**Supporting Information**

**Cationic Ring-Opening Polymerization of Protected Oxazolidine Imines Resulting in Gradient Copolymers of Poly(2-oxazoline) and Poly(urea)**

*Meike N. Leiske,[ab] Matthias Hartlieb,[‡ab] Fabian H. Sobotta,[ab] Renzo M. Paulus,[ab] Helmar Görls,[c] Peter Bellstedt,[a] and Ulrich S. Schubert*[ab]*

*[a]Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstraße 10, 07743, Jena, Germany. E-mail: ulrich.schubert@uni-jena.de*

*[b]Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany*

*[c]Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University Jena, Humboldtstraße 8, 07743 Jena*

*‡Current address: Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry, CV4 7AL, UK.*

**Correspondence to U. S. Schubert (ulrich.schubert@uni-jena.de)*

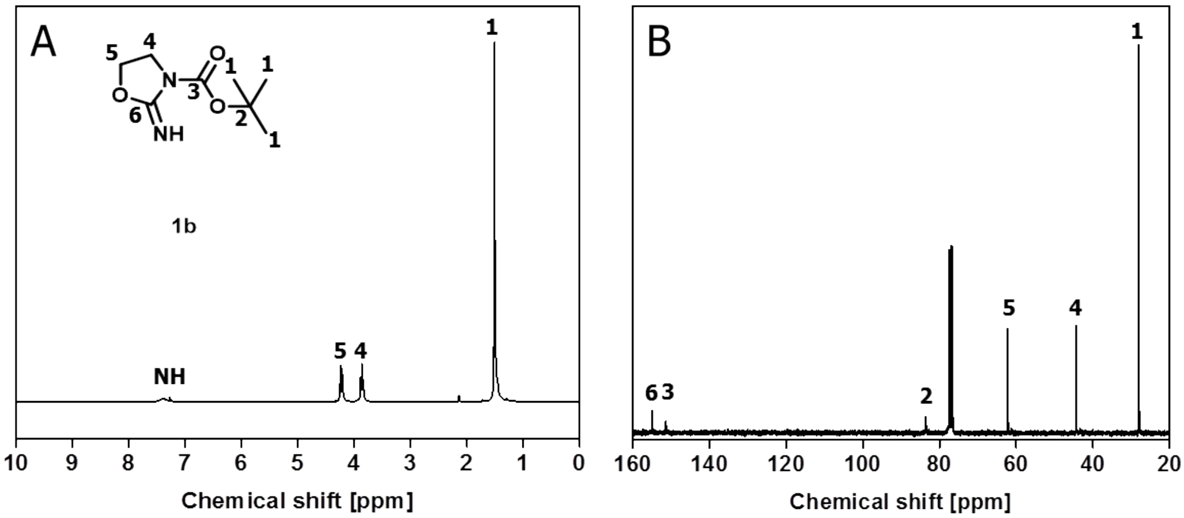



**Figure S1: A:** $^{1}$H-NMR ($CDCl_3$, 300 MHz) and **B:** $^{13}$C-NMR ($CDCl_3$, 300 MHz) of BocOI (**1b**).

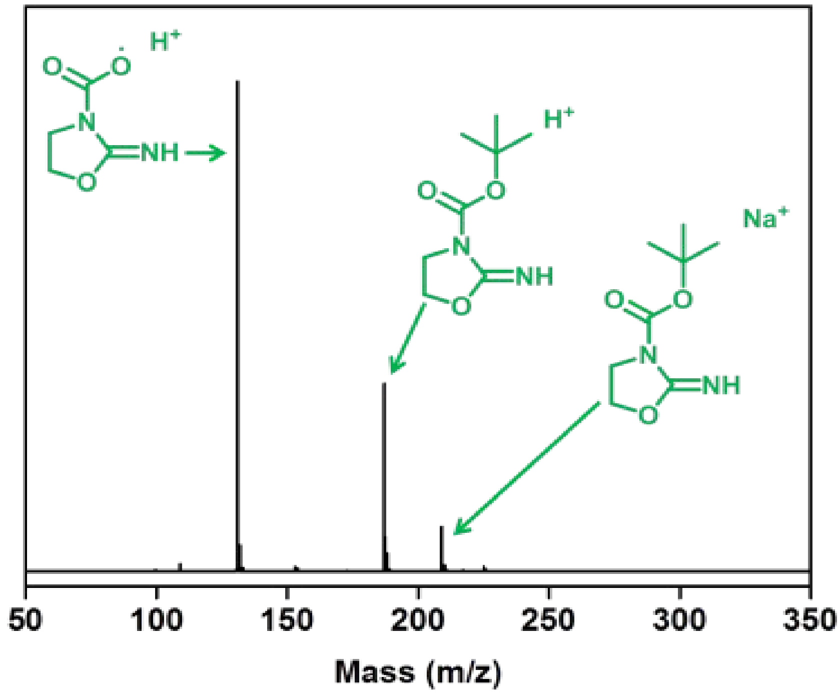



**Figure S2:** HR-ESI MS of BocOI (**1b**).

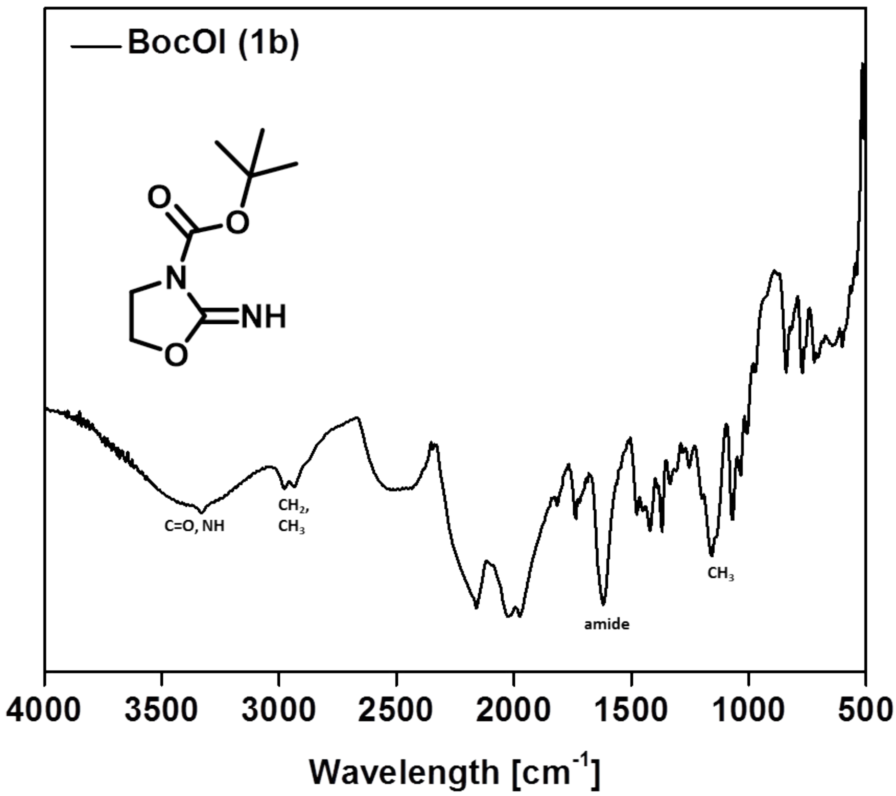
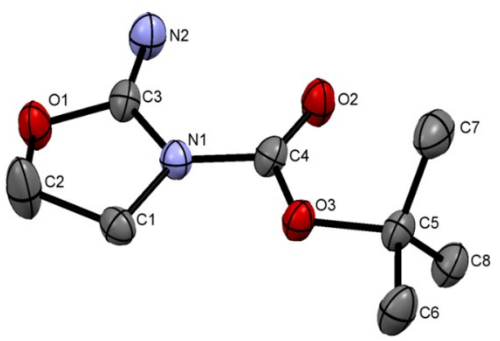



**Figure S3:** Normalized FTIR spectrum of BocOI (**1b**).

**Table S1:** Bond lengths and comparative bond angles of BocOI (**1b**) determined *via* X-ray crystal structure analysis.

| Atoms | Bond length [Å] | Atoms | Angle [°] |
|---|---|---|---|
| **O(1)-C(3)** | 1.357(3) | **C(3)-O(1)-C(2)** | 110.6(2) |
| **O(1)-C(2)** | 1.431(4) | **C(4)-O(3)-C(5)** | 120.40(19) |
| **O(2)-C(4)** | 1.210(3) | **C(4)-N(1)-C(3)** | 123.5(2) |
| **O(3)-C(4)** | 1.330(3) | **C(4)-N(1)-C(1)** | 124.4(2) |
| **O(3)-C(5)** | 1.490(3) | **C(3)-N(1)-C(1)** | 112.1(2) |
| **N(1)-C(4)** | 1.378(3) | **C(3)-N(2)-H(1N2)** | 108(2) |
| **N(1)-C(3)** | 1.401(3) | **N(1)-C(1)-C(2)** | 100.7(2) |
| **N(1)-C(1)** | 1.471(3) | **N(1)-C(1)-H(1B)** | 111.9(15) |
| **N(2)-C(3)** | 1.252(3) | **C(2)-C(1)-H(1B)** | 113.6(15) |
| **N(2)-H(1N2)** | 0.88(3) | **N(1)-C(1)-H(1A)** | 108.0(17) |
| **C(1)-C(2)** | 1.499(4) | **C(2)-C(1)-H(1A)** | 115.7(17) |
| **C(1)-H(1B)** | 0.99(3) | **H(1B)-C(1)-H(1A)** | 107(2) |
| **C(1)-H(1A)** | 0.97(3) | **O(1)-C(2)-C(1)** | 107.1(2) |
| **C(2)-H(2B)** | 0.91(4) | **O(1)-C(2)-H(2B)** | 112(3) |
| **C(2)-H(2A)** | 1.07(5) | **C(1)-C(2)-H(2B)** | 117(3) |
| **C(5)-C(7)** | 1.511(4) | **O(1)-C(2)-H(2A)** | 108(3) |
| **C(5)-C(8)** | 1.517(4) | **C(1)-C(2)-H(2A)** | 105(2) |
| **C(5)-C(6)** | 1.517(4) | **H(2B)-C(2)-H(2A)** | 108(3) |
| **C(6)-H(6C)** | 1.01(3) | **N(2)-C(3)-O(1)** | 120.7(2) |
| **C(6)-H(6B)** | 0.98(3) | **N(2)-C(3)-N(1)** | 132.1(2) |
| **C(6)-H(6A)** | 0.94(3) | **O(1)-C(3)-N(1)** | 107.2(2) |
| **C(7)-H(7C)** | 0.96(3) | **O(2)-C(4)-O(3)** | 127.2(2) |
| **C(7)-H(7B)** | 0.92(4) | **O(2)-C(4)-N(1)** | 123.8(2) |
| **C(7)-H(7A)** | 0.97(4) | **O(3)-C(4)-N(1)** | 109.0(2) |
| **C(8)-H(8C)** | 0.99(3) | **O(3)-C(5)-C(7)** | 109.3(2) |
| **C(8)-H(8B)** | 1.00(3) | **O(3)-C(5)-C(8)** | 109.7(2) |
| **C(8)-H(8A)** | 0.95(3) | **C(7)-C(5)-C(8)** | 113.0(3) |
| | | **O(3)-C(5)-C(6)** | 102.0(2) |
| | | **C(7)-C(5)-C(6)** | 111.4(3) |
| | | **C(8)-C(5)-C(6)** | 110.9(2) |
| | | **C(5)-C(6)-H(6C)** | 105.6(19) |
| | | **C(5)-C(6)-H(6B)** | 111.0(18) |
| | | **H(6C)-C(6)-H(6B)** | 110(3) |
| | | **C(5)-C(6)-H(6A)** | 108(2) |
| | | **H(6C)-C(6)-H(6A)** | 116(3) |
| | | **H(6B)-C(6)-H(6A)** | 106(3) |
| | | **C(5)-C(7)-H(7C)** | 111(2) |
| | | **C(5)-C(7)-H(7B)** | 108(2) |
| | | **H(7C)-C(7)-H(7B)** | 110(3) |
| | | **C(5)-C(7)-H(7A)** | 111(2) |
| | | **H(7C)-C(7)-H(7A)** | 110(3) |
| | | **H(7B)-C(7)-H(7A)** | 107(3) |
| | | **C(5)-C(8)-H(8C)** | 111.9(17) |



