

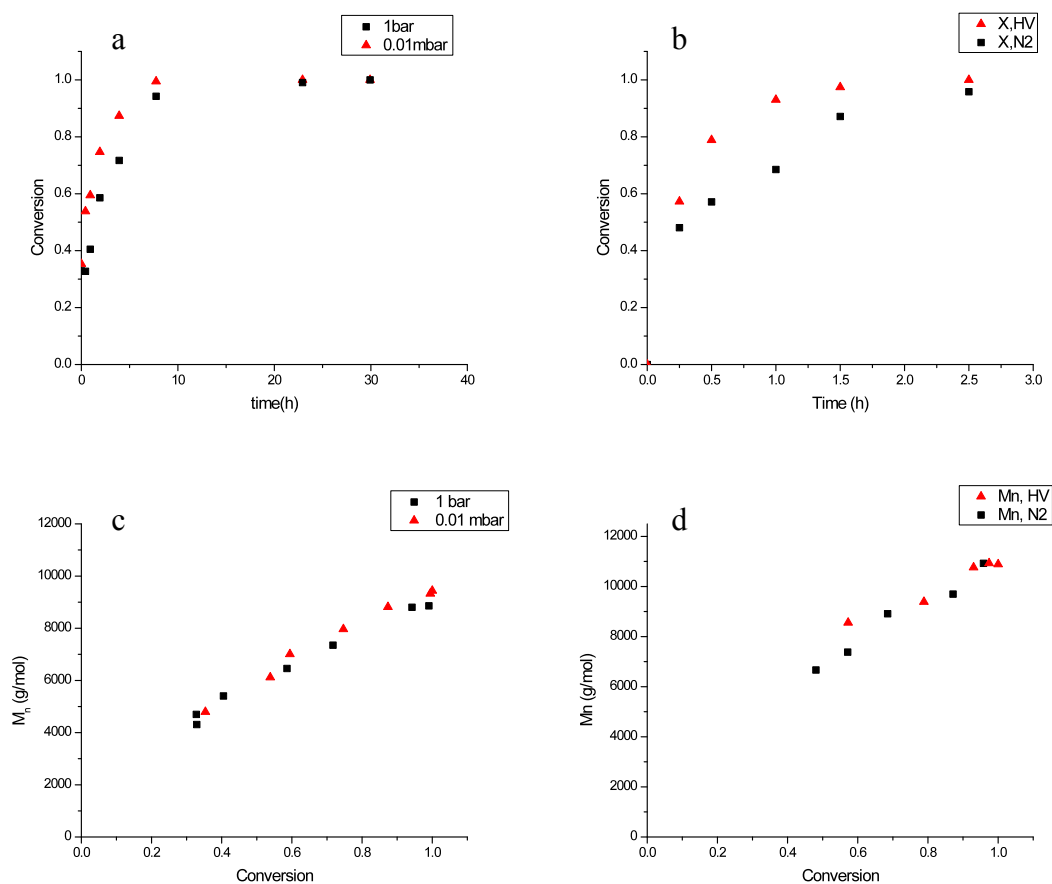
Supporting Information:

Optimization of N-Carboxyanhydride (NCA) Polymerization by Variation of Reaction Temperature and Pressure

Gijs J. M. Habraken¹, Karel H.R.M. Wilsens¹, Cor E. Koning¹ and Andreas Heise^{1,2}

¹Eindhoven University of Technology; Laboratory of Polymer Chemistry, Den Dolech 2, P.O.

Box 513, 5600 MB Eindhoven, The Netherlands. ²Dublin City University, School of Chemical Sciences, Glasnevin, Dublin 9, Ireland.



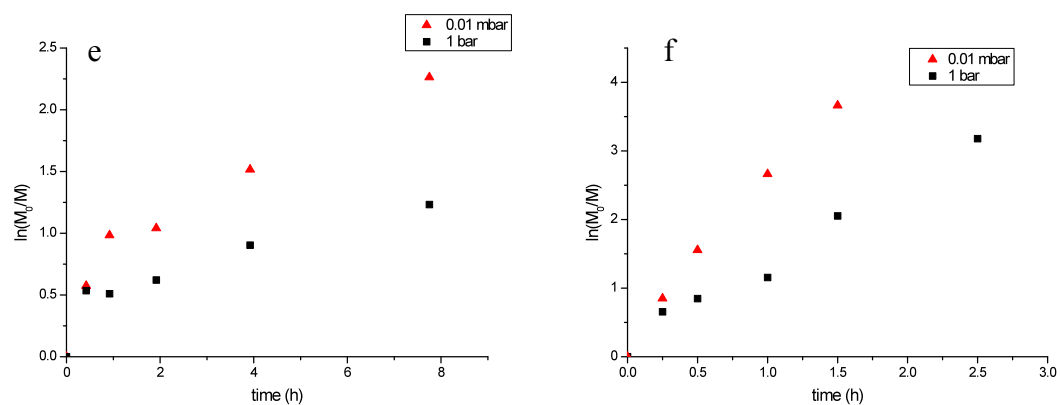


Figure SI 1: Polymerization of BLG NCA at a monomer to initiator ration of 40: (a) monomer conversion at 0 °C, (b) monomer conversion at 20 °C, (c) M_n vs conversion at 0 °C, (d) M_n vs conversion at 20 °C, (e) kinetic plot of the reaction at 0 °C and (f) kinetic plot of the reaction at 20 °C. (▲) reaction under high vacuum of 0.01 mbar and (■) reaction under nitrogen at 1 bar.

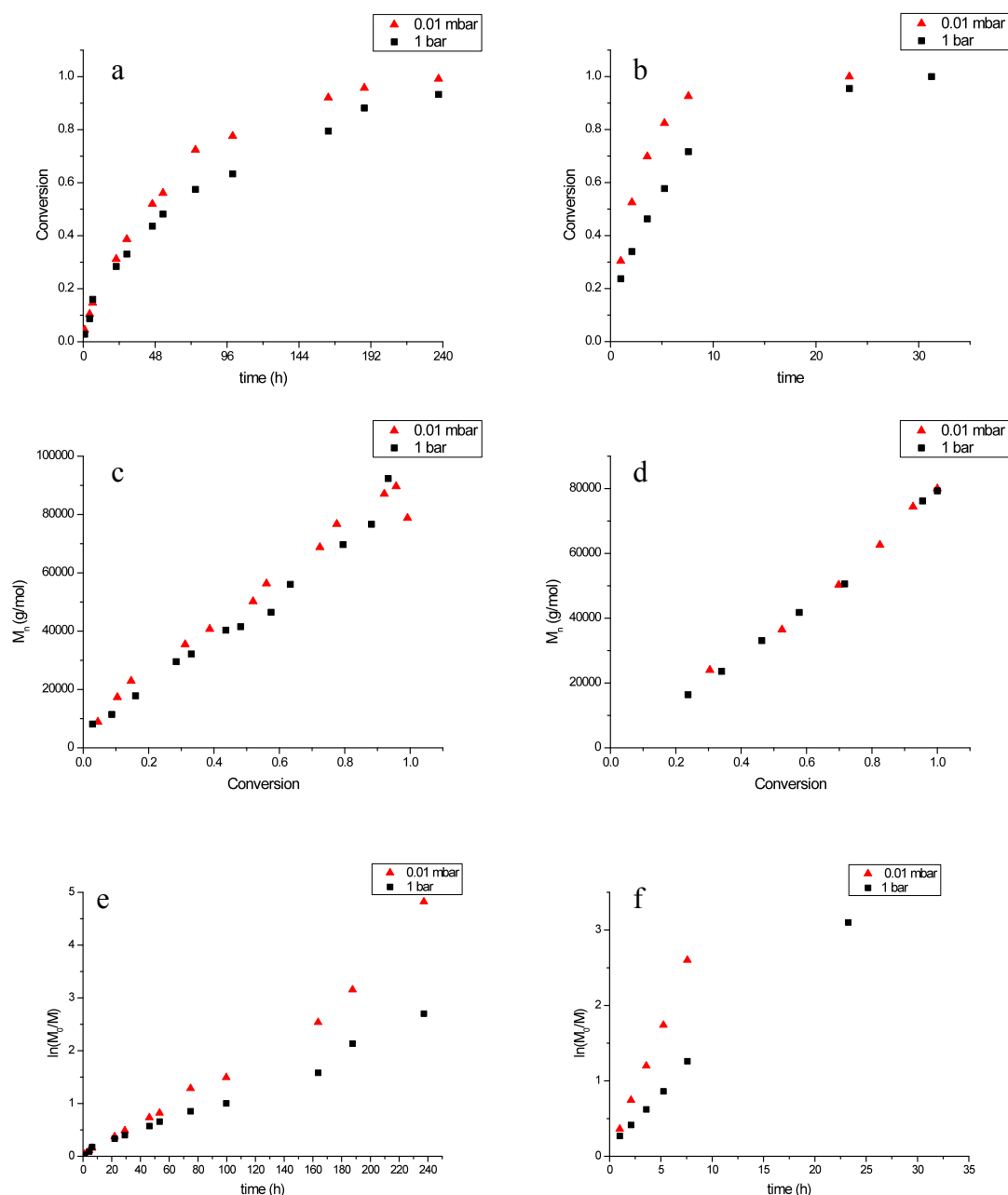


Figure SI 2: Polymerization of BLG NCA at a monomer to initiator ratio of 400: (a) monomer conversion at 0 °C, (b) monomer conversion at 20 °C, (c) M_n vs conversion at 0 °C, (d) M_n vs conversion at 20 °C, (e) kinetic plot of the reaction at 0 °C and (f) kinetic plot of the reaction at 20 °C. (▲) reaction under high vacuum of 0.01 mbar and (■) reaction under nitrogen at 1 bar.

