— —Supporting Information — —

Degradable Vinyl Copolymers Featuring Backbone Dithiocarbonates by Radical Copolymerization of a Cyclic Xanthate

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Synthesis of BOT

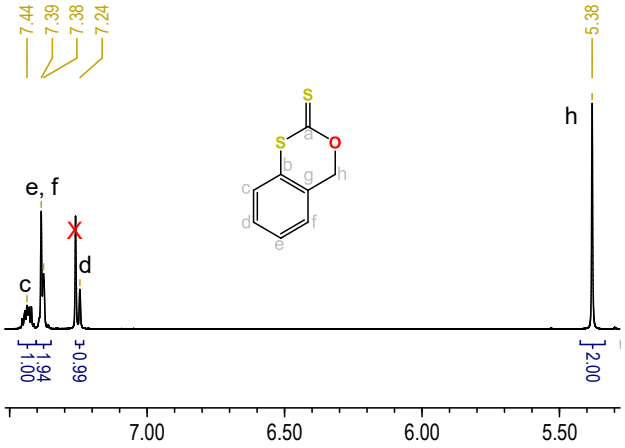

Figure S1. ^{1}H NMR spectrum of BOT

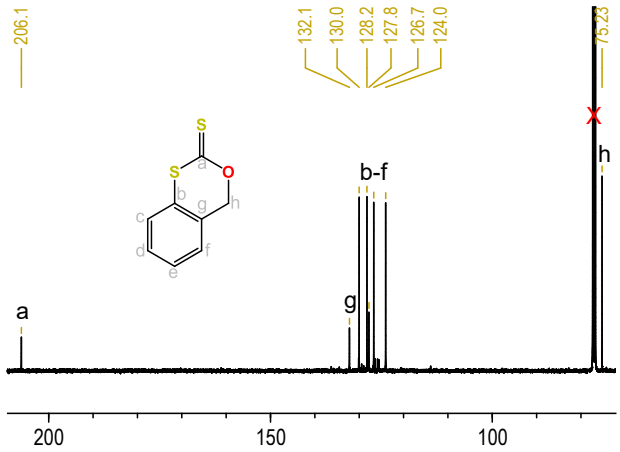

Figure S2. ^{13}C NMR spectrum of BOT

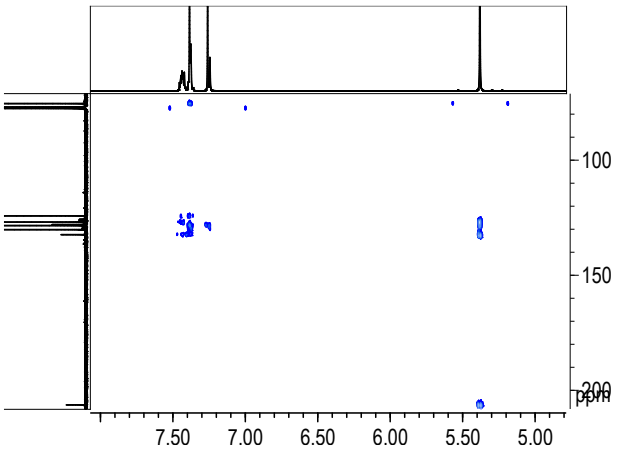

Figure S3. $^{1}H–^{13}C$ HMBC spectrum of BOT

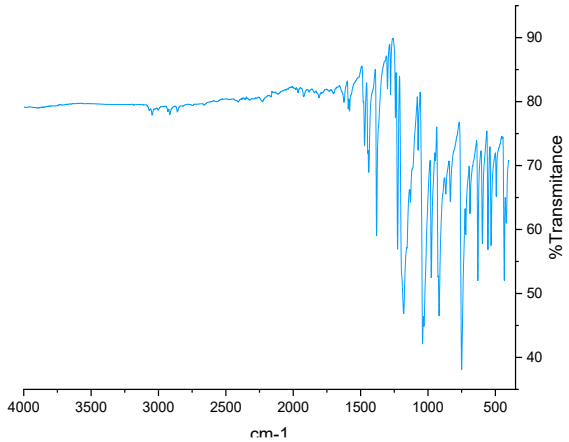

Figure S4. FT-IR spectrum of BOT

Spiro Side Product