| | |
|---|---|
| **C(5)-C(8)-H(8B)** | 113.6(19) |
| **H(8C)-C(8)-H(8B)** | 106(3) |
| **C(5)-C(8)-H(8A)** | 109(2) |
| **H(8C)-C(8)-H(8A)** | 106(3) |
| **H(8B)-C(8)-H(8A)** | 110(3) |

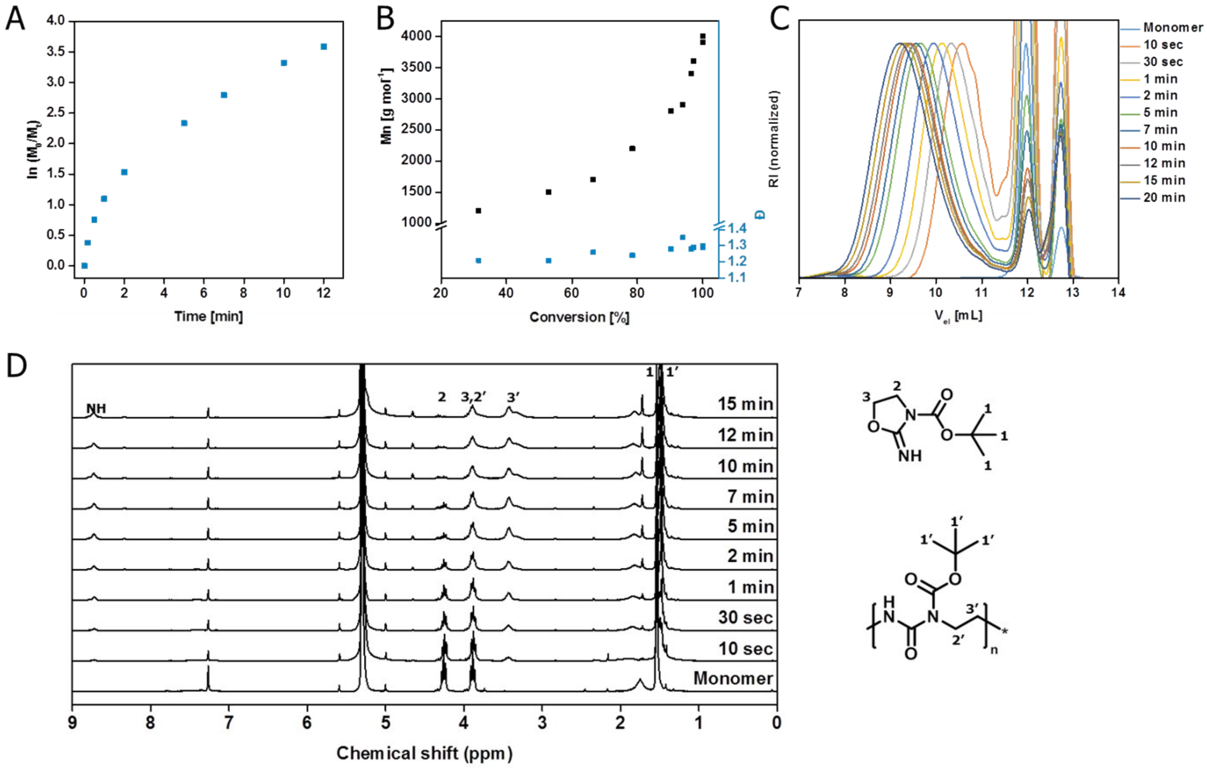



**Figure S4:** Kinetic studies of BocOI ([M]/[I] = 60) in $CH_2Cl_2$ at 140 °C. **A:** Time-dependent polymerization kinetics calculated by the monomer conversion obtained from the GC-analytics.. **B:** Increase in molar mass and the stability of Đ dependent on the monomer conversion. **C:** SEC-traces ($CHCl_3$-*i*-PrOH-TEA, PS-cal.; 1st system peak after 12 mL) of the reaction mixture after several polymerization times. **D:** $^1$H-NMR (300 MHz, $CDCl_3$) after several polymerization times.

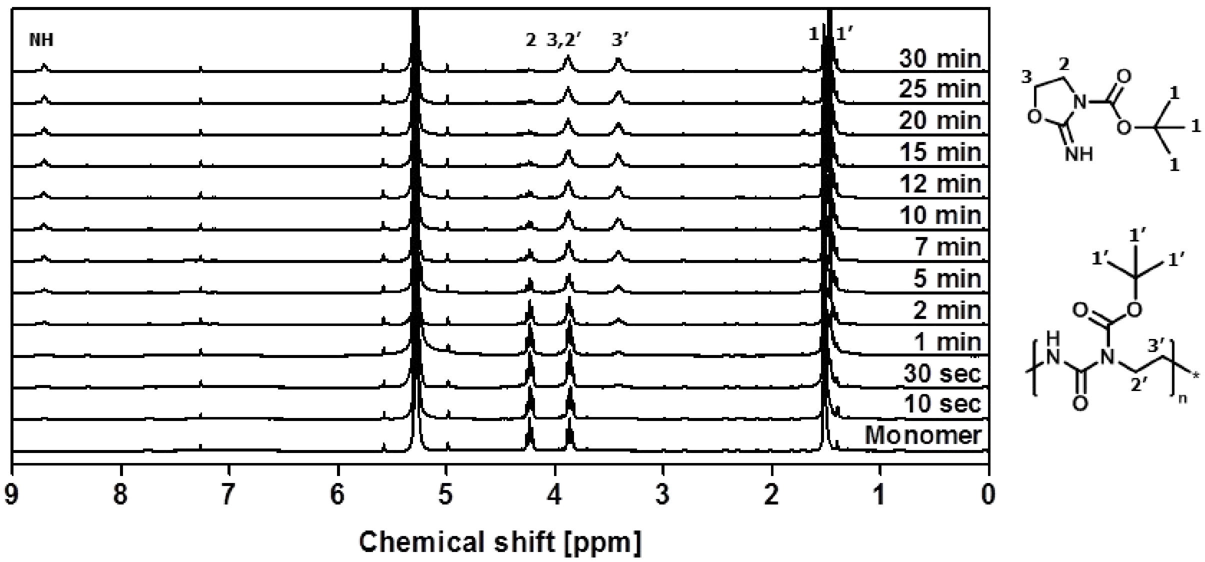



**Figure S5:** Kinetic studies of BocOI in $CH_2Cl_2$ at 100 °C showing the $^1$H-NMR (300 MHz, $CDCl_3$) shifts recorded at RT.