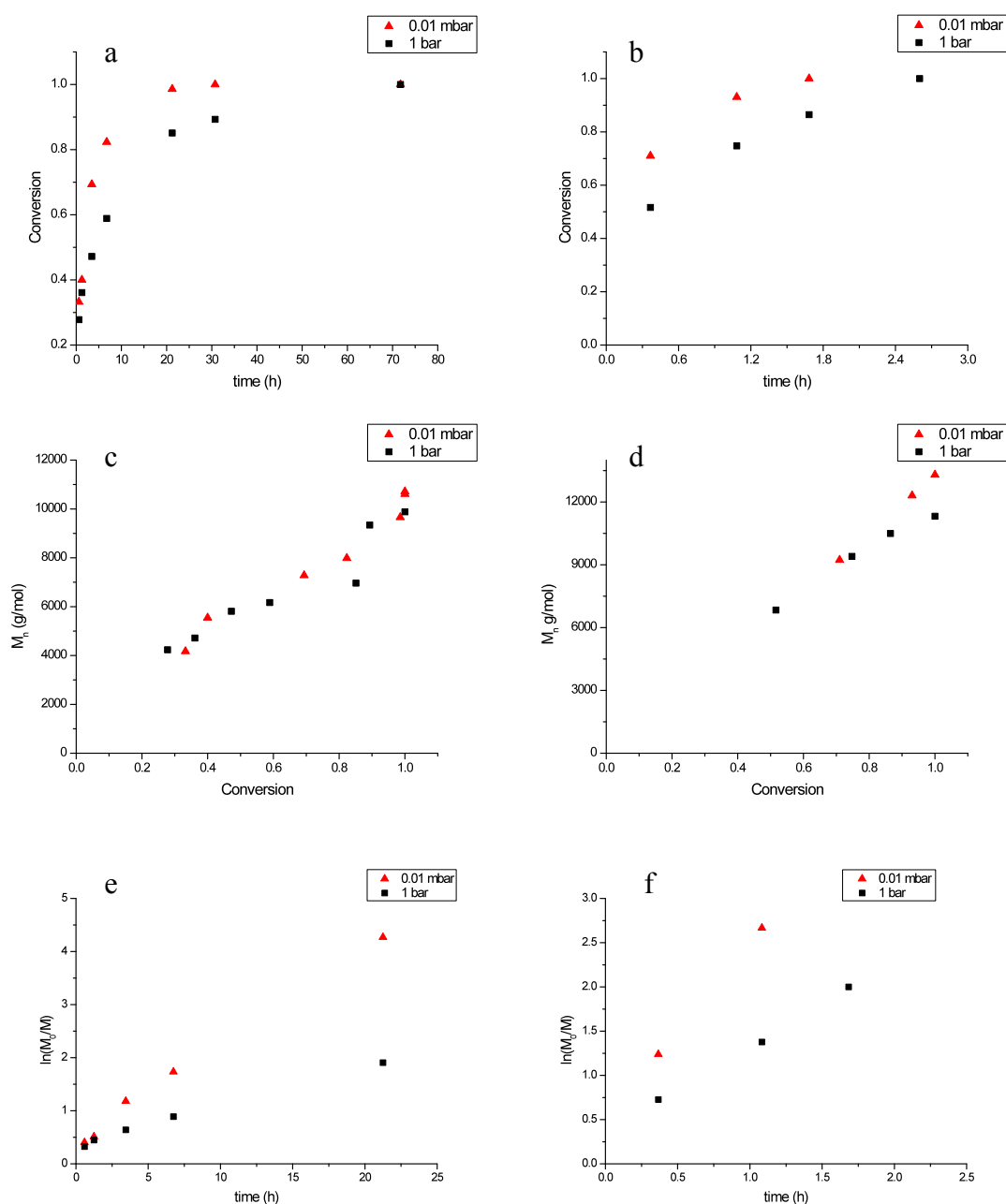


Figure SI 3: Polymerization of ZLL NCA at a monomer to initiator ratio of 40: (a) monomer conversion at 0 °C, (b) monomer conversion at 20 °C, (c) M_n vs conversion at 0 °C, (d) M_n vs conversion at 20 °C, (e) kinetic plot of the reaction at 0 °C and (f) kinetic plot of the reaction at 20 °C. (▲) reaction under high vacuum of 0.01 mbar and (■) reaction under nitrogen at 1 bar.

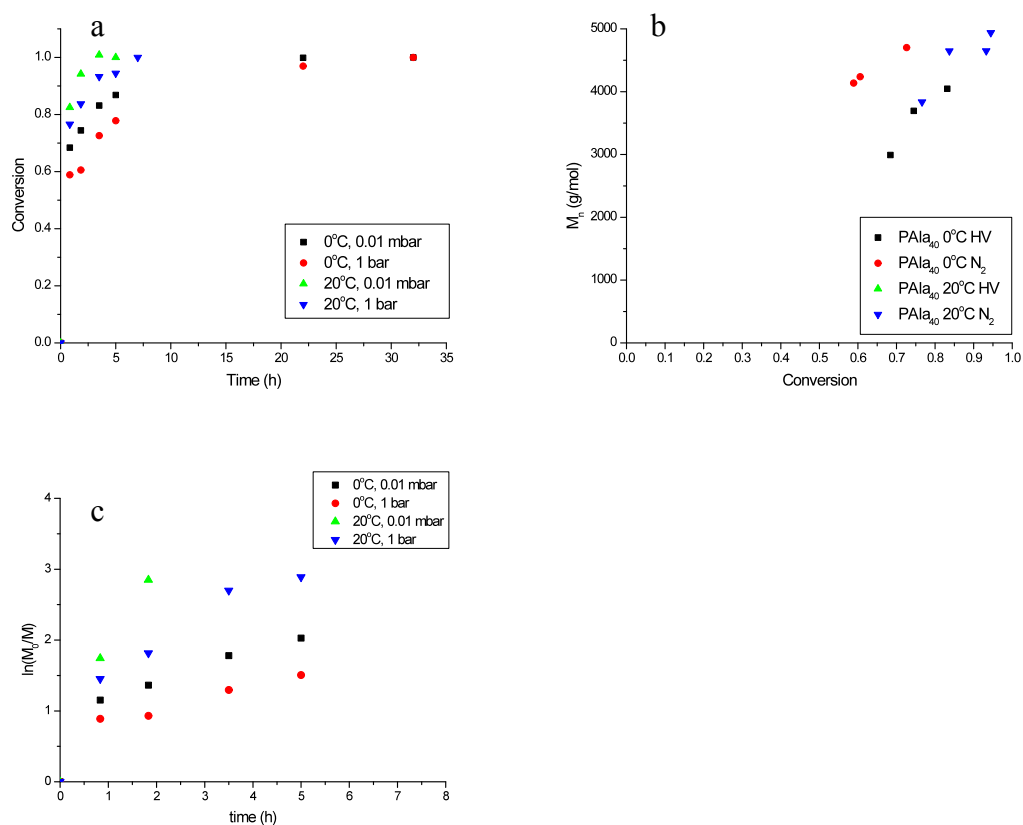


Figure SI 4: Polymerization of Ala NCA at a monomer to initiator ratio of 40: (a) monomer conversion at 0 °C and 20 °C, (b) M_n vs conversion at 0 °C and 20 °C and (c) kinetic plot of the reaction at 0 °C and 20 °C. (■) reaction under nitrogen at 0.01 mbar and 0 °C, (●) reaction under high vacuum of 1 bar and 0 °C (▲) reaction under high vacuum of 0.01 mbar and 20 °C and (▼) reaction under nitrogen at 1 bar and 20 °C.