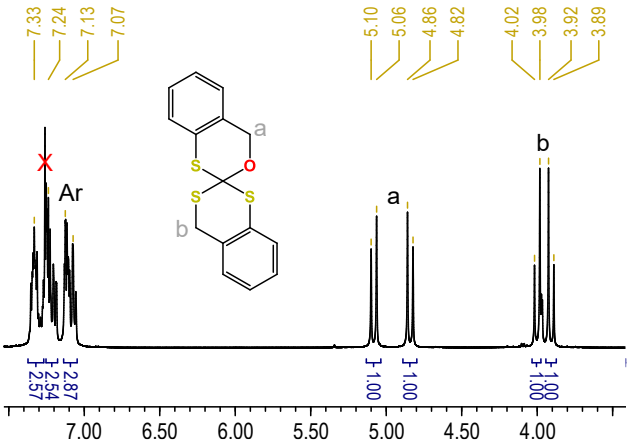

Figure S5. ^{1}H NMR spectrum of side product presumed to be 1-oxa-1',3,3'-trithia-2,2'-spirobi(1,2,3,4-tetrahydronaphthalene).

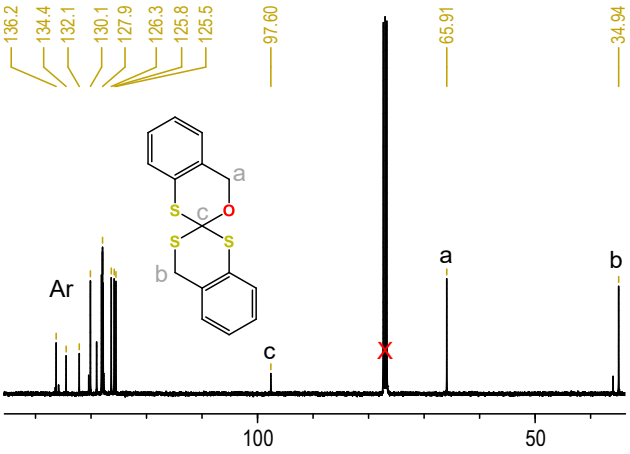

Figure S6. ^{13}C NMR spectrum of side product.

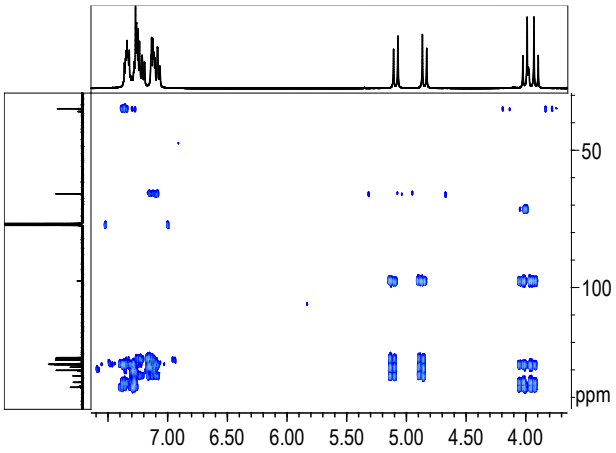

Figure S7. $^{1}H–^{13}C$ HMBC spectrum of side product. It shows both methylene groups coupling to the central carbon at δ_C = 97.6 ppm and to different sets of aromatic carbons.

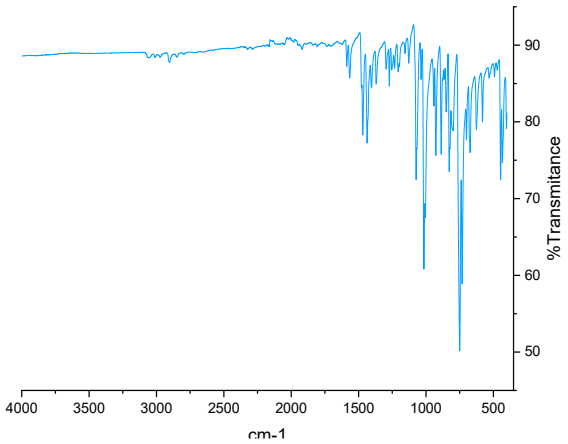

Figure S8. IR spectrum of side product.