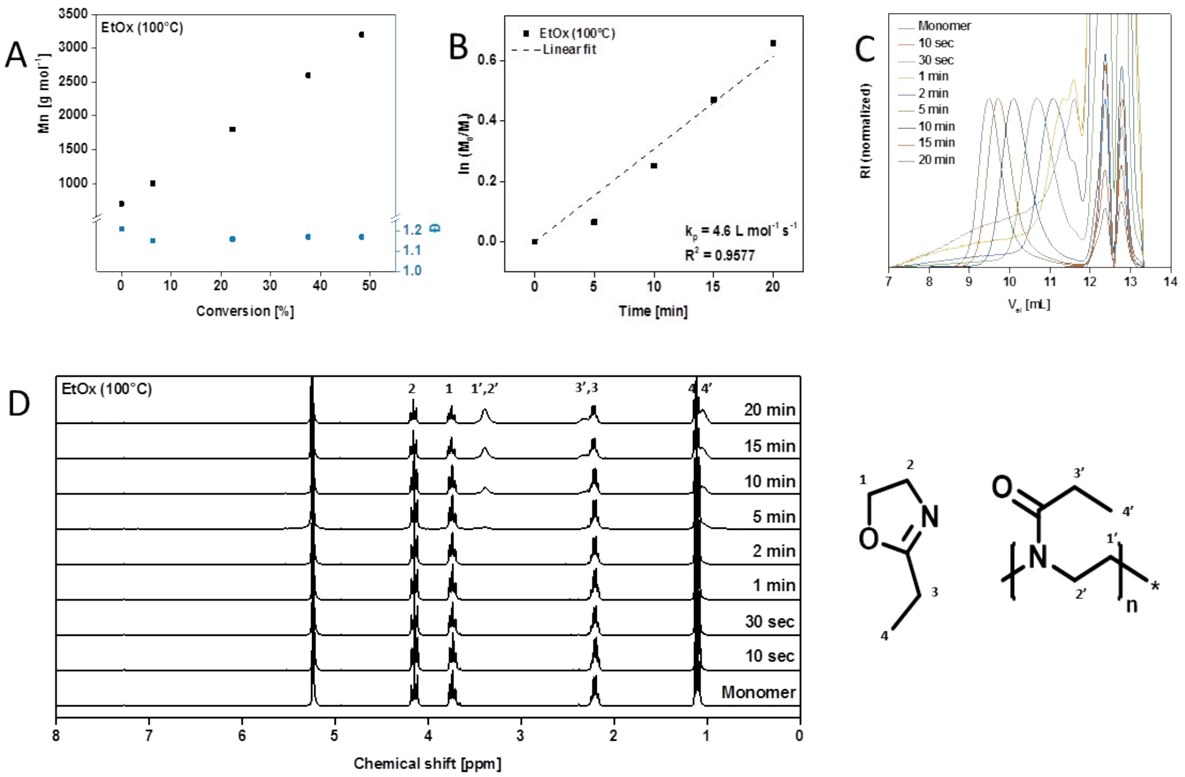



**Figure S6:** Kinetic studies of EtOx ([M]/[I] = 60) in $CH_2Cl_2$ at 100 °C showing **A:** The increase in molar mass and the stability of Đ dependent on the monomer conversion. **B:** The time-dependent polymerization kinetics calculated by the monomer conversion obtained from the GC-analytics. **C:** The SEC-traces ($CHCl_3$-*i*-PrOH-TEA, PS-cal.; 1st system peak after 12 mL). **D:** The $^1$H-NMR shifts ($CDCl_3$, 300 MHz) recorded at RT.

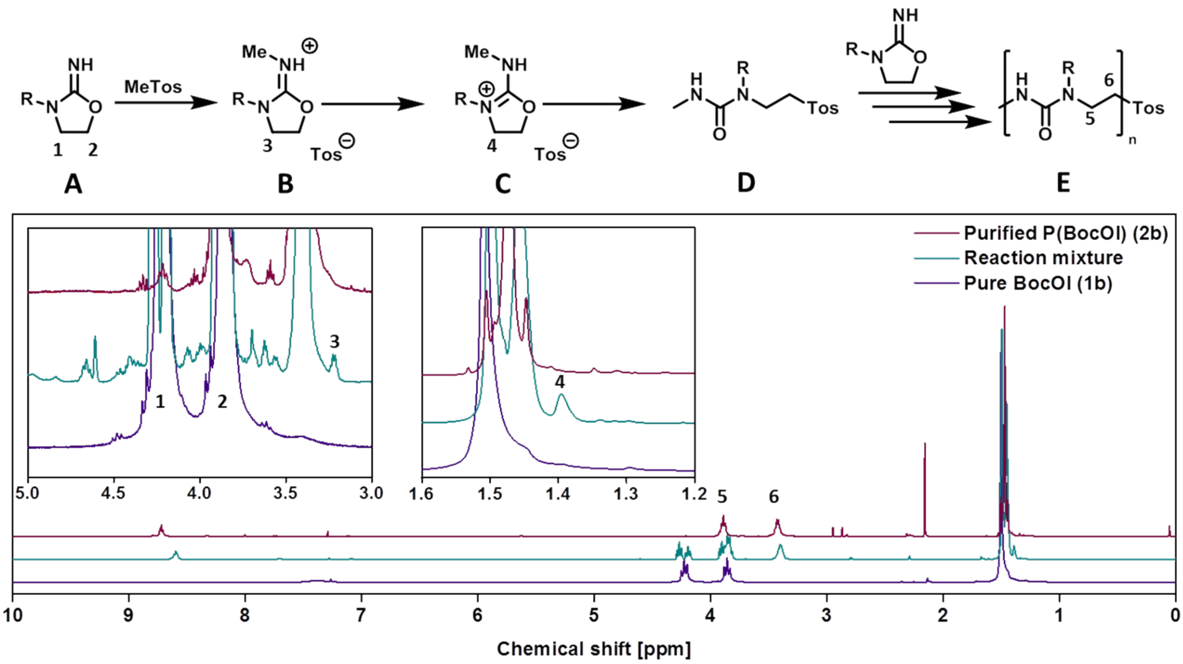



**Figure S7:** $^{1}$H-NMR ($CDCl_3$, 300 MHz) of the BocOI, the CROP of BocOI initiated by MeTos and the purified P(BocOI), showing the active species during polymerization; R = Boc-protection group.