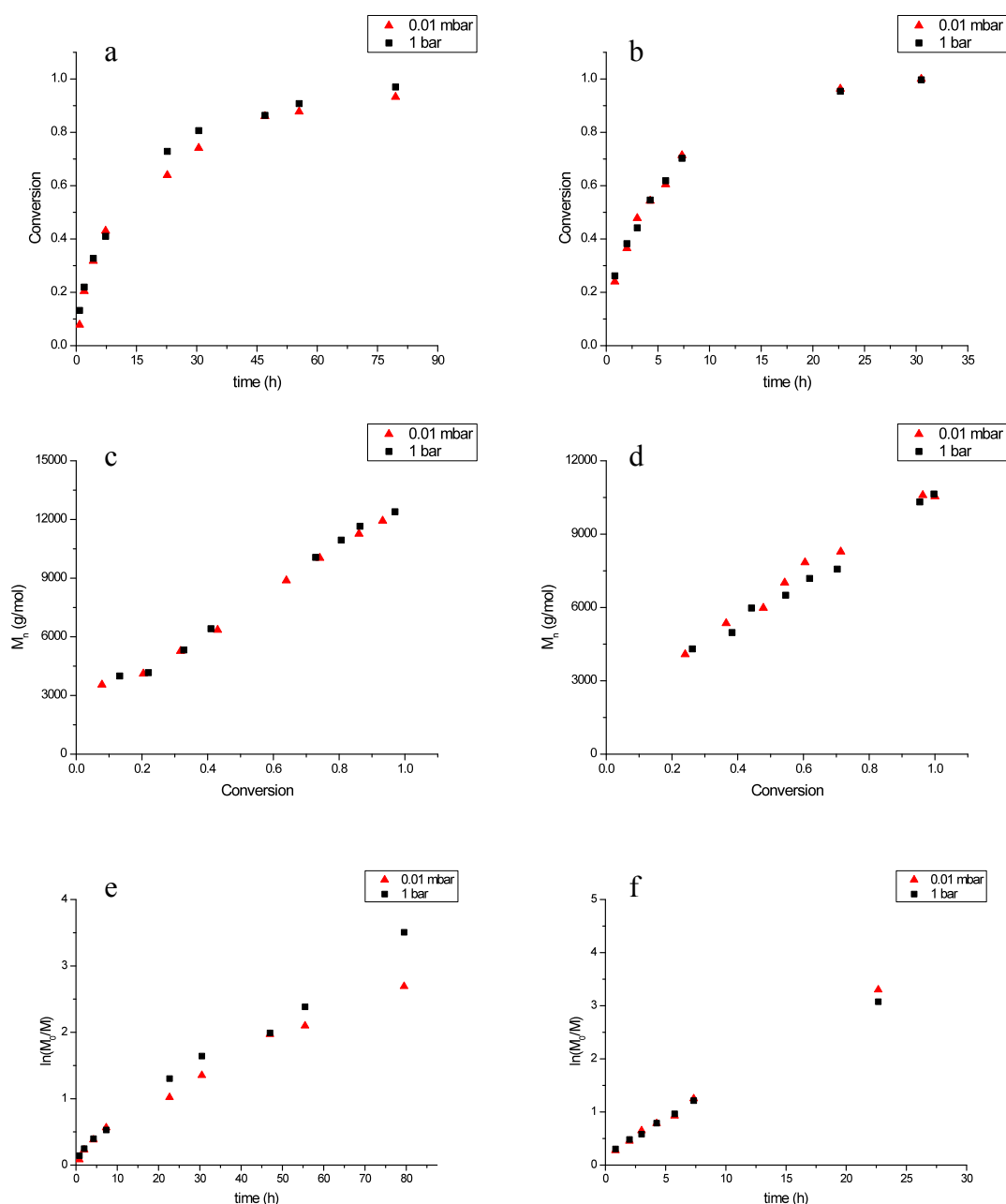


Figure SI 5: Polymerization of BLA NCA at a monomer to initiator ratio of 40: (a) monomer conversion at 0 °C, (b) monomer conversion at 20 °C, (c) M_n vs conversion at 0 °C, (d) M_n vs conversion at 20 °C, (e) kinetic plot of the reaction at 0 °C and (f) kinetic plot of the reaction at 20 °C. (▲) reaction under high vacuum of 0.01 mbar and (■) reaction under nitrogen at 1 bar.

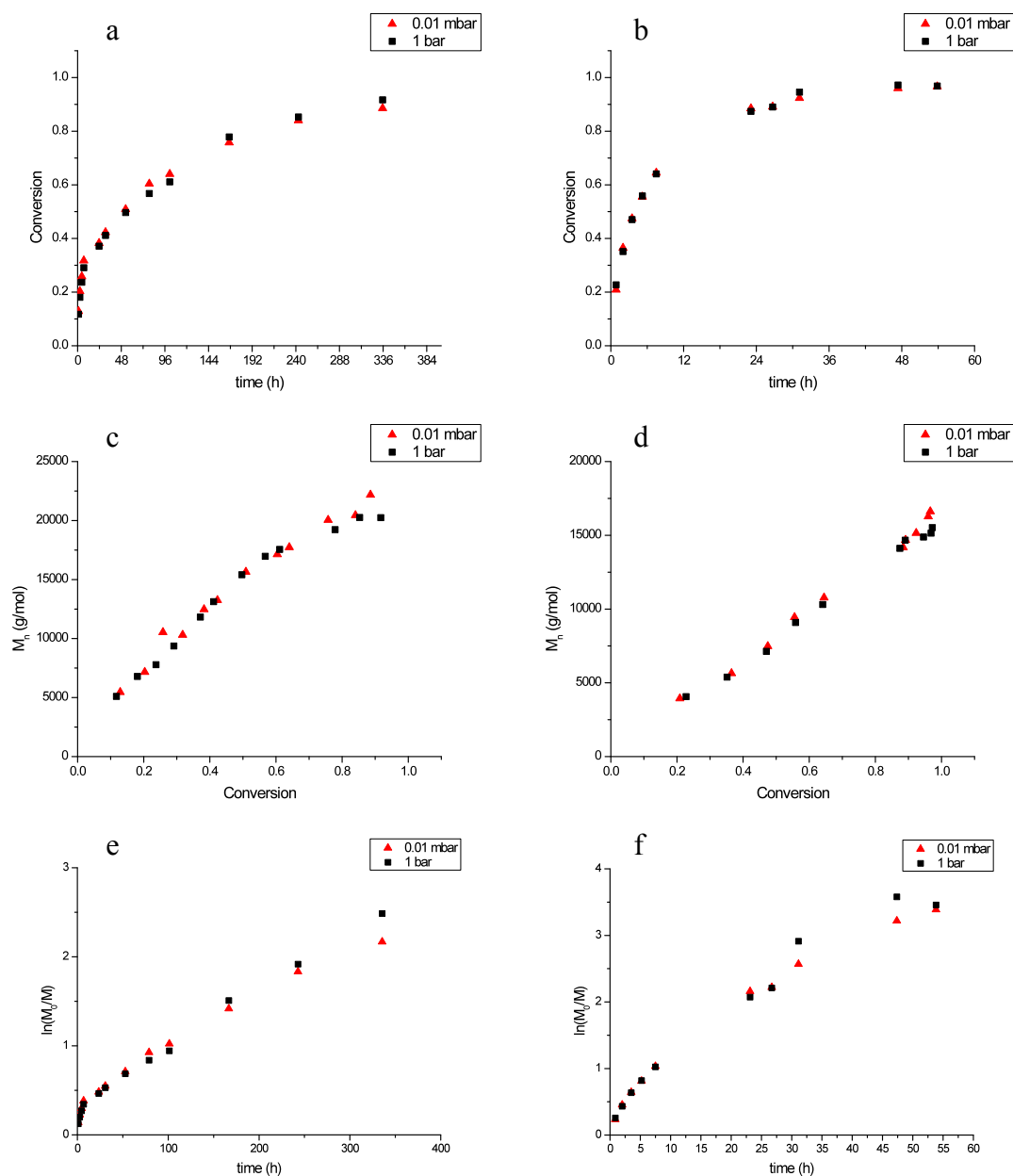


Figure SI 6: Polymerization of BLA NCA at a monomer to initiator ration of 100: (a) monomer conversion at 0 °C, (b) monomer conversion at 20 °C, (c) M_n vs conversion at 0 °C, (d) M_n vs conversion at 20 °C, (e) kinetic plot of the reaction at 0 °C and (f) kinetic plot of the reaction at 20 °C. (▲) reaction under high vacuum of 0.01 mbar and (■) reaction under nitrogen at 1 bar.

