Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Integration of Metal-Free Ring-Opening Metathesis Polymerization and Organocatalyzed Ring Opening Polymerization through a Bifunctional Initiators

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Materials and Methods

Dimethylformamide (DMF), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF) were obtained from a solvent purification system. For MF-ROMP procedure, CH_2Cl_2 was dried over 4Å molecular sieves before use. Norbornene was sublimed prior to use. 3,6-dimethyl-1,4-dioxane-2,5-dione (rac-LA) was recrystallized from dry toluene (3 times) prior to use and stored at -20 °C under inert atmosphere. Ɛ-caprolactone (CL) was distilled over CaH_2 (×2) and stored under inert atmosphere. The pyrylium tetrafluoroborate was prepared according to literature procedure.[1] 1,3-(2,4,6-trimethylphenyl)imidazolium chloride and 1,3-dimethylimidazolium iodide were prepared according to previous literature procedure.[2-3] Initiator **1** was prepared as previously described.[4] All other reagents and solvents were obtained from commercial sources and used as received unless otherwise noted. All polymerizations were carried out in standard borosilicate glass vials with magnetic stirring. Irradiation of photochemical reactions was done using a 2W Miracle Blue LED indoor gardening bulb purchased from Amazon. ^1H and ^{13}C NMR spectra were recorded on Bruker AVance 300 MHz or 500 MHz spectrometers. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protio-solvent as an internal standard (CDCl3, ^1H: 7.26 ppm and ^{13}C: 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplets, q = quartet, m = multiplet, br = broad peak), coupling constants (Hz) and integration. Gel Permeation Chromatography (GPC) was performed using a GPC setup consisting of: an Agilent pump, 3 in-line columns, and Wyatt light scattering and refractive index detectors with THF as the mobile phase. Number average molecular weight (M_n) and weight average molecular weight (M_w) were calculated from refractive index data and light scattering, respectively, using Astra software from Wyatt Technology Corp. Thermogravimetric analysis (TGA) was performed on a TA TGA Q50 under nitrogen from room temperature to 600 °C at a rate of 5 °C/min. Differential Scanning Calorimetry (DSC) was performed on a TA DSC Q250 calorimeter under nitrogen. Heat flow as watts from the second heating was recorded and reported after normalizing by mass of the sample (W/g).

General Procedure for MF-ROMP from Macroinitiator

To a 2-dram vial containing a magnetic stir bar was added pyrylium salt (1.3 mg, 0.003 mmol) followed by corresponding macroinitiator (0.01 mmol) and norbornene (141 mg, 1.50 mmol). CH_2Cl_2 was then added. The vial was sealed with a PTFE-lined cap and irradiated with blue LEDs (λ = 450 nm, 2 W) at a distance of 2.0 cm. Aliquots were taken for analysis to determine the conversion of norbornene by ^1H-NMR spectrometry. The contents of the vial were then diluted with CH_2Cl_2 and filtered over neutral alumina to remove pyrylium salts. The filtrate was then partially concentrated and then added slowly into an excess of methanol, causing the polymer to precipitate. The solids were collected by filtration, washed with methanol, and then dried under reduced pressure to give the final polymer.

General Procedure for "one-pot" Block Copolymer Synthesis

All organocatalytic ring-opening polymerizations were set up inside glove box at ambient temperature. To a 2-dram vial containing a magnetic stir bar was added TBD (0.3 mg, 0.002 mmol) followed by adding bifunctional initiator **1** (3.0 mg, 0.02 mmol). CH_2Cl_2 was then added, followed by corresponding monomer. The vial was sealed with a PTFE-lined cap and aliquots were taken for determining monomer conversion. After there was no more increase of monomer conversion, the vial was pumped out of glove box and the reaction was open to air. The contents of the vial were then diluted with CH_2Cl_2 and pyrylium salts (3.0 mg, 0.006 mmol) were then added. Aliquots were taken for analysis to determine the molecular weight of macroinitiator. Norbornene was then added and the vial was sealed again with a PTFE-lined cap. At room temperature, the reaction was irradiated with blue LEDs (λ = 450 nm, 2 W) with a distance of 2.0 cm. Aliquots were taken for analysis to determine the conversion of norbornene by ^{1}H-NMR spectrometry. The contents of the vial were then diluted with CH_2Cl_2 and filtered over neutral alumina to remove pyrylium salts. The filtrate was then partially concentrated and then added slowly into an excess of methanol, causing the polymer to precipitate. The solids were collected by filtration, washed with methanol, and then dried under reduced pressure to give the final polymer.

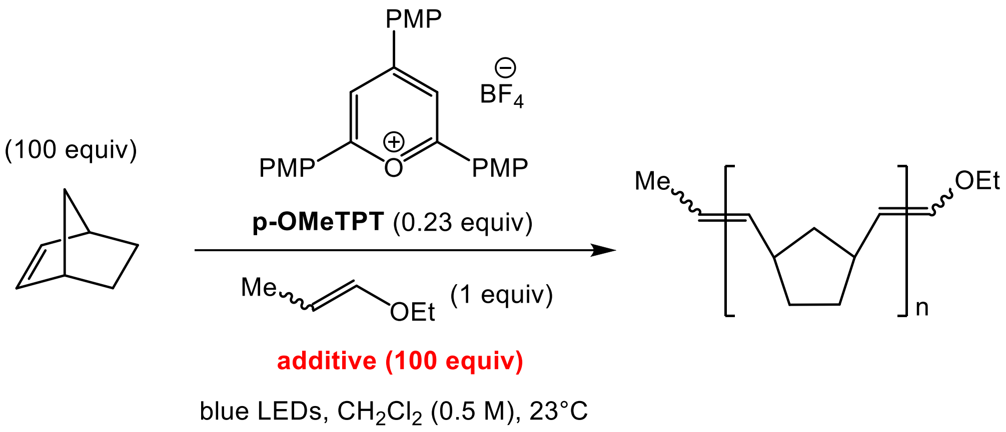
Determination of MF-ROMP monomer conversion

For tracking the conversion of monomer by ^{1}H-NMR spectroscopy (in $CDCl_3$), the following signals were used,

For **M1** (norbornene), the monomer signal at δ = 5.97 ppm (2H) was integrated against the polymer signal at δ = 2.90 to 2.30 ppm (2H total after subtracting monomer peak at 2.83 ppm).