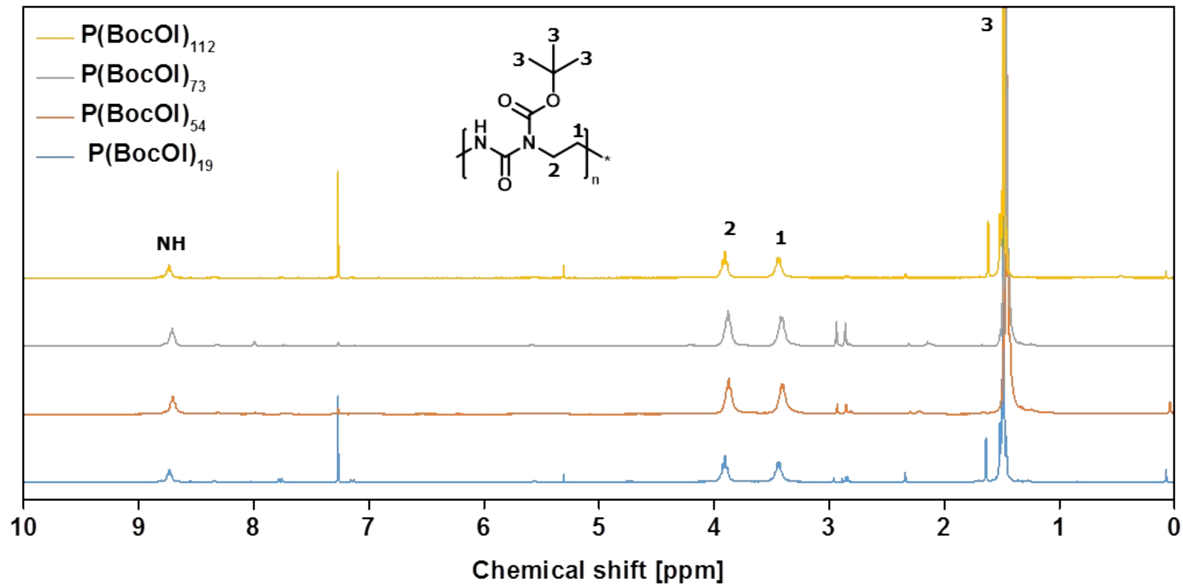



**Figure S8:** $^{1}$H-NMR ($CDCl_3$, 300 MHz) of the purified $P(BocOI)_n$ precursors (**2a-d**).

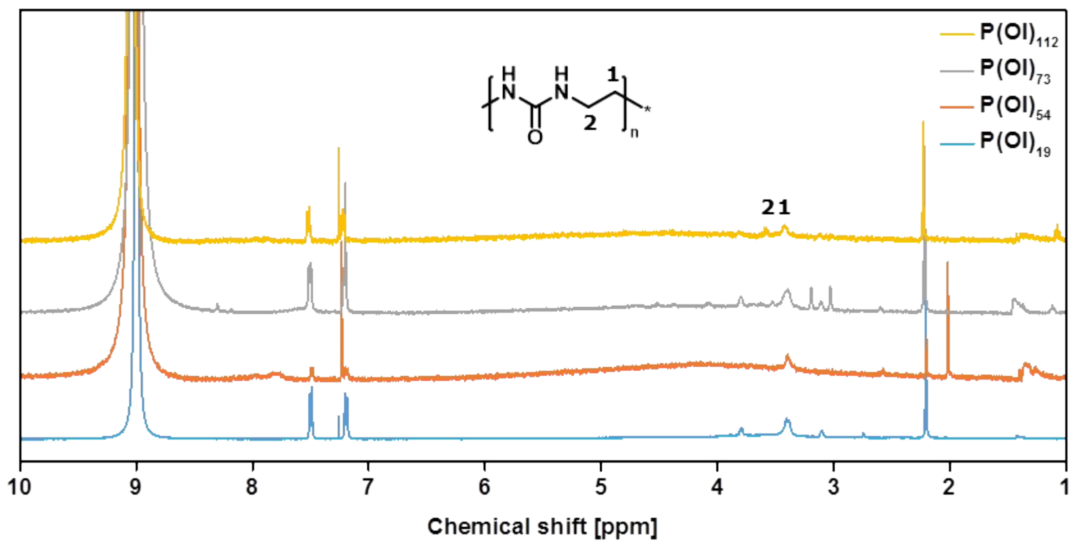



**Figure S9**: $^{1}$H-NMR (35% DCl in $D_2O$, 300 MHz) of the purified $P(OI)_n$ (**3a-d**).

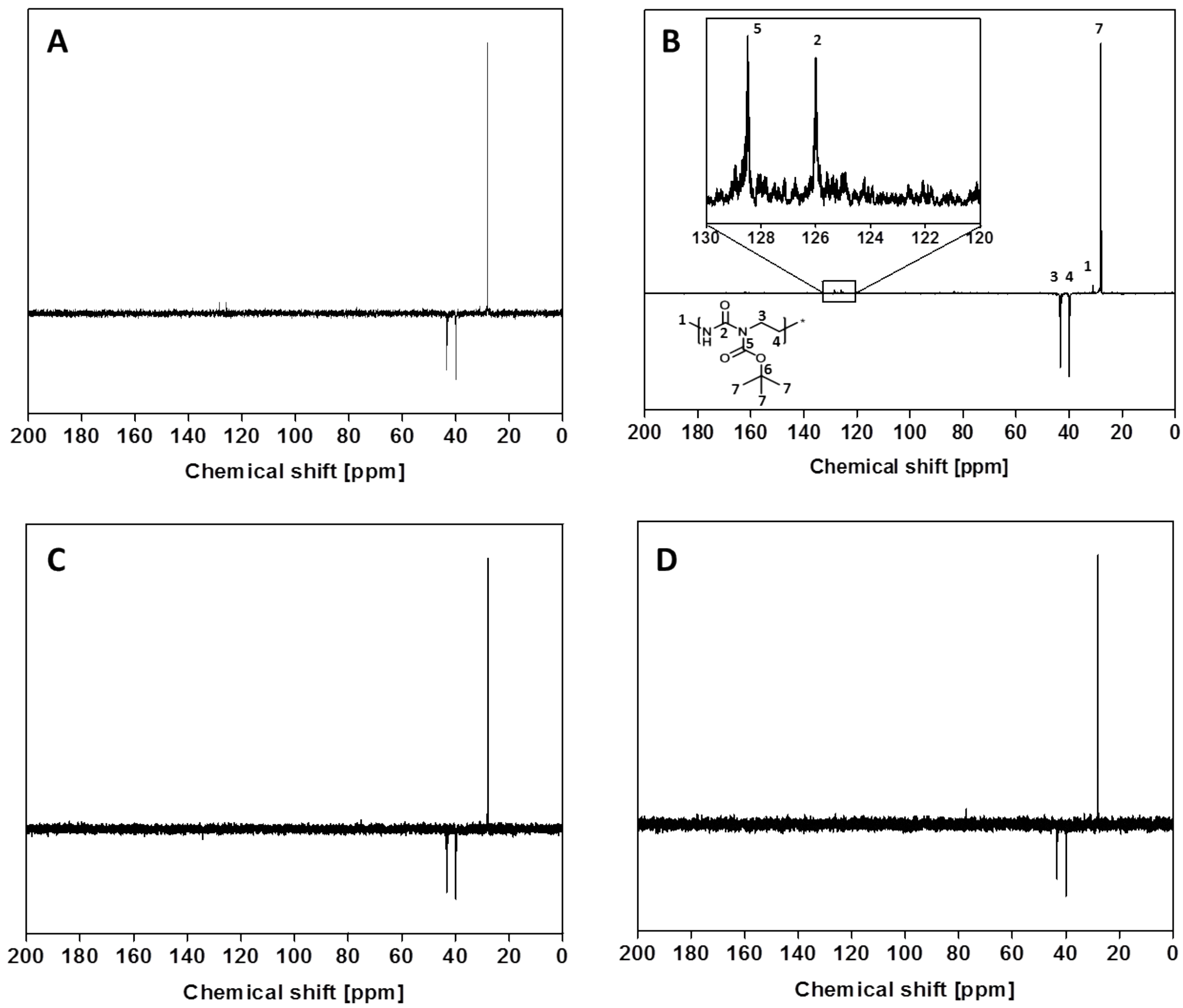



**Figure S10:** $^{13}$C-NMR ($CDCl_3$, 300 MHz) spectra of the purified $P(BocOI)_n$. **A: 2a. B: 2b. C: 2c. D: 2d.**

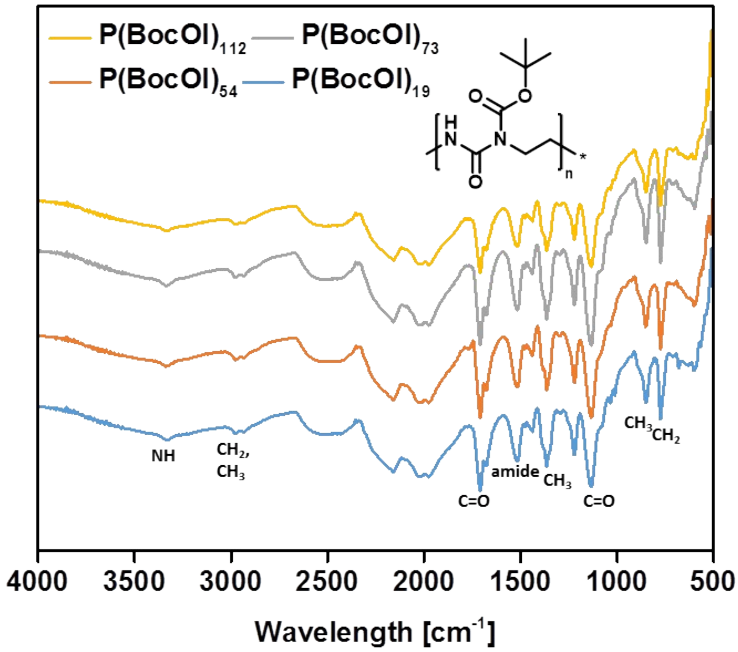



**Figure S11:** Normalized FTIR spectra of the purified $P(BocOI)_n$ precursors (**2a-d**).

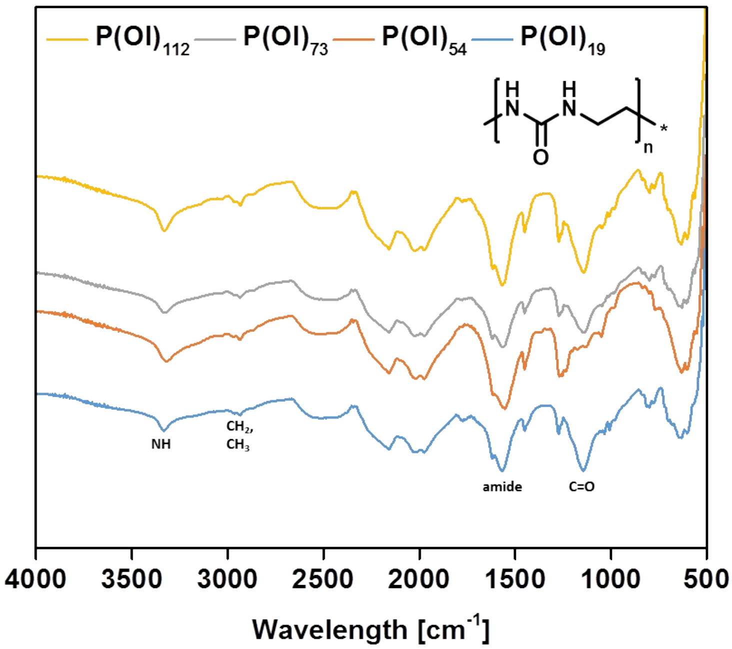



**Figure S12:** Normalized FTIR spectra of the purified $P(OI)_n$ (**3a-d**).

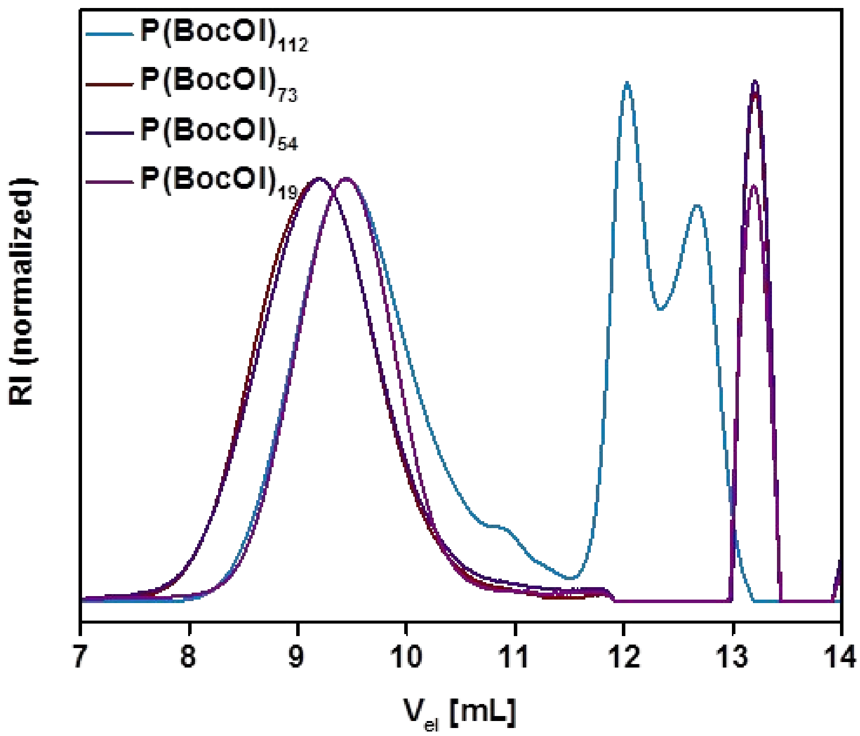



**Figure S13:** SEC-traces ($CHCl_3$-*i*-PrOH, PS-cal.; 1st system peak after 12 mL) of the purified Boc-protected homopolymer precursors (**2a-d**)