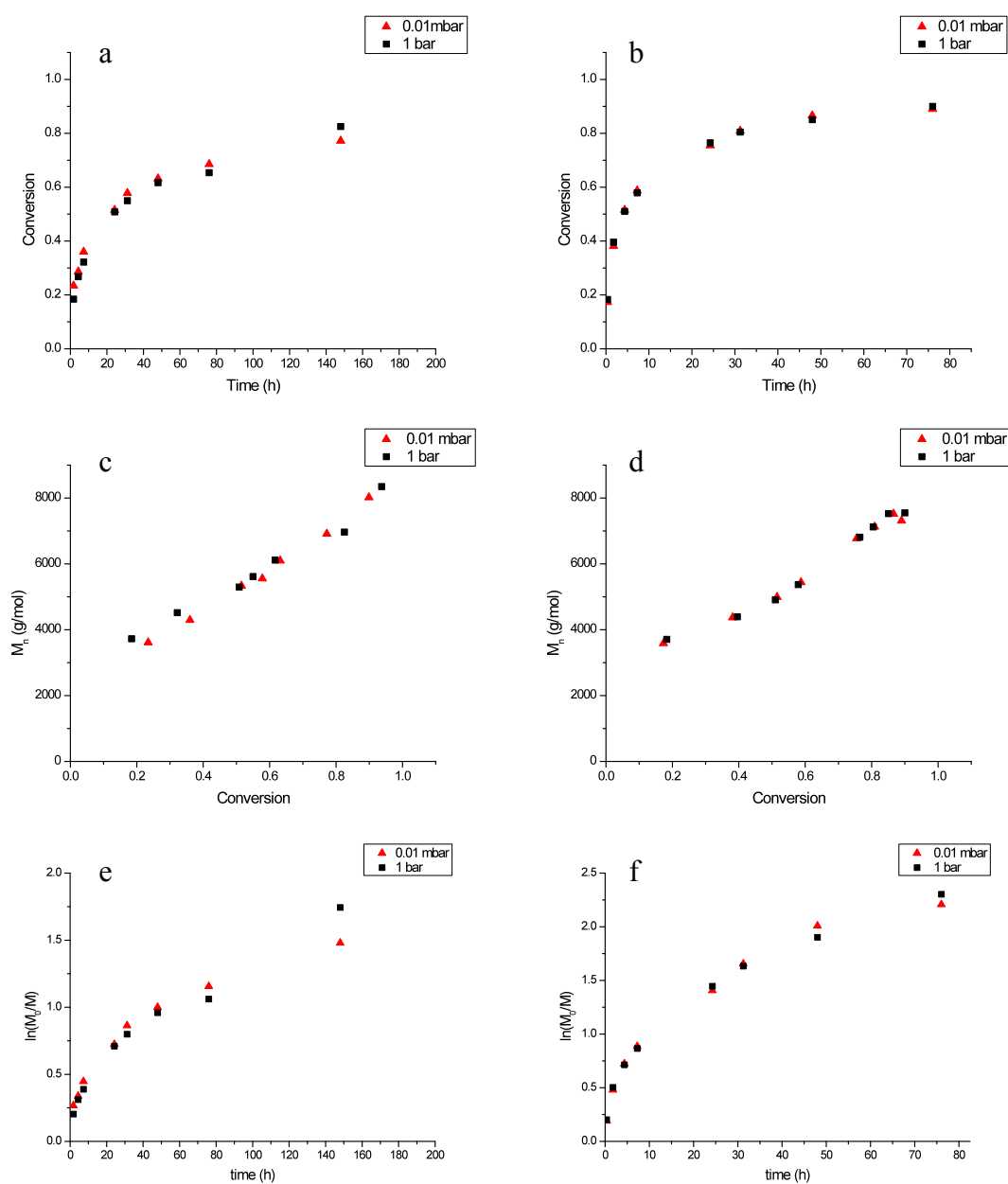


Figure SI 7: Polymerization of BLS NCA at a monomer to initiator ratio of 40: (a) monomer conversion at 0 °C, (b) monomer conversion at 20 °C, (c) M_n vs conversion at 0 °C, (d) M_n vs conversion at 20 °C, (e) kinetic plot of the reaction at 0 °C and (f) kinetic plot of the reaction at 20 °C. (▲) reaction under high vacuum of 0.01 mbar and (■) reaction under nitrogen at 1 bar.

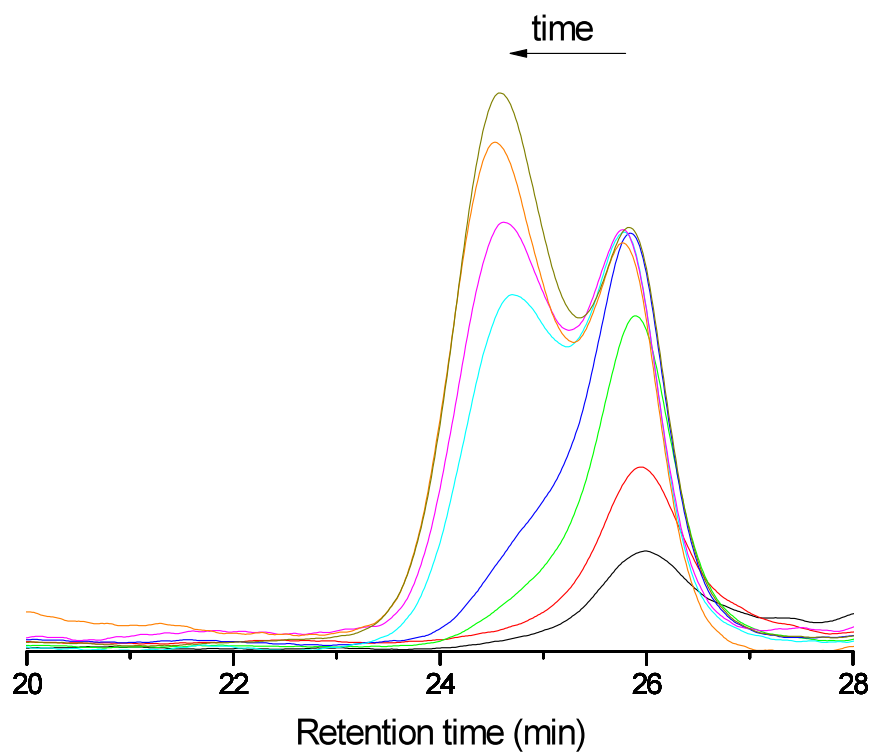


Figure SI 8: HFIP SEC results of BLS polymerization (DP: 40) at 20 °C under high vacuum at different reaction times.