BOT Homopolymer

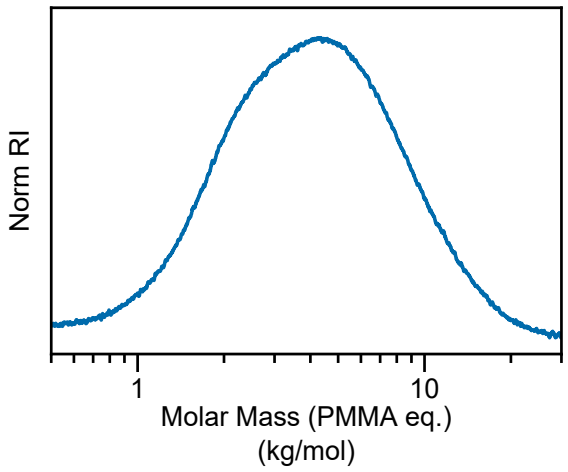

Figure S9. SEC trace of pBOT homopolymer (Table 1, entry 1).

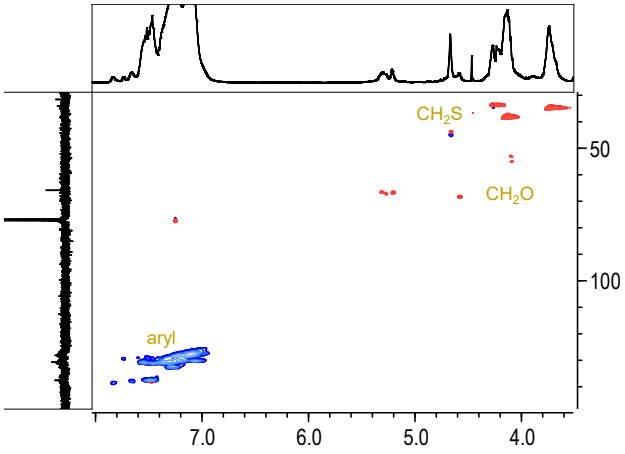

Figure S10. ^{1}H–^{13}C HSQC spectrum of pBOT homopolymer (Table 1, entry 1).

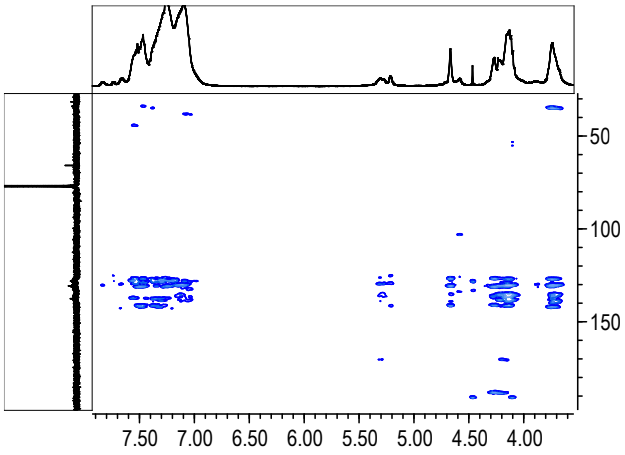

Figure S11. $^{1}H–^{13}C$ HMBC spectrum of pBOT homopolymer (Table 1, entry 1).

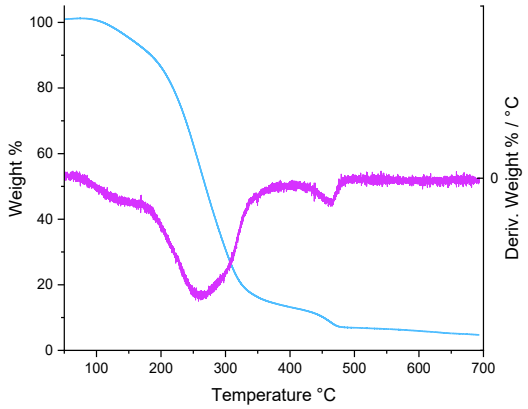

Figure S12. Thermogravimetric analysis of pBOT homopolymer (Table 1, entry 1) (blue curve, left axis) and derivate weight (purple curve, right axis).