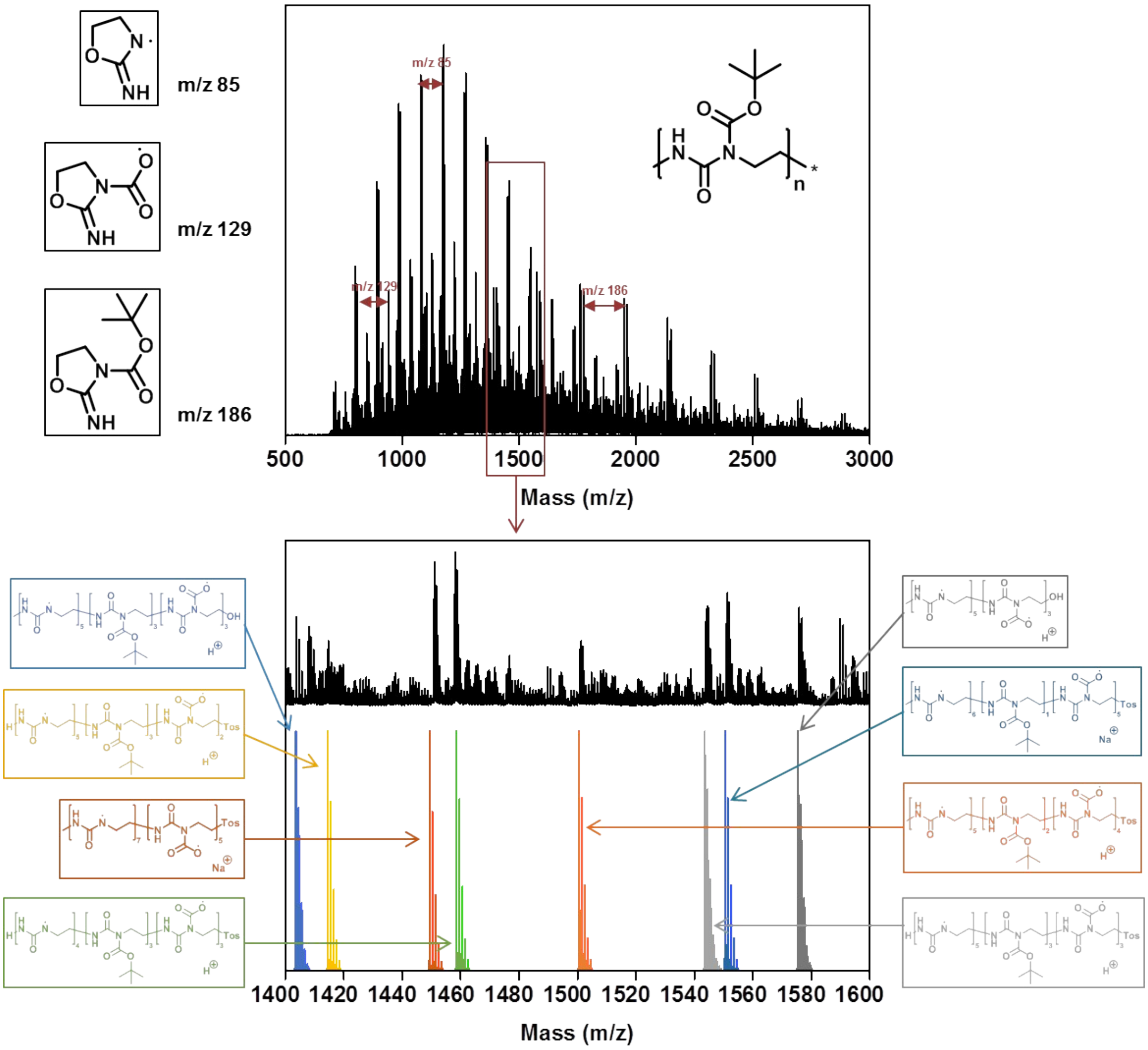



**Figure S14:** ESI-MS of P(BocOI)$_{19}$ (**2a**).

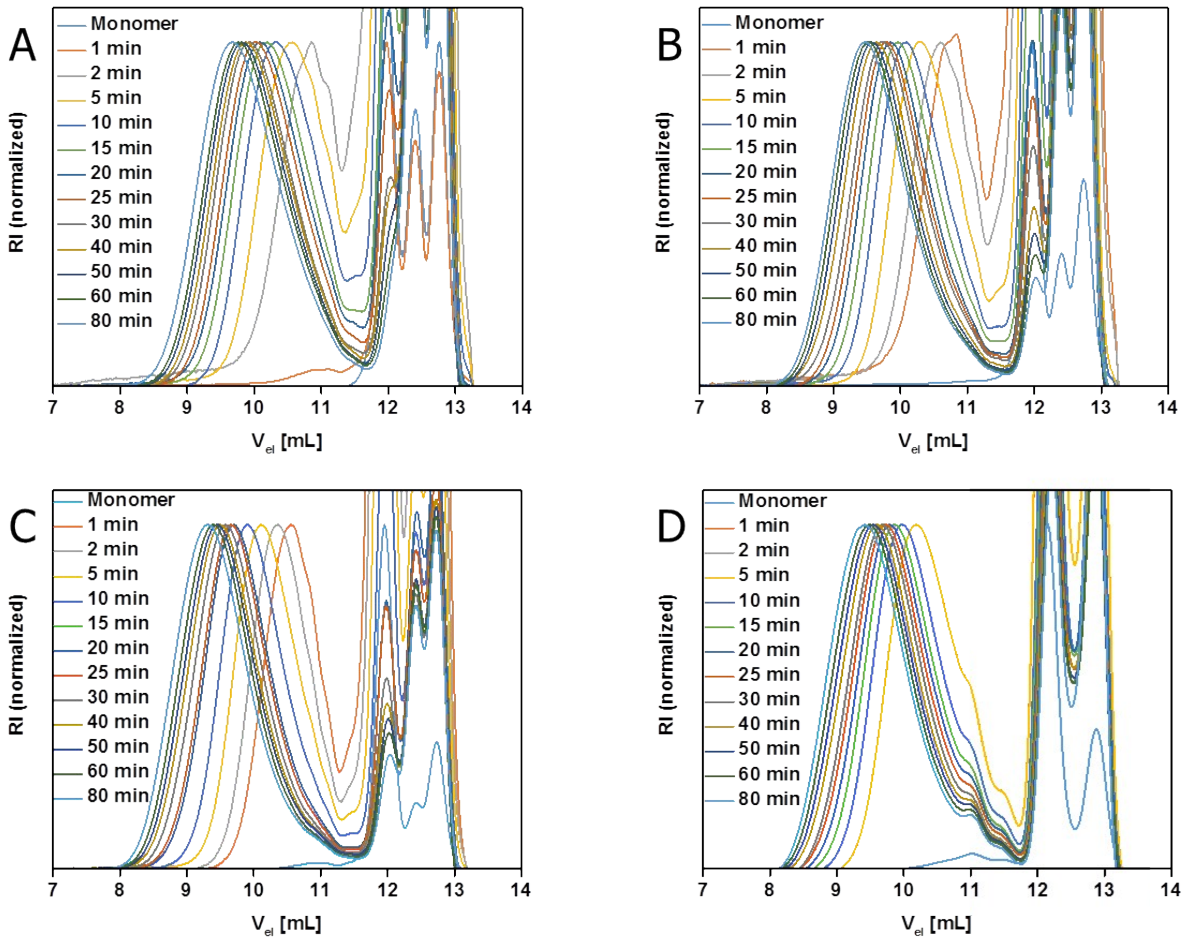



**Figure S15:** SEC-traces ($CHCl_3$-*i*-PrOH, PS-cal.; 1st system peak after 12 mL) of time dependent P(BocOI$_n$-*co*-EtOx$_m$) kinetics in $CH_2Cl_2$ at 100 °C bearing different monomer ratios (**A**: 20% BocOI, **B**: 40% BocOI, **C**: 60% BocOI, **D**: 80% BocOI).

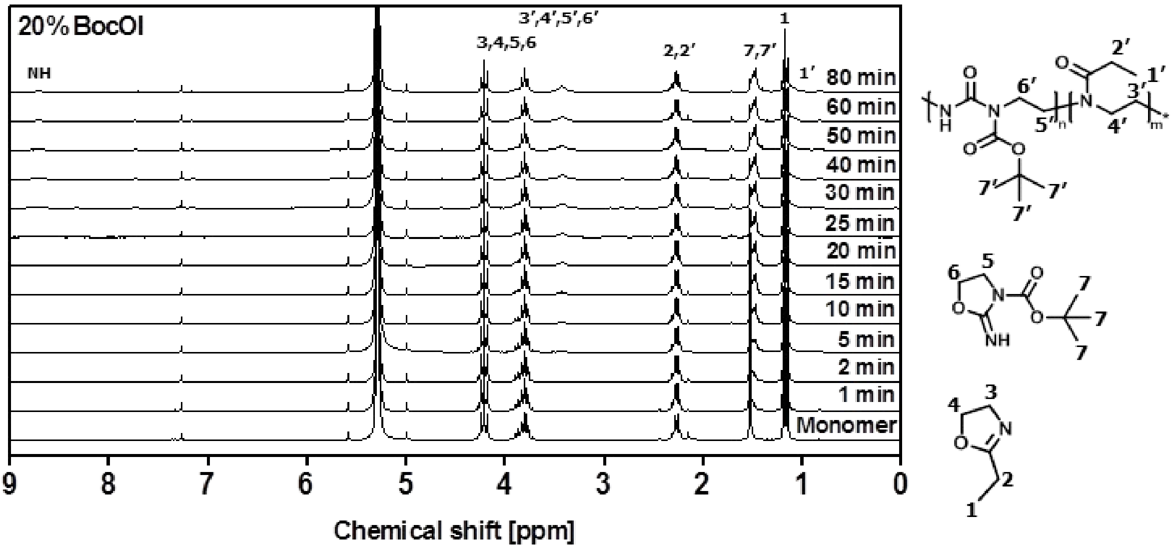



**Figure S16:** $^1$H-NMR shifts ($CDCl_3$, 300 MHz) of time dependent P(BocOI-*co*-EtOx) kinetics in $CH_2Cl_2$ at 100 °C with [M]/[I] = 60 aiming 20% BocOI, recorded at RT.

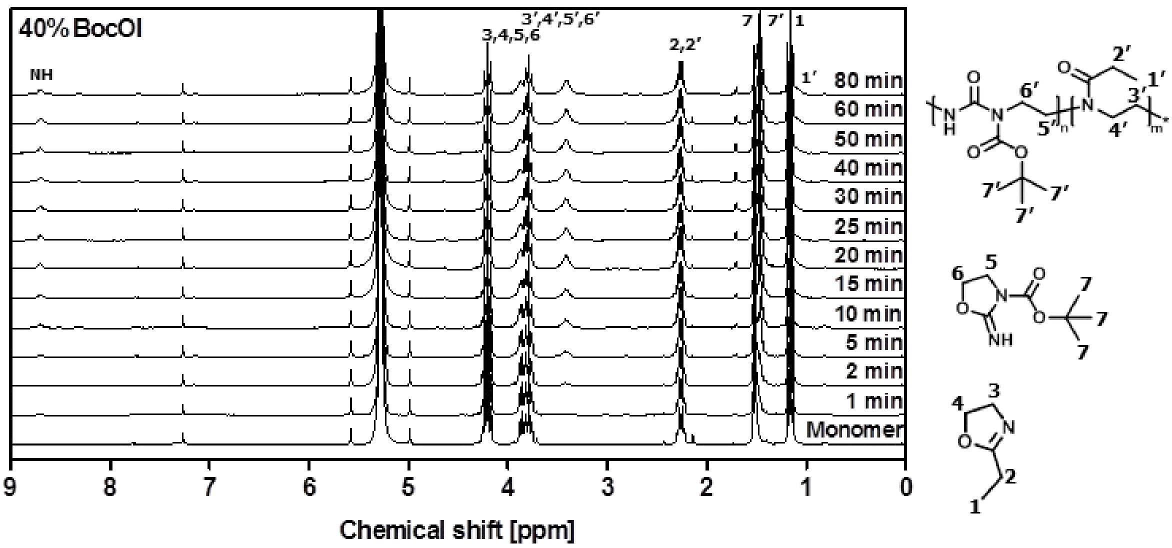



**Figure S17:** $^1$H-NMR shifts ($CDCl_3$, 300 MHz) of time dependent P(BocOI-*co*-EtOx) kinetics in $CH_2Cl_2$ at 100 °C with [M]/[I] = 60 aiming 40% BocOI, recorded at RT.