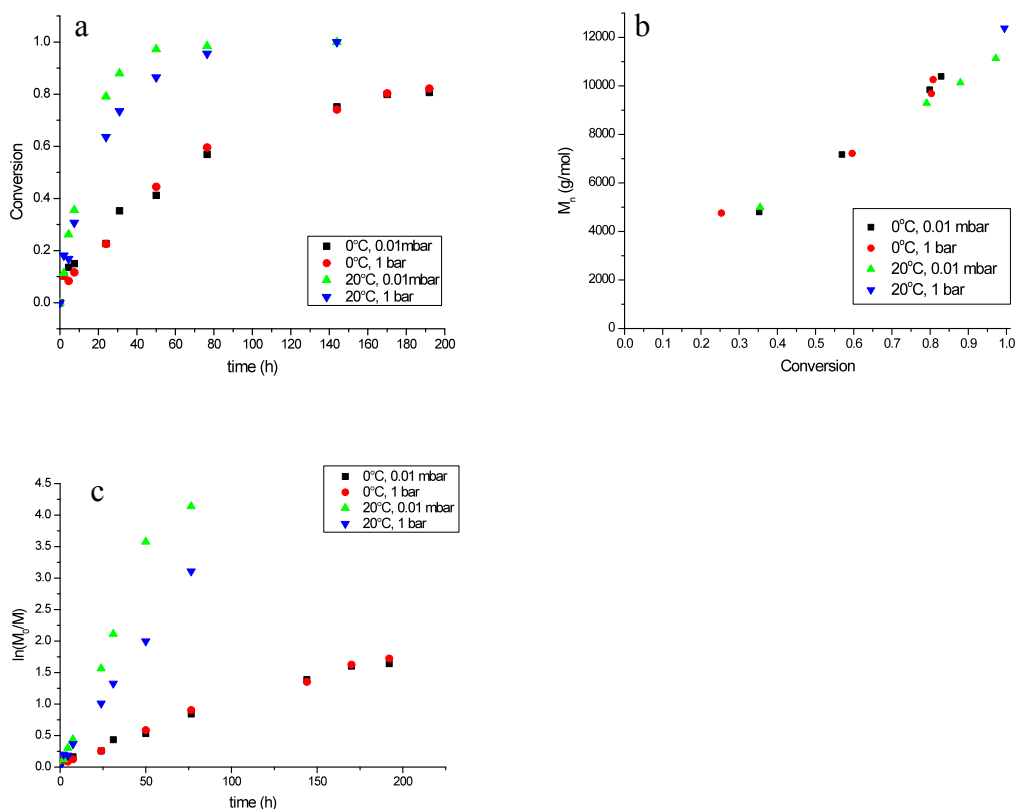


Figure SI 9: Polymerization of BLT NCA ($C_{\text{NCA}} = 0.76\text{M}$) at a monomer to initiator ratio of 40: (a) monomer conversion at 0 °C and 20 °C, (b) M_n vs conversion at 0 °C and 20 °C, (c) kinetic plot of the reaction at 0 °C and 20 °C. ($\blacksquare$) reaction under nitrogen at 0.01 mbar and 0 °C, ($\bullet$) reaction under high vacuum of 1 bar and 0 °C ($\blacktriangle$) reaction under high vacuum of 0.01 mbar and 20 °C and ($\blacktriangledown$) reaction under nitrogen at 1 bar and 20 °C.

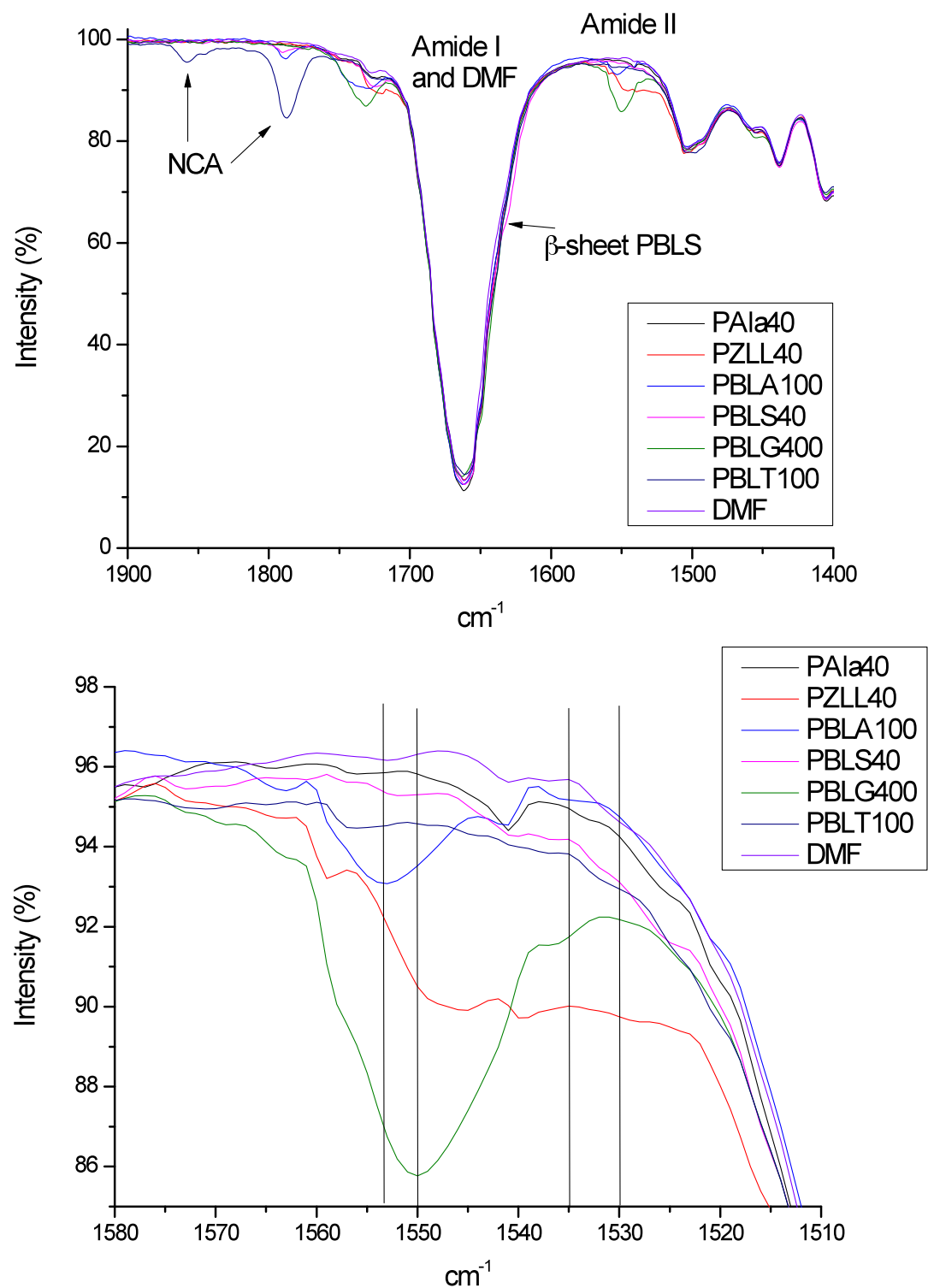


Figure SI 10: FTIR spectra of polypeptides in DMF.

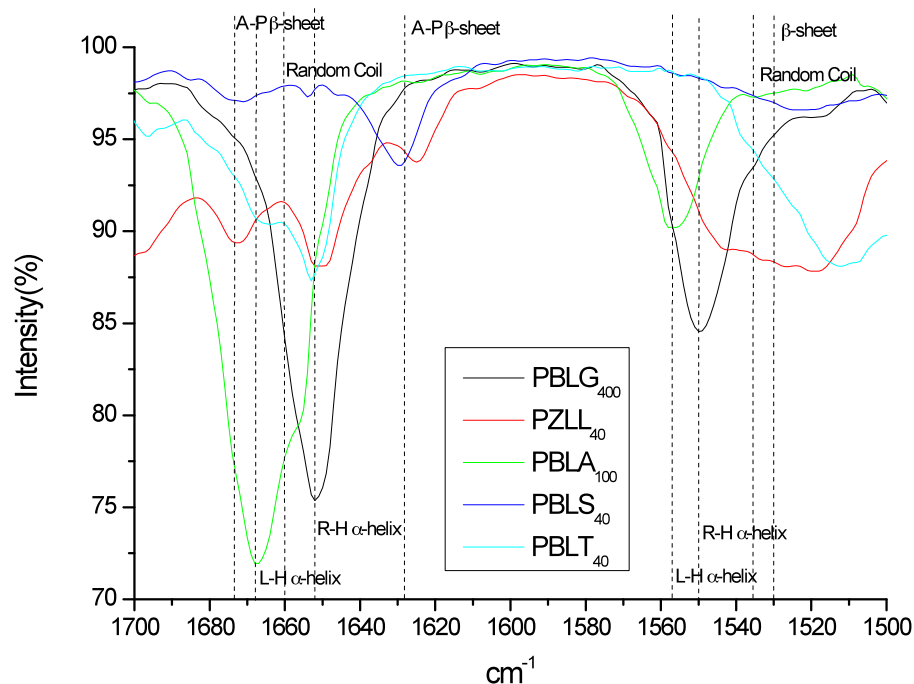
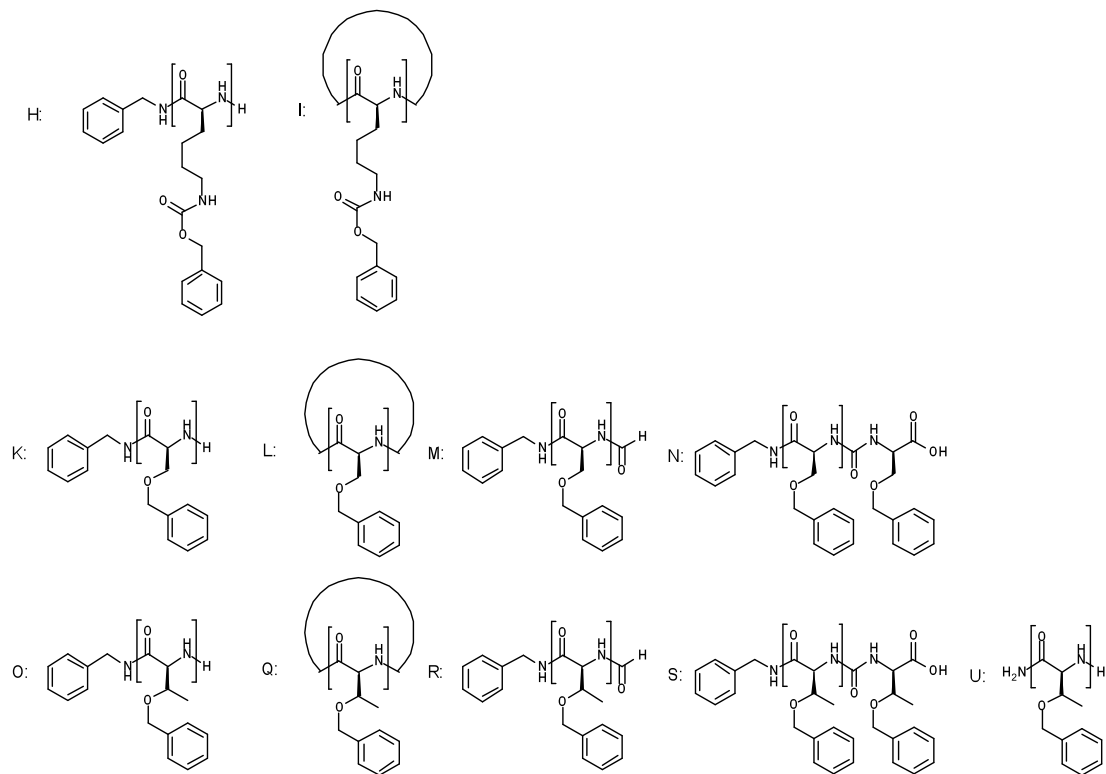


