Electronic Supplementary Information for

Mild synthesis of environment-friendly thermoplastic triblock copolymer elastomers through combination of ring-opening and RAFT polymerization⁺

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Fig. S1 Peak deconvolutions of the ¹H NMR spectra for (a) PLA-CTA, (b) PI10k and (c) PLA-PI98k-PLA triblock copolymer. The experimental data points are represented by black open circles. The peak signals from PLA and PI blocks are represented by olive and blue curves, respectively and the sums of all the peak signals are represented by magenta curves.

Sample code	1,4-addition ($P_{1,4}$ %)	1,2-addition (P _{1,2} %)	3,4-addition (<i>P</i> _{3,4} %)
PI10k	89.9	4.2	5.9
PLA-PI29k-PLA	89.7	4.5	5.8
PLA-PI48k-PLA	89.5	4.3	6.2
PLA-PI80k-PLA	89.0	4.7	6.3
PLA-PI98k-PLA	88.9	4.9	6.2
PLA-PI106k-PLA	89.2	5.0	5.8

Table S1 The 1,4-, 1,2- and 3,4-addition ratios for isoprene unit in PI10k andPLA-b-PI-b-PLA triblock copolymers



Fig. S2 DSC derivative heat flow curves for PLA-*b*-PI-*b*-PLA triblock copolymers during the second heating scan with a heating rate of 10 °C /min in a temperature range from -75 to 180 °C. The curves are vertically shifted for clarity.



Fig. S3 Heat flow curves for (a) PLA-CTA and (b) PI10k during the second heating scan with a heating rate of 10 °C/min.



Fig. S4 Change of glass transition temperature of PI block with molecular mass of PI block for PLA-*b*-PI-*b*-PLA triblock copolymers.



Fig. S5 TEM micrograph for PLA-PI80k-PLA.



Fig. S6 DSC heat flow curves during the heating scan of the four cycles for (a) PLA-CTA and (b) PLA-PI106k-PLA. For examination of the sample thermal stability, a cyclic DSC heating-cooling–heating scan was applied. PLA-CTA sample was firstly heated from 40 to 160 °C to eliminate thermal history, and then cooled to 20 °C followed by heating up again to 160 °C. For PLA-PI106k-PLA, the sample was firstly heated from 40 to 150 °C to eliminate thermal history, and then cooled to -80 °C followed by heating up again to 150 °C. For PLA-PI106k-Four cycles with the ramping rate of 10 °C/min were applied to these samples.