## Anionic Polymerization of Styrene and 1,3-Butadiene in the Presence of Phosphazene Superbases

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Figure S1. SEC traces obtained from withdrawn aliquots at 10 min and 20 min {[t-BuP4]/[sec-BuLi]:1/1, styrene}.



Figure S2. <sup>1</sup>H-NMR spectra after 30 min, 2h and 4h (100% conversion) {[t-BuP2]/[sec-BuLi]:0.5/1, styrene}.



Figure S3. SEC traces obtained from withdrawn aliquots during the polymerization of styrene with [t-BuP2]/[sec-BuLi]:0.5/1.



Figure S4. SEC traces obtained from withdrawn aliquots during the polymerization of styrene with [t-BuP1]/[sec-BuLi]:0.5/1.



Figure S5. 1H-NMR spectra after 30 min, 2h and 4h (100% conversion) {[t-BuP<sub>1</sub>]/[sec-BuLi]:1/1, styrene}.



Figure S6. <sup>1</sup>H-NMR spectra after 2h, 4h and 6h (100% conversion) {[t-BuP<sub>1</sub>]/[sec-BuLi]:0.5/1, styrene}.



Figure S7. SEC traces obtained from withdrawn aliquots during the polymerization of styrene in the absence of phosphazene base.



Figure S8. 1H-NMR spectra after 2h, 4h and 6h (100% conversion) {styrene in the absence of phosphazene base}.



Figure S9. <sup>1</sup>H-NMR spectra after 2h, 8h and 12h (100% conversion) {[t-BuP<sub>1</sub>]/[sec-BuLi]:1/1, 1,3-butadiene}.



Figure S10. <sup>1</sup>H-NMR spectra after 4h, 8h and 16h (100% conversion) {1,3-butadiene in the absence of phosphazene base}.



Figure S11. SEC traces obtained from withdrawn aliquots during the polymerization of 1,3-butadiene in the absence of phosphazene base.



**Figure S12.** *A*: SEC traces of PS (black line) synthesized with [t-BuP<sub>2</sub>]/[sec-BuLi]:1/1 and the corresponding PS-b-PLLA (red line). **B**:<sup>1</sup>H-NMR spectrum of the final diblock copolymer in CDCl<sub>3</sub>.



**Figure S13.** *A*: SEC traces of PS (black line) synthesized by [t-BuP<sub>1</sub>]/[sec-BuLi]:1/1 and of the corresponding PS-b-PCL (green line). B: <sup>1</sup>H-NMR spectrum of the final diblock copolymer in CDCl<sub>3</sub>.