BOT Copolymerization with DMA

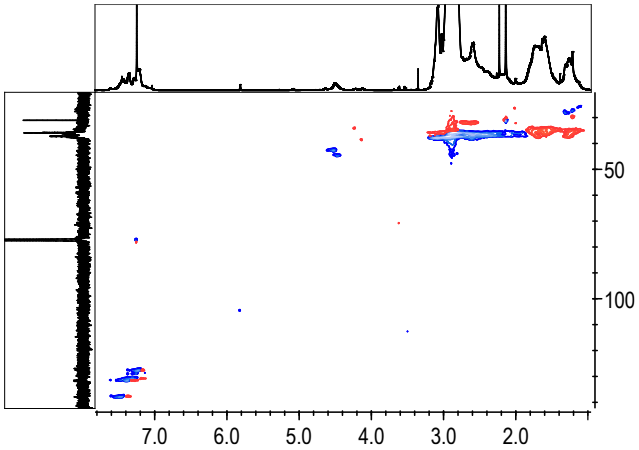

Figure S13. $^{1}H–^{13}C$ HSQC spectrum of $p(DMA_{0.89}\text{-}BOT_{0.11})_n$ (Table 1, entry 5).

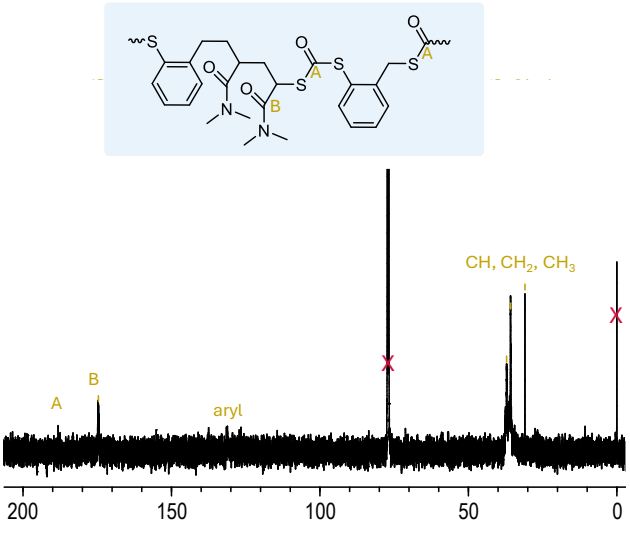

Figure S14.^{13}C NMR spectrum of $p(DMA_{0.89}\text{-}BOT_{0.11})_n$ (Table 1, entry 5).

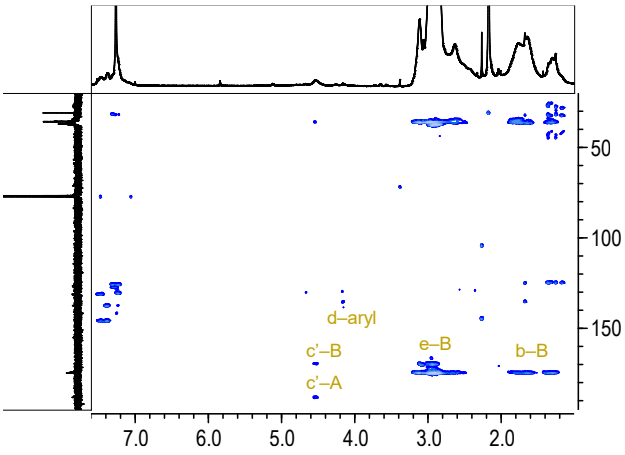

Figure S15. HMBC spectrum of $p(DMA_{0.89}\text{-}BOT_{0.11})_n$ (Table 1, entry 5). Refer to previous figures and Figure 2 for peak assignment.