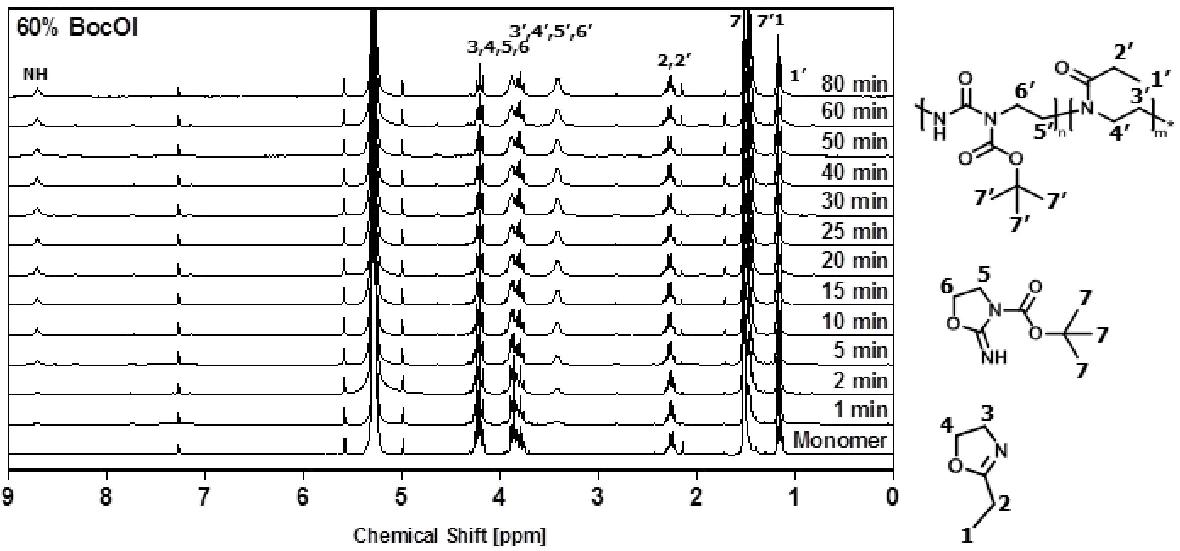



**Figure S18:** $^{1}$H-NMR shifts ($CDCl_3$, 300 MHz) of time dependent P(BocOI-*co*-EtOx) kinetics in $CH_2Cl_2$ at 100 °C with [M]/[I] = 60 aiming 60% BocOI, recorded at RT.

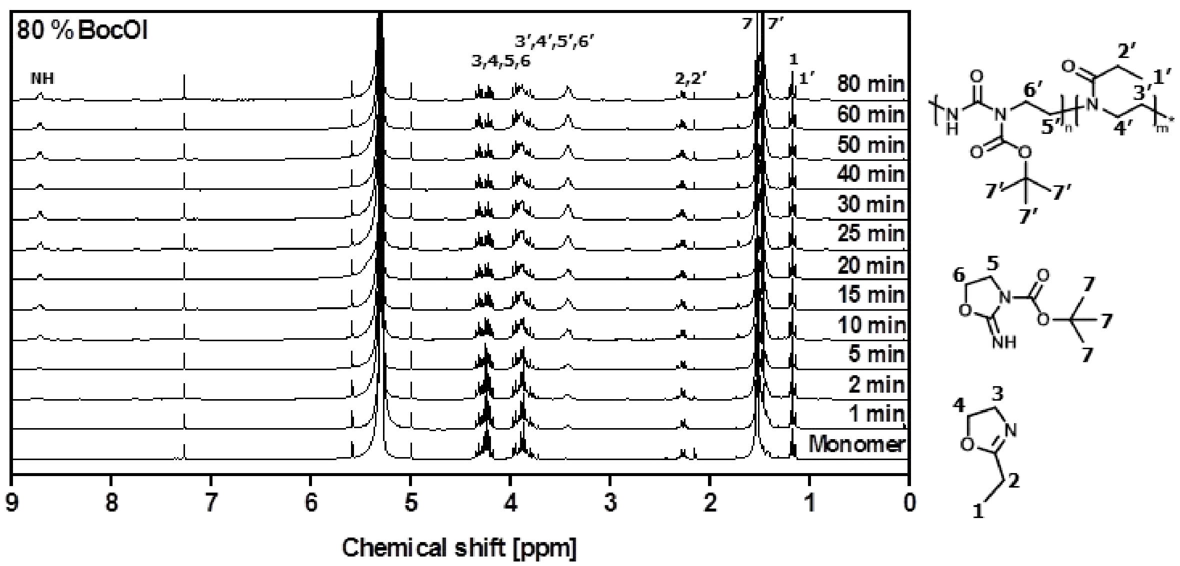



**Figure S19:** $^{1}$H-NMR shifts ($CDCl_3$, 300 MHz) of time dependent P(BocOI-*co*-EtOx) kinetics in $CH_2Cl_2$ at 100 °C with [M]/[I] = 60 aiming 80% BocOI, recorded at RT.

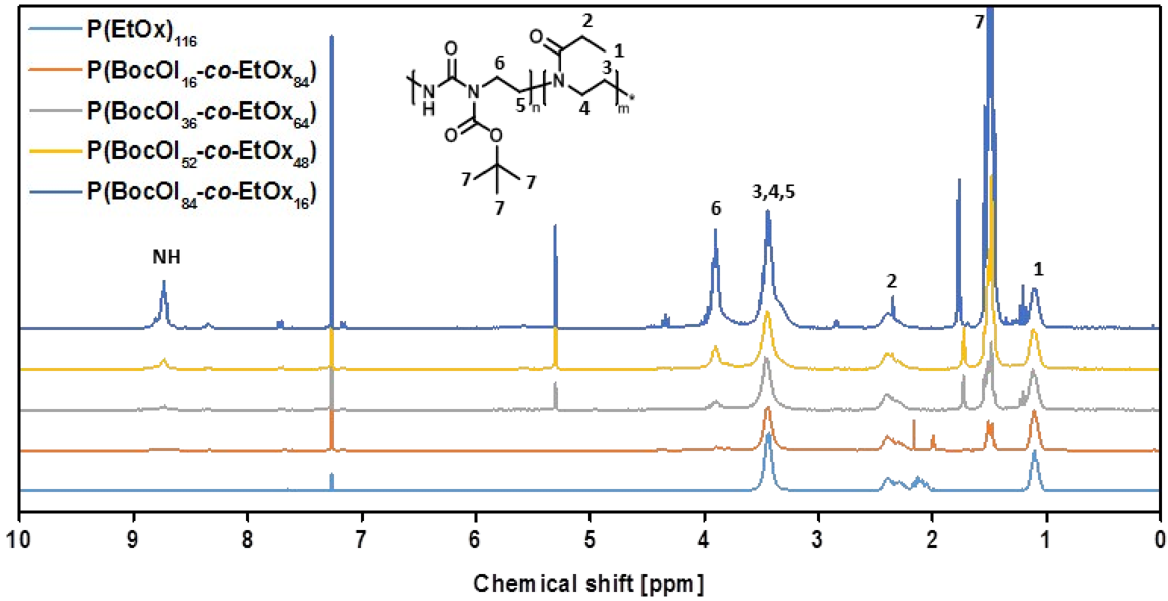



**Figure S20:** $^{1}$H-NMR ($CDCl_3$, 300 MHz) of the purified P(BocOI$_n$-*co*-EtOx$_m$) (**4a-d**) precursors and P(EtOx)$_{116}$ (**6**).

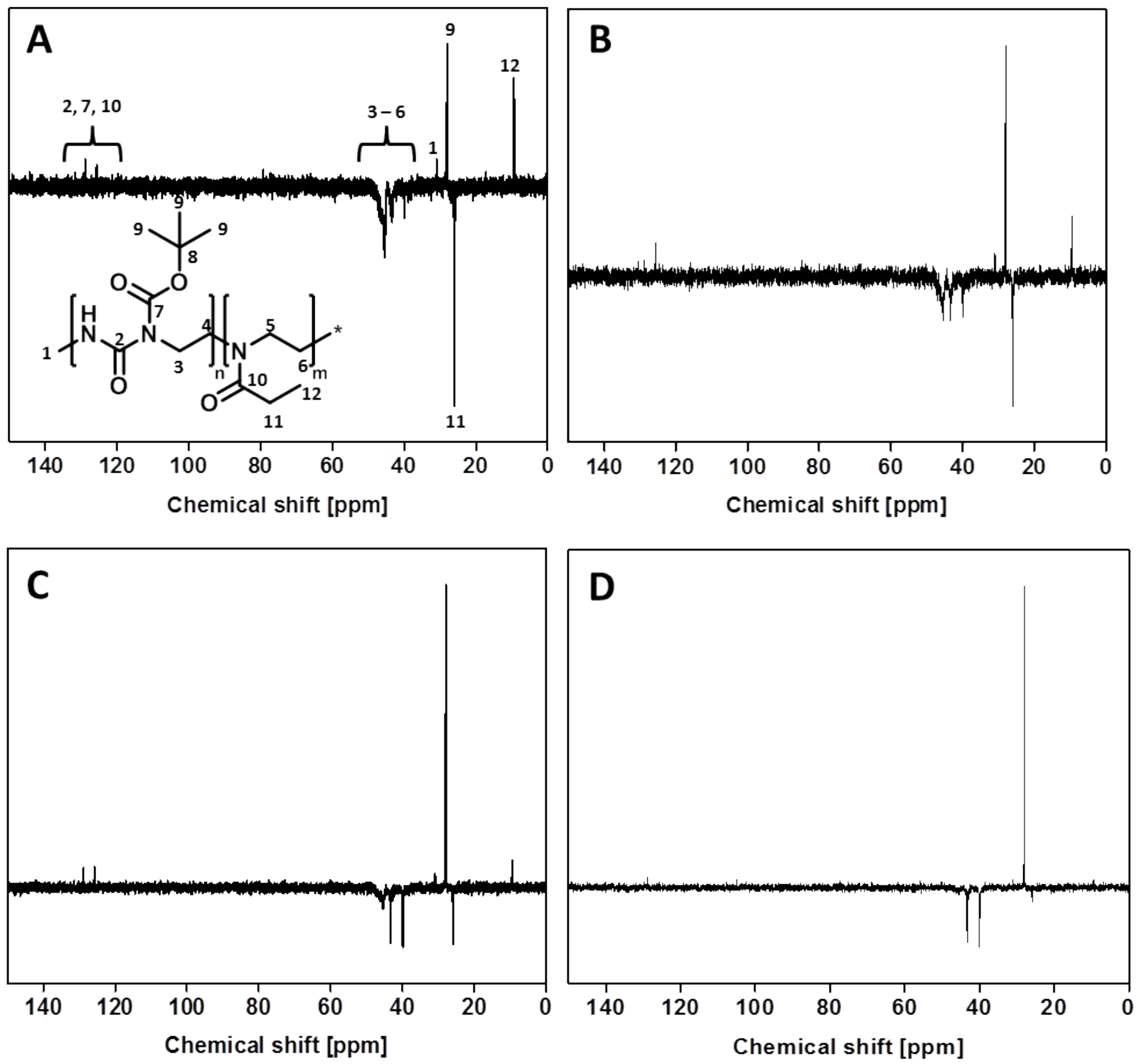



**Figure S21:** $^{13}$C-NMR ($CDCl_3$, 300 MHz) spectra of the purified P(BocOI$_n$-*co*-EtOx$_m$). **A: 4a. B: 4b. C: 4c. D: 4d.**