Figure SI 11: FTIR spectra of polypeptides re-dissolved in CHCl_3 . The lines indicate the expected position of IR bands of the secondary structures.



Scheme SI 1: Structures of reaction products formed in various NCA polymerizations. Letters refer to structural assignments in MALDI-ToF-MS spectra, presented in SI Figures 11 to 18.

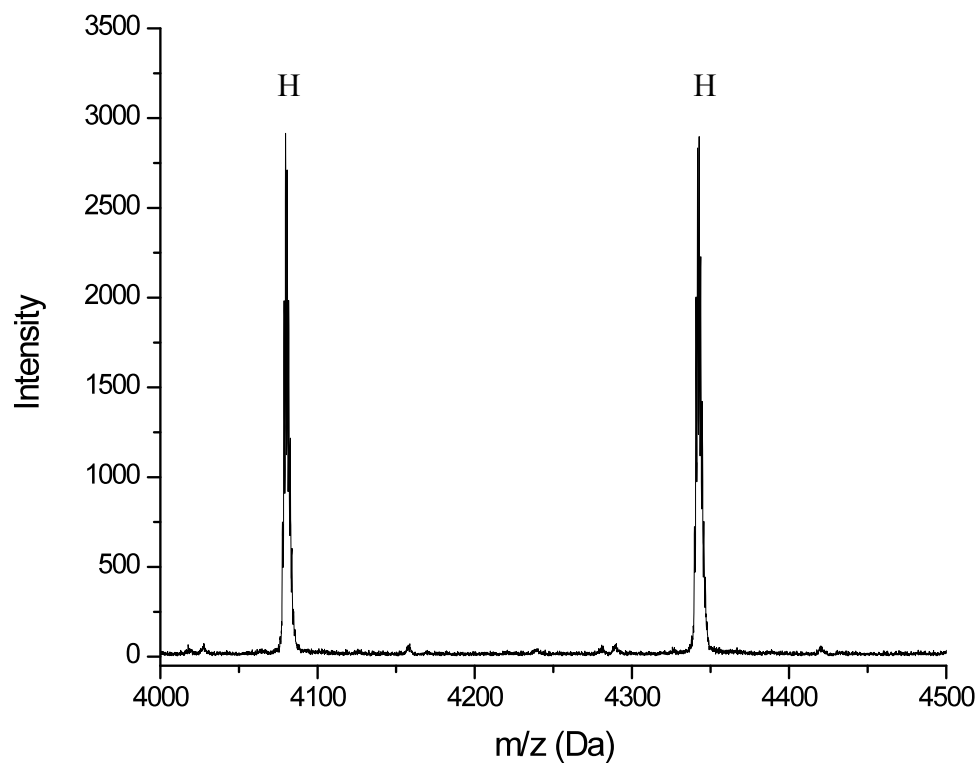


Figure SI 12: MALDI-ToF-MS after PZLL NCA ROP under nitrogen at 1 bar and 0° C.

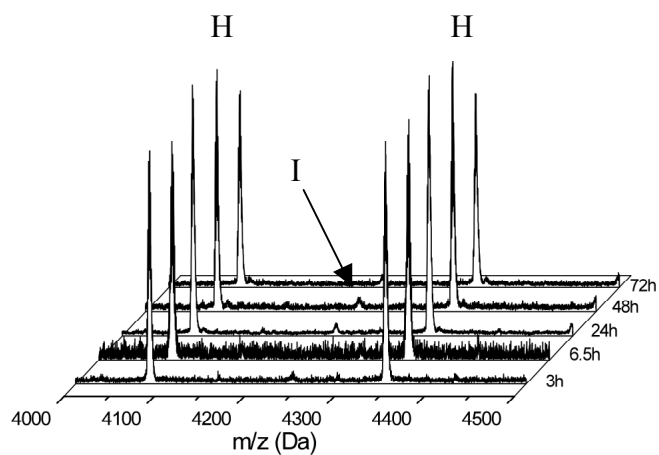


Figure SI 13: MALDI-ToF-MS spectra of samples taken from the polymerization reaction of ZLL NCA at 20 °C and 0.01 mbar at different reaction times.

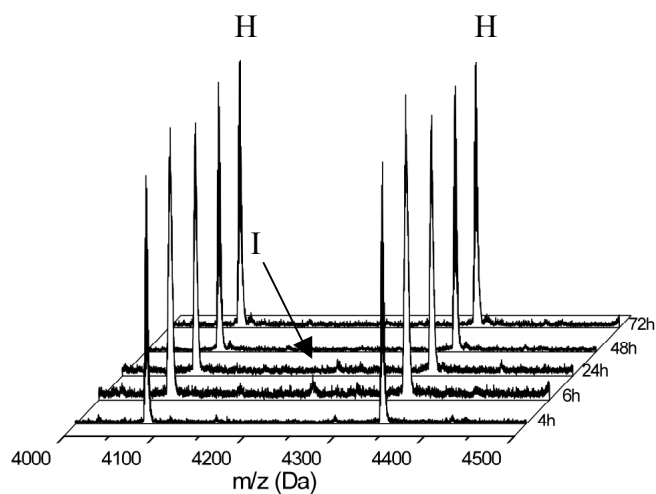


Figure SI 14: MALDI-ToF-MS spectra of samples taken from the polymerization reaction of ZLL NCA at 20 °C under nitrogen at different reaction times.

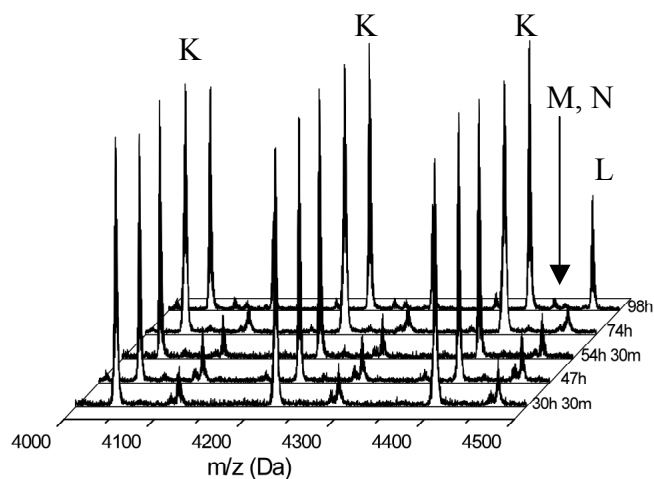


Figure SI 15: MALDI-ToF-MS spectra of samples taken from the polymerization reaction of BLS NCA at 20 °C and 0.01 mbar at different reaction times.