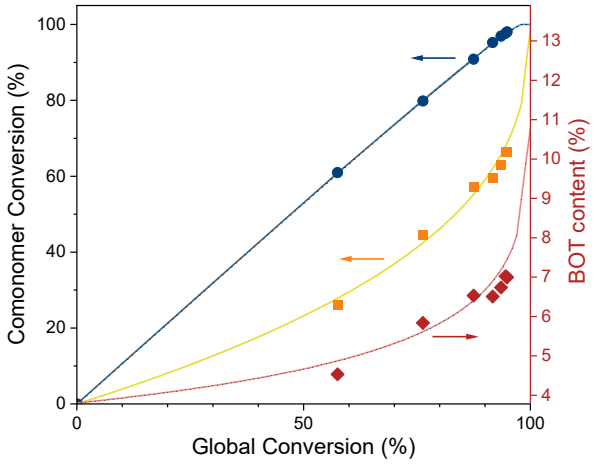

Figure S16. Plot of comonomer conversion (left axis) for DMA (blue) and BOT (orange/yellow) and cumulative copolymer BOT content (right axis, red/pink data) versus global conversion for the copolymerization kinetics of $p(DMA_{0.93}\text{-}BOT_{0.07})_n$ (Table 1, entry 4). Data points are experimental data estimated from ^{1}H NMR spectra of withdrawn aliquots; continuous lines are least square fits obtained from a numerical calculation: the global conversion was divided in 100 steps, at each of which fractions of both comonomers totalling 1 are consumed as estimated by the Mayo-Lewis equation using the instantaneous mole fractions. After each step, the new mole fractions were calculated after subtracting the consumed fractions from the remaining comonomer stock.[1] The formation of side product was ignored for this estimation. Negative mole fractions were prevented by setting the amount of a fully consumed comonomer to zero. Comonomer conversions and the cumulative comonomer content were calculated from the initial versus residual comonomer contents at each of the 100 global conversion steps. The fits use the reactivity ratios $r_{BOT} = 0.04$ and $r_{DMA} = 2.73$. Despite the low estimated reactivity ratio of BOT, it is incorporated into the copolymer; the calculated cumulative BOT content in the polymer product is 3.8 mol-% in the first percentile of the copolymerization (left end of pink curve) and reached 7.0 mol-% after 95% global conversion (right-most red data point).

BOT Copolymerization with DEVP

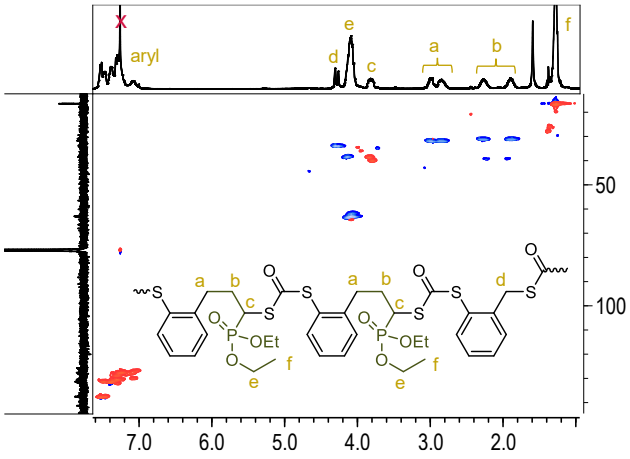

Figure S17. $^{1}H–^{13}C$ HSQC spectrum of p($DEVP_{0.4}$-$BOT_{0.6}$)$_n$ (Table 1, entry 8).

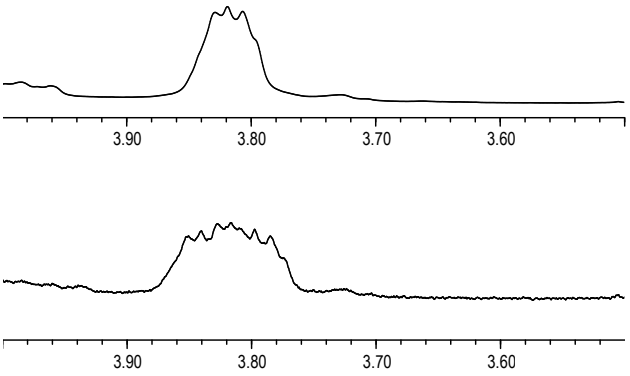

Figure S18. Sections of ^{1}H NMR (bottom) and ^{1}H $\{^{31}P\}$ NMR (top) spectra of the δ_H = 3.82 ppm resonance of p($DEVP_{0.4}$-$BOT_{0.6}$)$_n$ (Table 1, entry 8) showing $^{1}H–^{31}P$ coupling in the bottom spectrum. All other signals (not shown) did not differ between the two spectra.