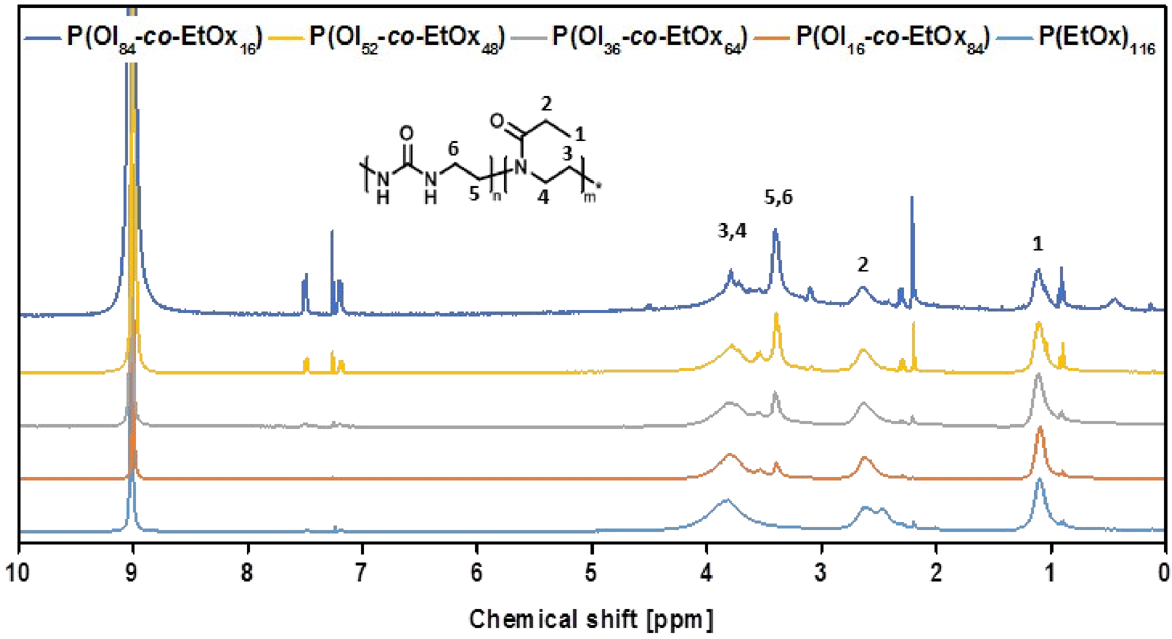



**Figure S22:** $^1$H-NMR (35% DCl in $D_2O$, $CDCl_3$-standard, 300 MHz) of P($OI_n$-*co*-$EtOx_m$) (**5a-d**) and P$(EtOx)_{116}$ (**6**).

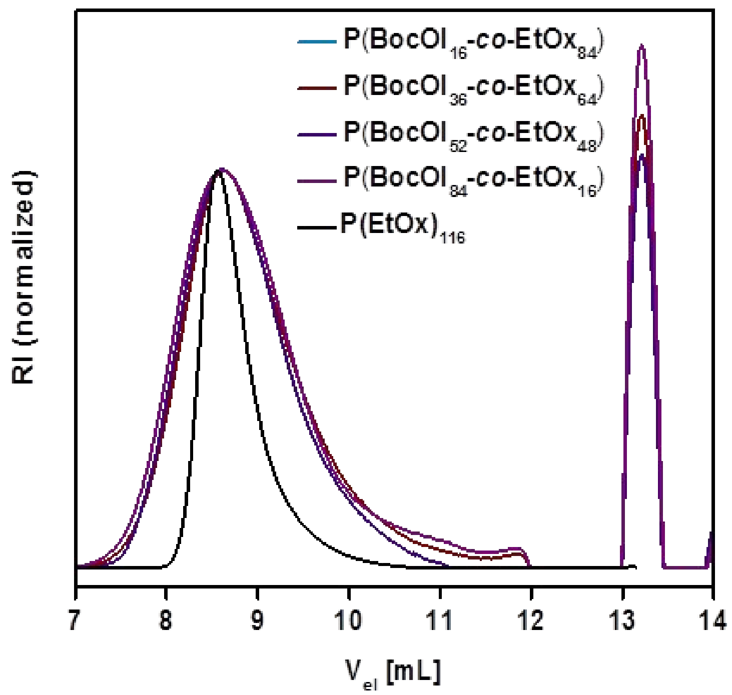



**Figure S23:** SEC-traces ($CHCl_3$-*i*-PrOH, PS-cal.; 1st system peak after 12 mL) of the purified Boc-protected copolymer precursors (**4a-d**).

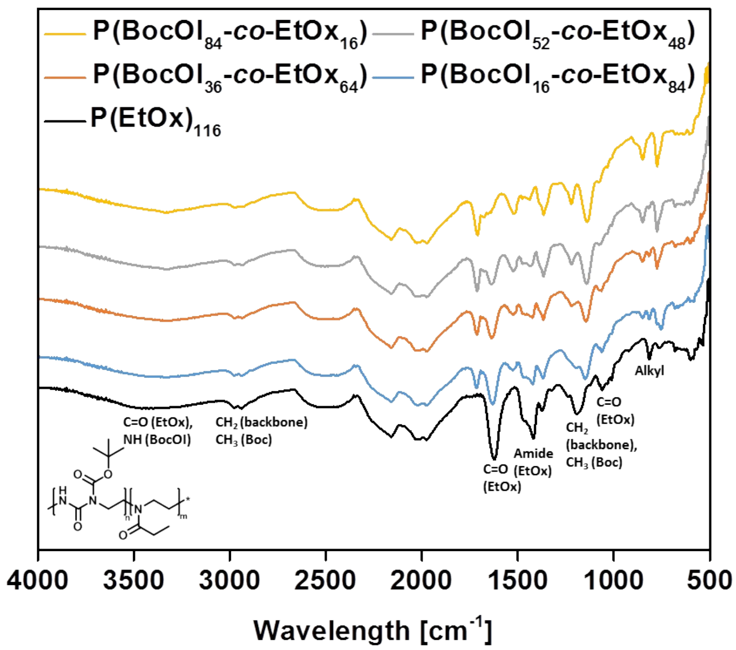



**Figure S24**: Normalized FTIR spectra of the purified P(BocOI$_n$-*co*-EtOx$_m$) precursors (**4a-d**) and P(EtOx)$_{116}$ (**6**).

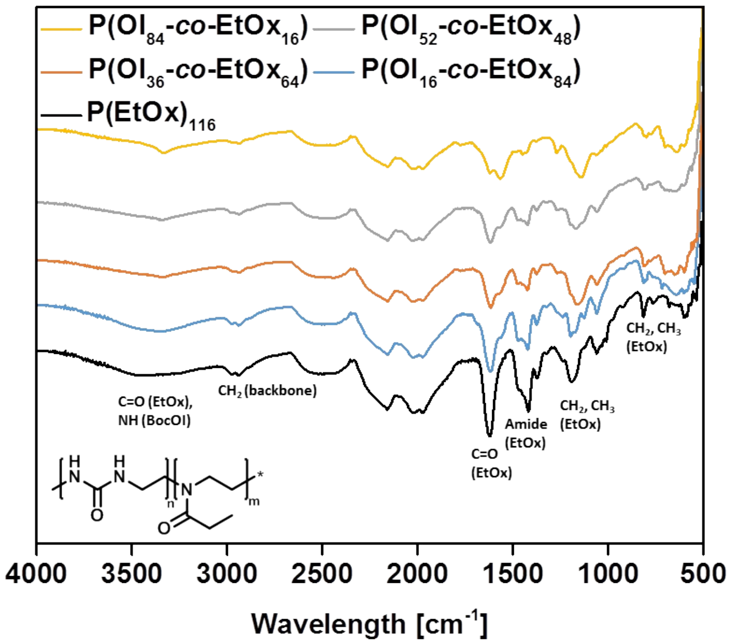



**Figure S25**: Normalized FTIR spectra of the purified P(OI$_n$-*co*-EtOx$_m$) (**5a-d**) and P(EtOx)$_{116}$ (**6**).

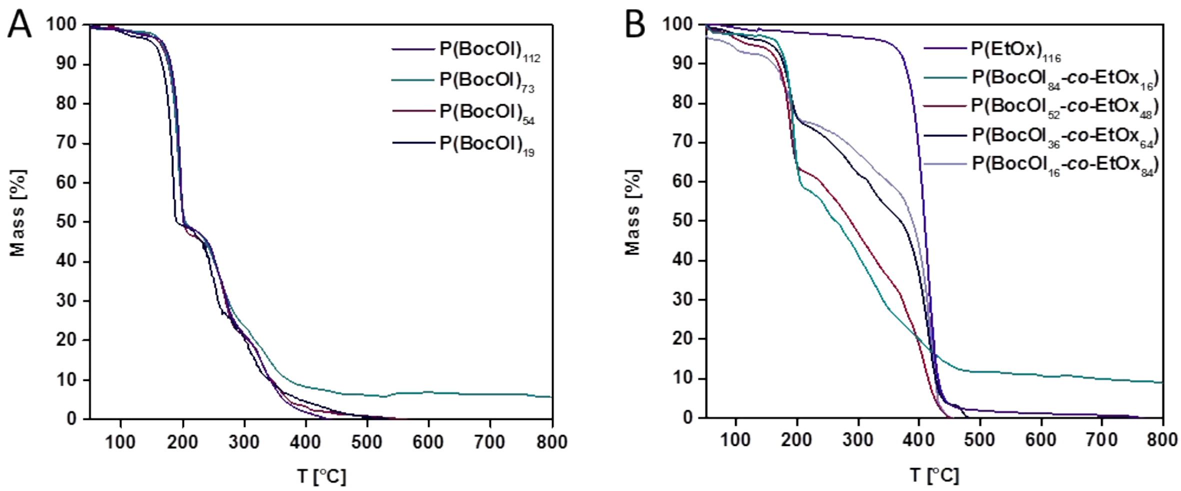



**Figure S26:** TGA traces of the Boc protected A: homopolymers (2a-d) and B: copolymers (**4a-d**) and P(EtOx)$_{116}$ (**6**).

