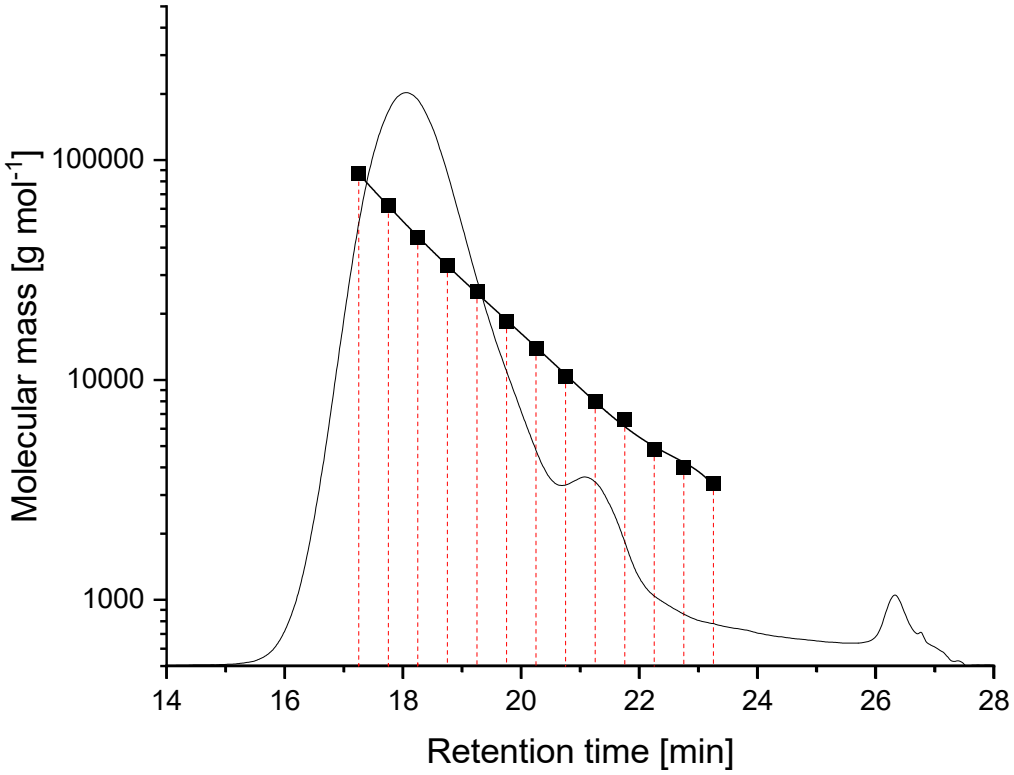



**Figure S8** GPC elution curve of the PLA prepared with $SnOct_2$ at 160°C/42d with indication of the fractionation (red dotted line) and calibration based on MALDI fractions shown in Figures S2 and S3 (polynomial fitting 5$^{th}$ order)

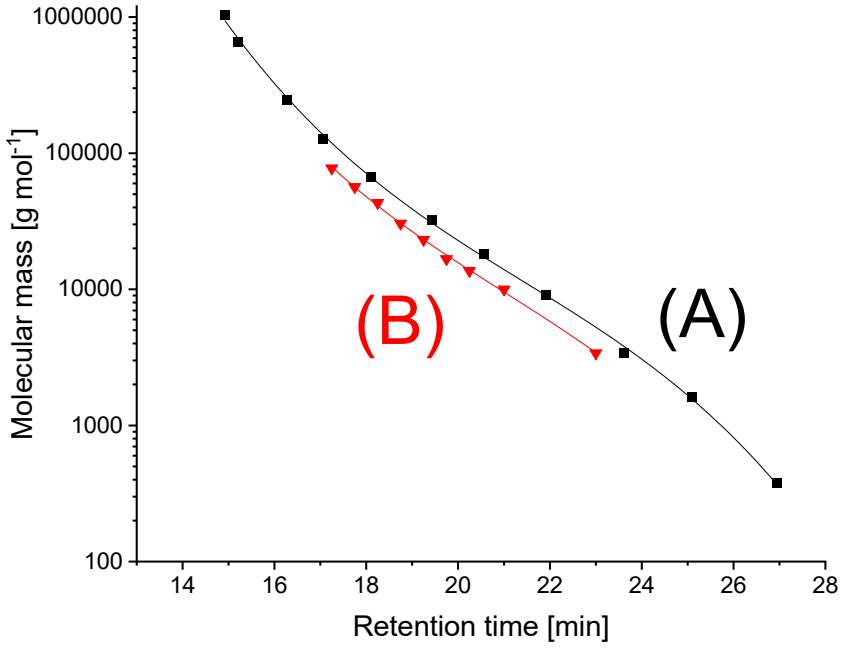
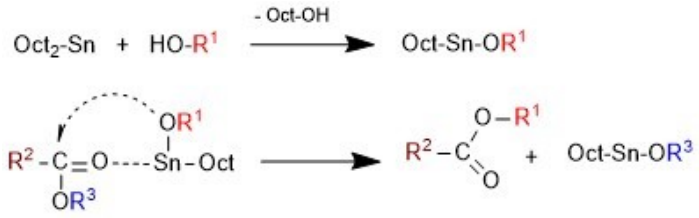
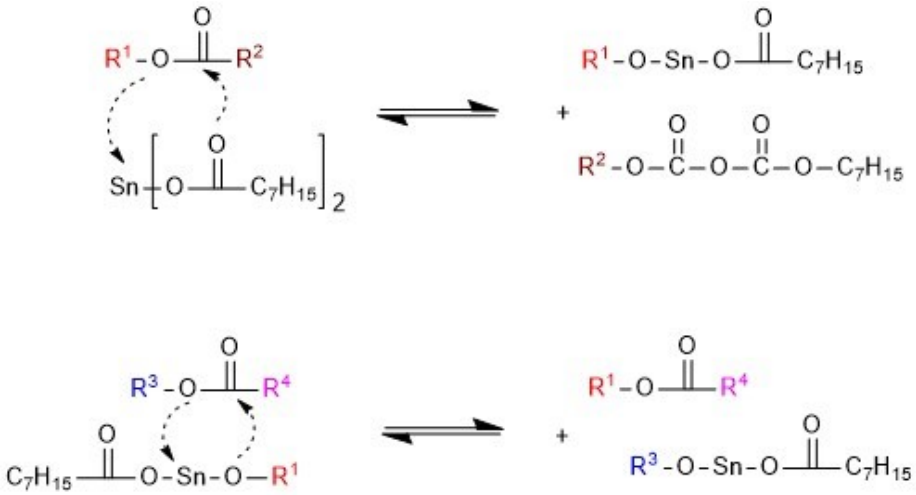



**Figure S9** GPC calibration curves: (A) based on polystyrene standards, (B) based on fractions of PLA 4C, Table 1.




**Scheme S1** Mechanism of alcoholytic transesterification




**Scheme S2** Mechanism of ester-ester-interchange reactions