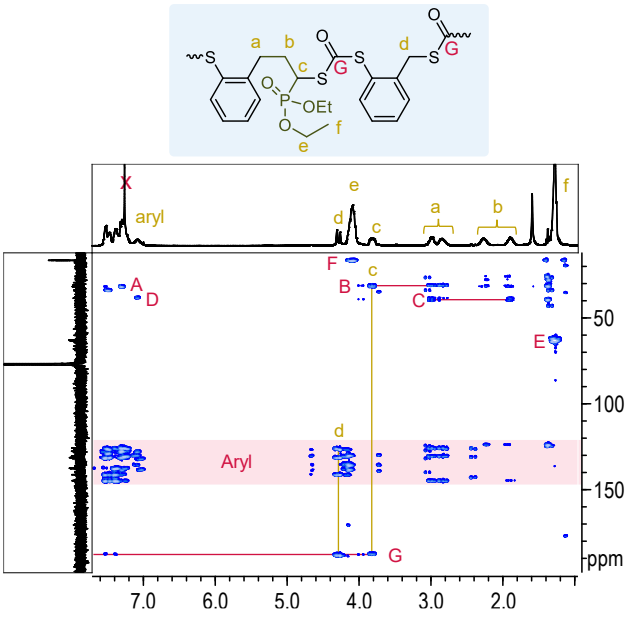

Figure S19. $^{1}H–^{13}C$ HMBC spectrum of $p(DEVP_{0.4}\text{-}BOT_{0.6})_n$ (Table 1, entry 8).

Capital letters and red lines refer to ^{13}C NMR signals

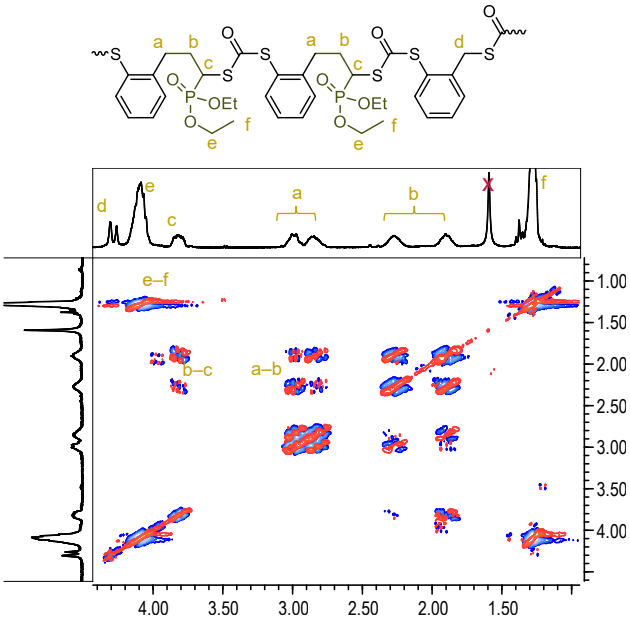

Figure S20. $^{1}H–^{1}H$ COSY NMR spectrum of $p(DEVP_{0.4}\text{-}BOT_{0.6})_n$ (Table 1, entry 8).

BOT Copolymerization with Styrene

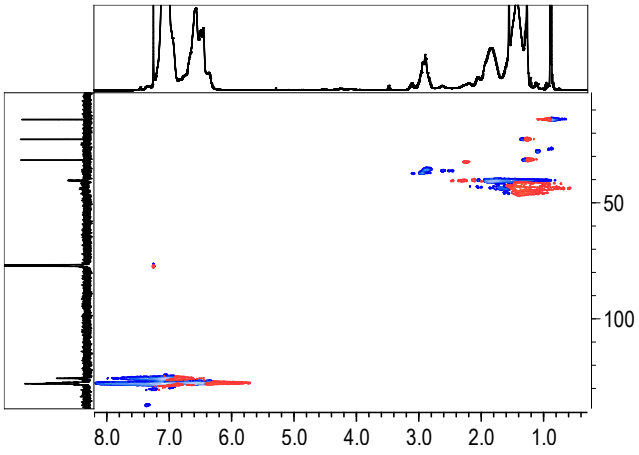

Figure S21. $^{1}H–^{13}C$ HSQC spectrum of $p(Sty_{0.98}\text{-}BOT_{0.02})_n$ (Table 1, entry 9).