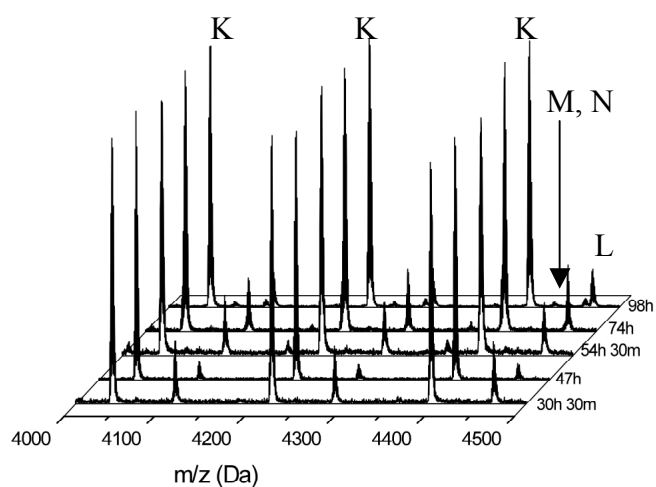


Figure SI 16: MALDI-ToF-MS spectra of samples taken from the polymerization reaction of BLS NCA at 20 °C under nitrogen at different reaction times.

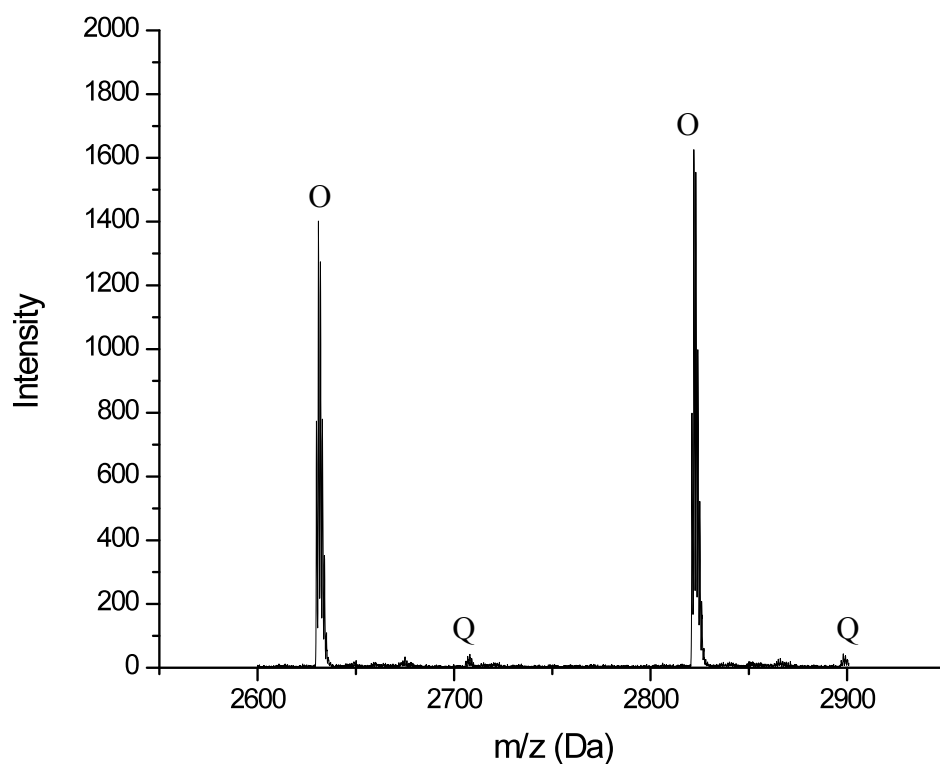


Figure SI 17: MALDI-ToF-MS of PBLT NCA ROP under nitrogen at 1 bar and 0° C.

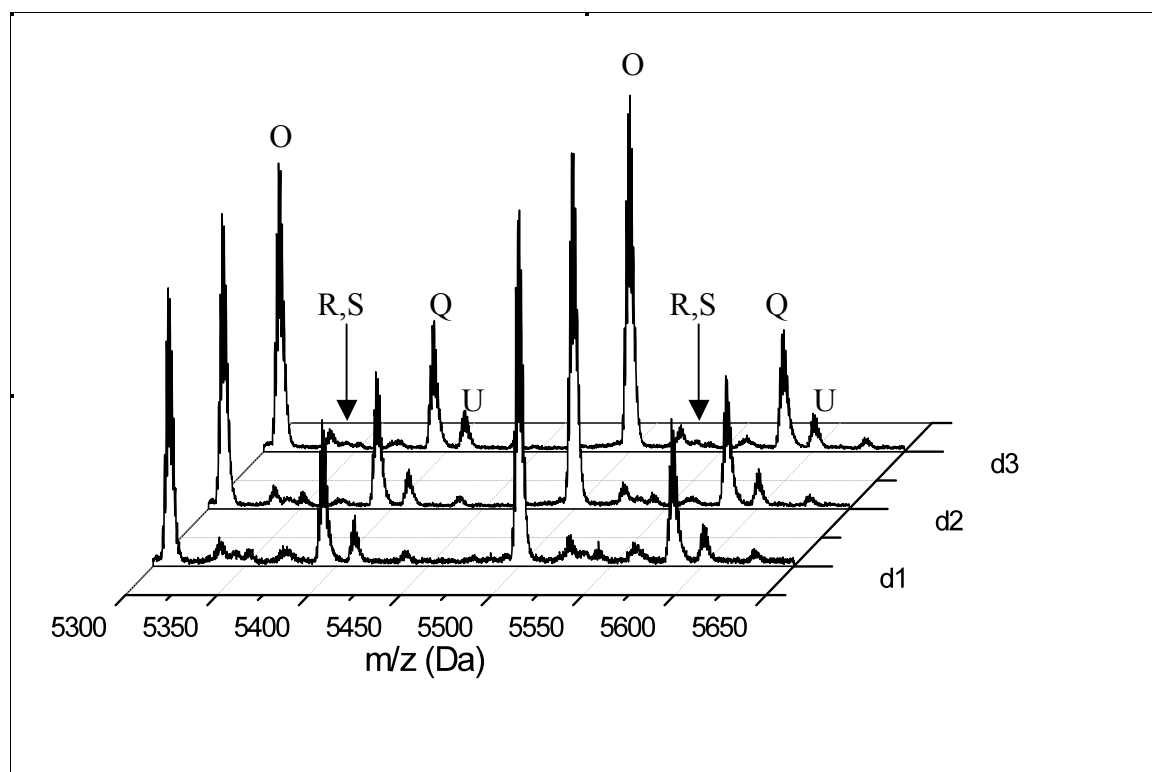


Figure SI 18: MALDI-ToF-MS spectra of samples taken from the polymerization reaction of BLT NCA at 20 °C and 0.01 mbar at different reaction times.

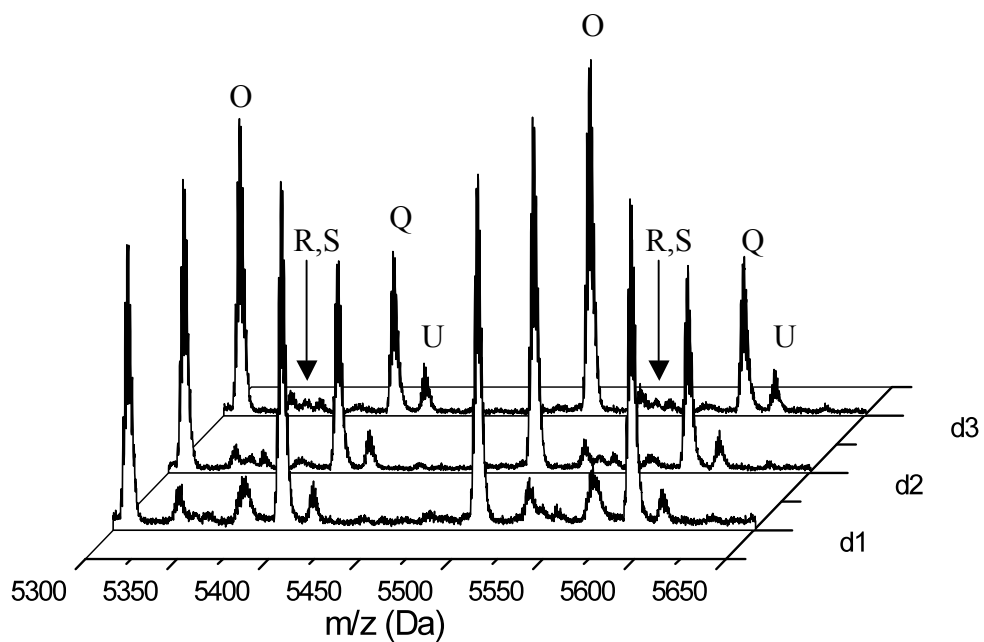


Figure SI 19: MALDI-ToF-MS spectra of samples taken from the polymerization reaction of BLT NCA at 20 °C under nitrogen at different reaction times.