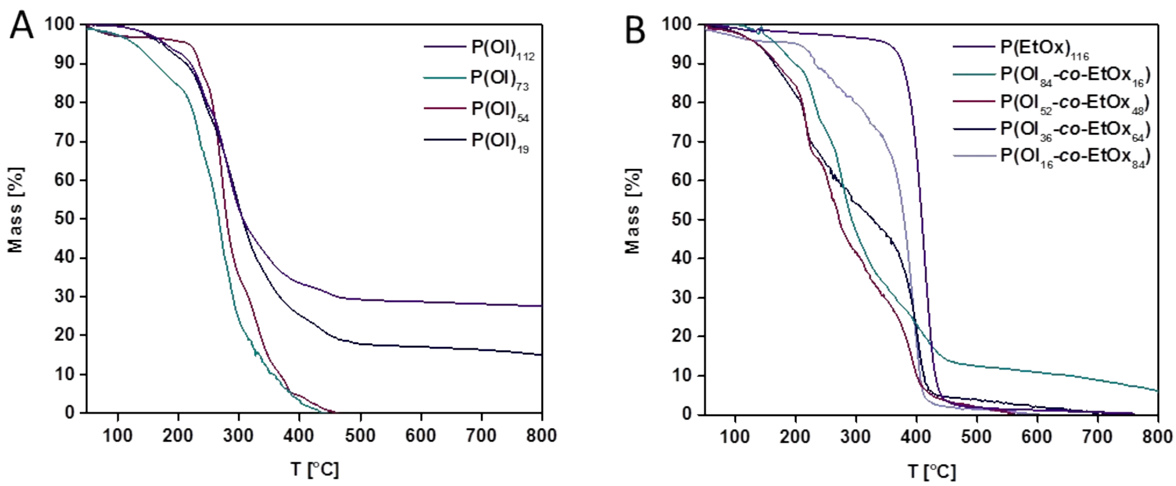



**Figure S27:** TGA traces of the deprotected **A:** homopolymers (**3a-d**) and **B:** copolymers (**5a-d**) and $P(EtOx)_{116}$ (**6**).

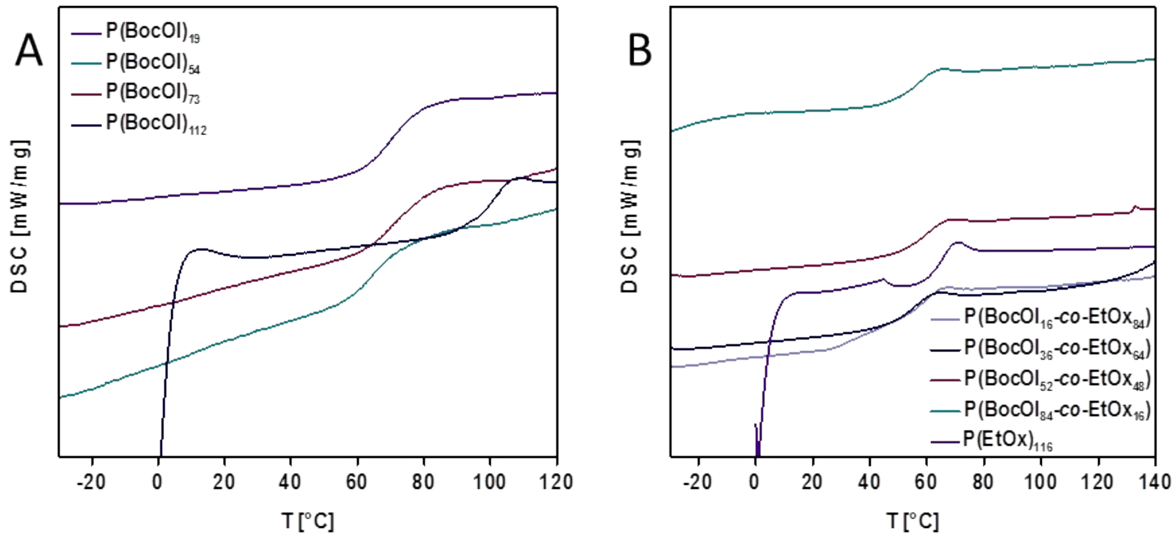



**Figure S28:** DSC traces of the Boc-protected **A:** homopolymers (**2a-d**) and **B:** copolymers (**4a-d**) and $P(EtOx)_{116}$ (**6**).

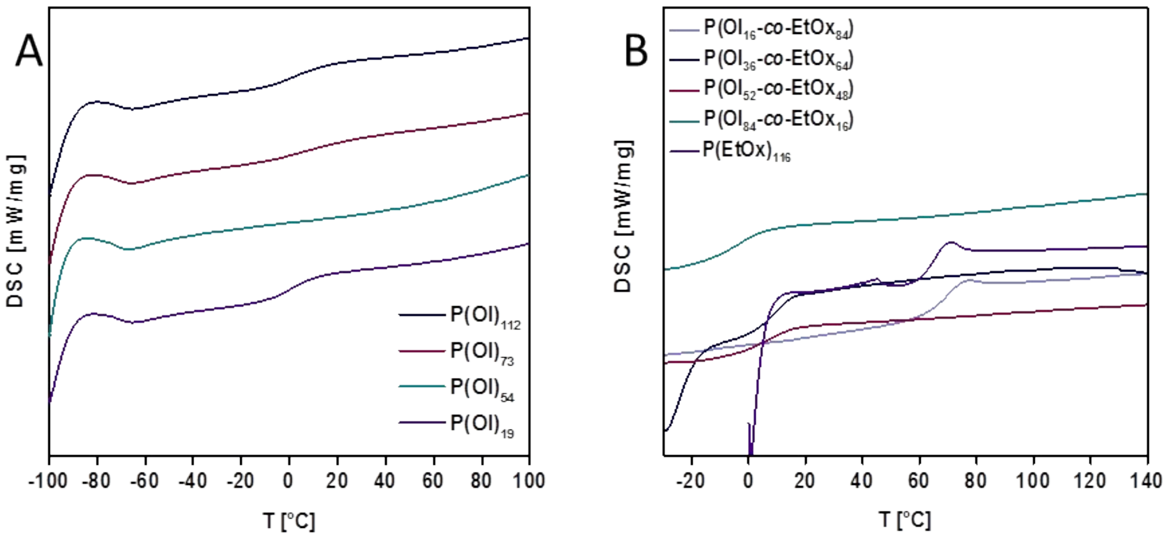



**Figure S29:** DSC traces of the deprotected **A:** homopolymers (**3a-d**) and **B:** copolymers (**5a-d**) and P(EtOx)$_{116}$ (**6**).

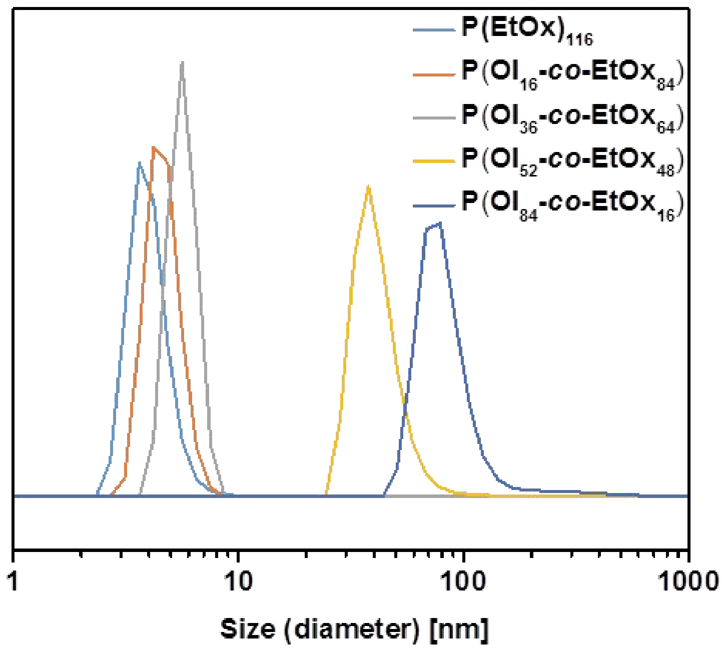



**Figure S30:** Size distribution of the self-assembled structures measured *via* DLS (number PSD).

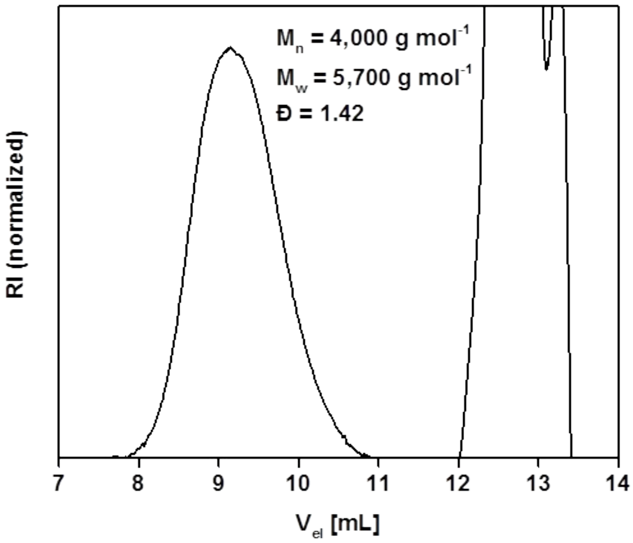



**Figure S31:** SEC-trace ($CHCl_3$-*i*-PrOH, PS-cal.; 1st system peak after 12 mL) of $P(BocOI)_{300}$.