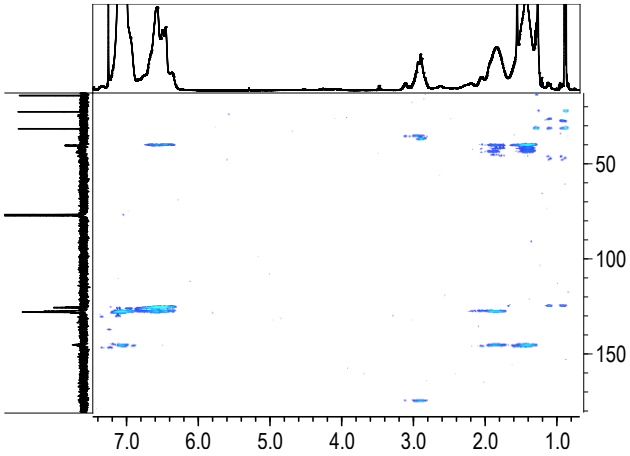

Figure S22. $^{1}H–^{13}C$ HMBC spectrum of $p(Sty_{0.98}\text{-}BOT_{0.02})_n$ (Table 1, entry 9).

Degradation

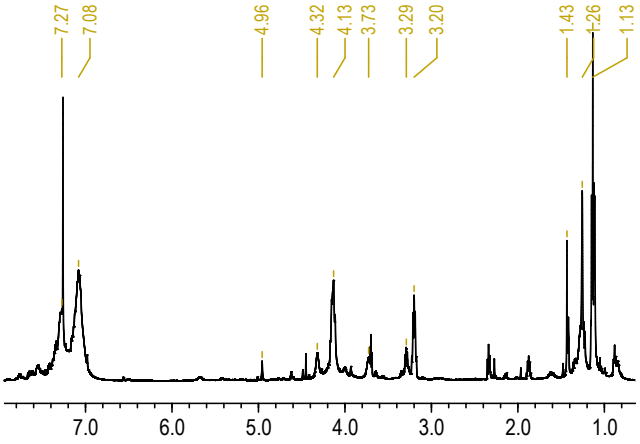

Figure S23. ^{1}H NMR spectrum of pBOT (table 1, entry 1) after ethylamine degradation.

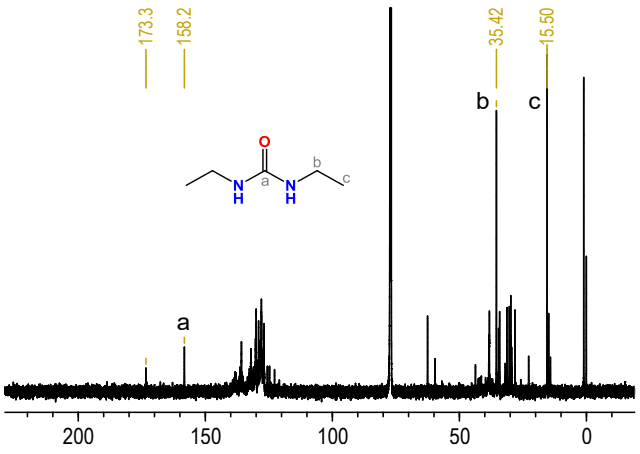

Figure S24. ^{13}C NMR spectrum of pBOT (Table 1, entry 1) after ethylamine degradation.

References

1. Kazmi, T.; Hepburn, K. S.; Nisa, Q.; Neogi, S.; Bingham, N. M.; Roth, P. J. Single Unit Comonomer Insertion Initiates Radical Polymerization of Thionolactone to Give Chemically and Thermally Degradable Polythioesters. *Macromolecules* **2025**.