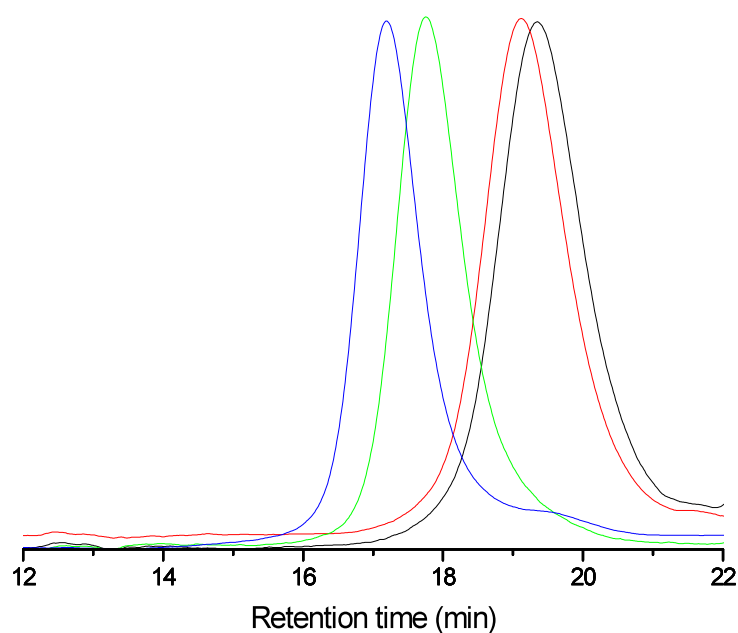


Figure SI 20: DMAC-SEC results of tetrablock $\text{PBLG}_{50}\text{-}b\text{-PAIa}_{15}\text{-}b\text{-PZLL}_{50}\text{-}b\text{-PBLA}_{40}$ copolymerization. Traces represent the sequentially extended block copolymers from right to left (entry 3 in Table 3).

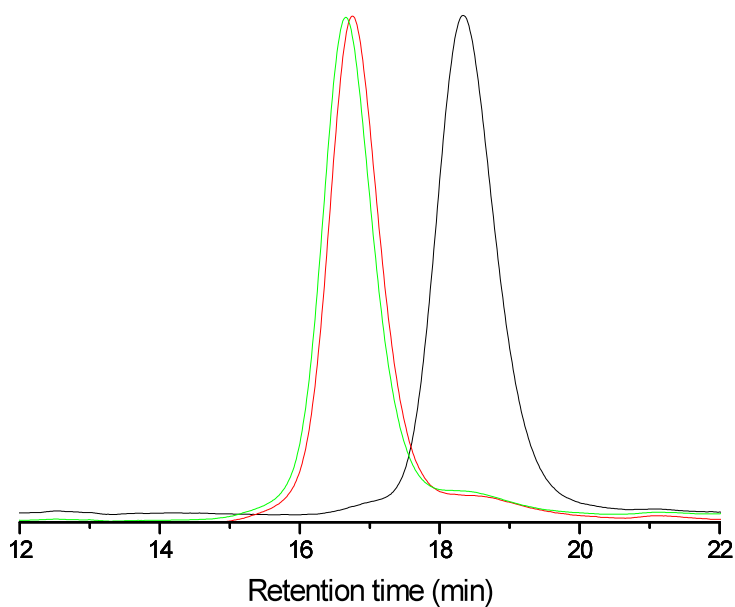


Figure SI 21: DMAC-SEC results of $\text{PBLG}_{100}\text{-}b\text{-PZLL}_{100}\text{-}b\text{-PAIa}_{20}$ triblock copolymerization. Traces represent the sequentially extended block copolymers from right to left (entry 2 in Table 3).

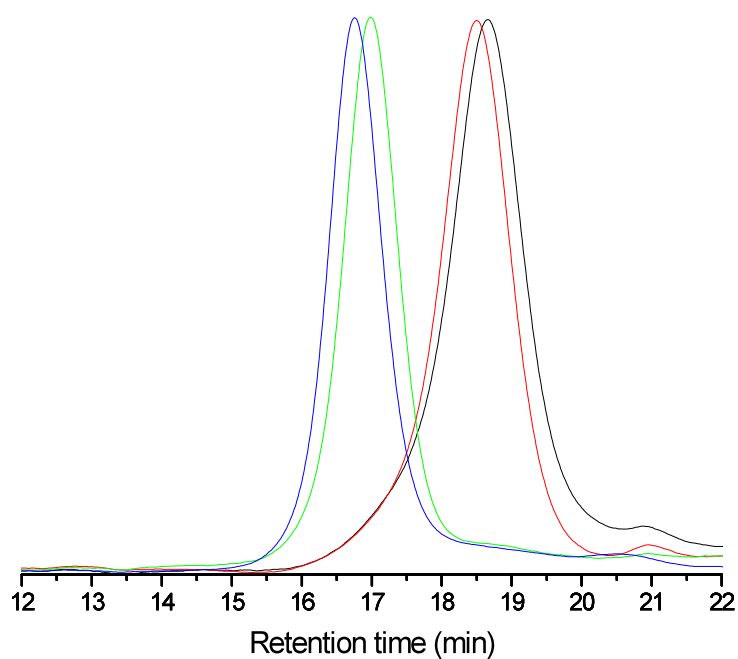


Figure SI 22: DMAc-SEC results of PBLG₁₀₀-*b*-PAla₁₅-*b*-PZLL₁₀₀-*b*-PBLA₄₀ tetra-block copolymerization. Traces represent the sequentially extended block copolymers from right to left (entry 4 in Table 3).

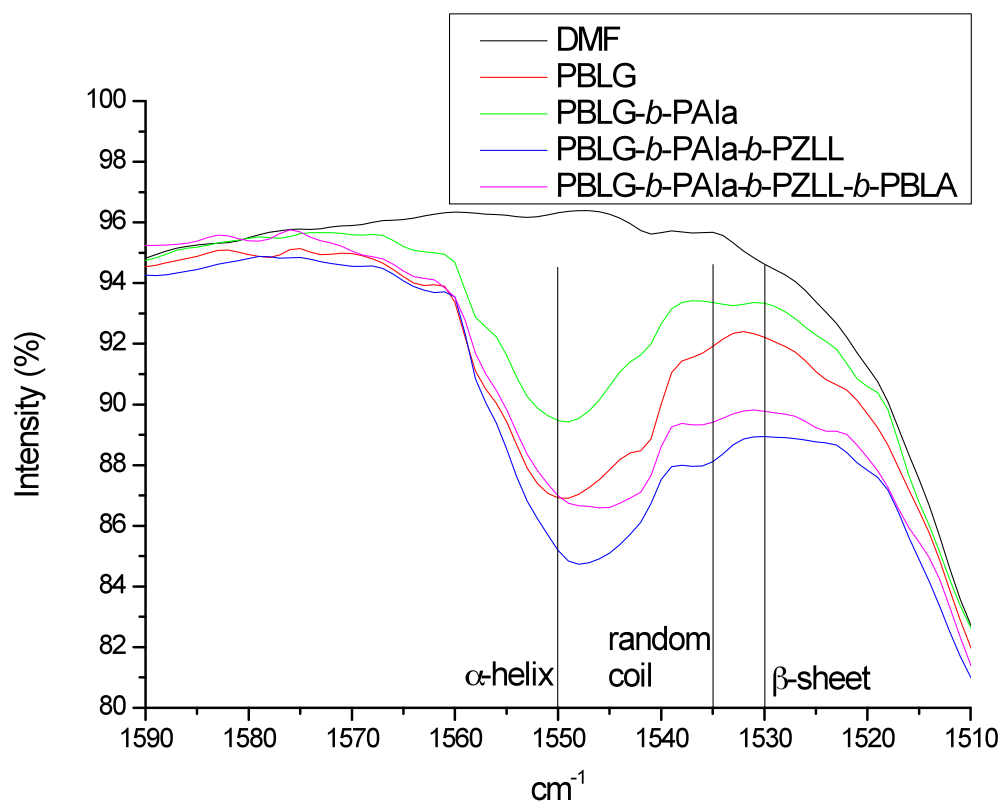


Figure SI 23: FTIR of amide II bonds of PBLG₁₀₀-*b*-PAla₁₅-*b*-PZLL₁₀₀-*b*-PBLA₄₀.