For **M2** (exo-dihydroDCPD), the monomer signal at δ = 0.95 ppm (2H) was integrated against the polymer signal at δ = 1.18 ppm (1H).

Table S1. Effect of Additives on Polymerization of norbornene to polynorbornene



additive	equivalents[a]	conversion (%)[b]
N/A	0	86
rac-lactide (M2)	100	54
caprolactone (M3)	100	45
cyclic trimethylene carbonate (M4)	100	58

[a] Relative to enol ether initiator. [b] Determined using 1H-NMR spectroscopy by comparison of monomer and polymer peaks. PMP = p-methoxyphenyl. All reaction times = 90 min.

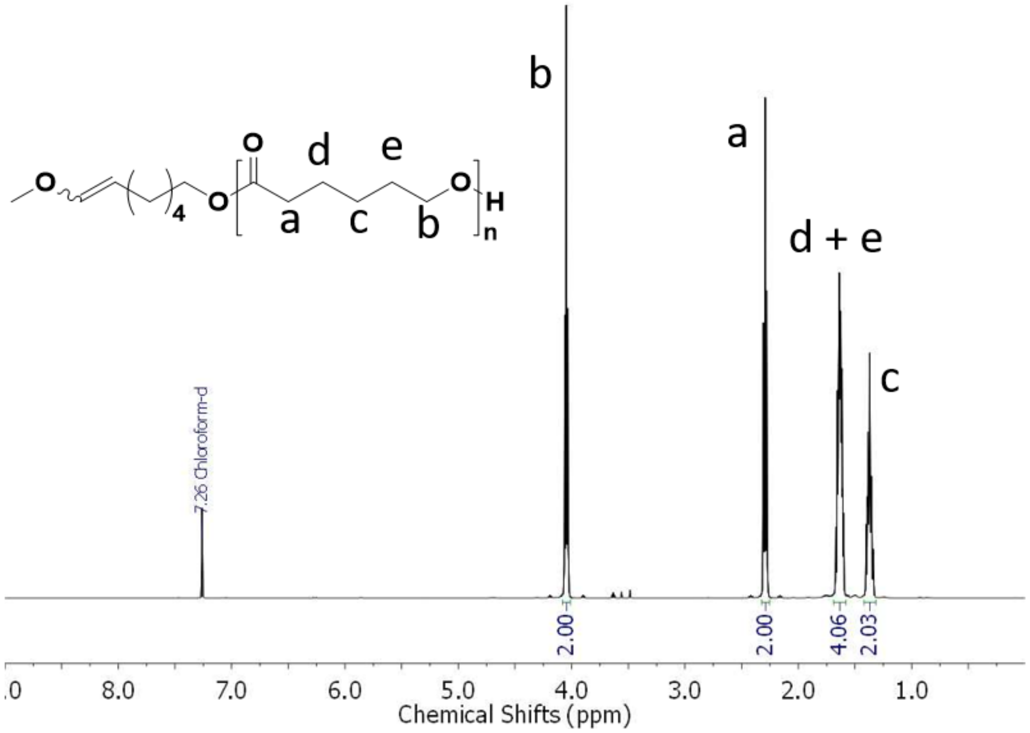


Figure S1. ^{1}H-NMR spectrum PCL macroinitiator

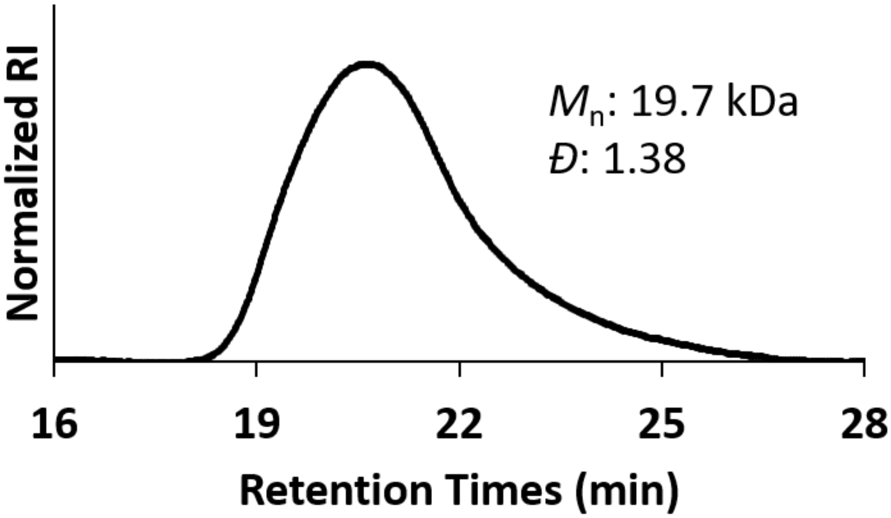


Figure S2. SEC chromatogram of PCL macroinitiator

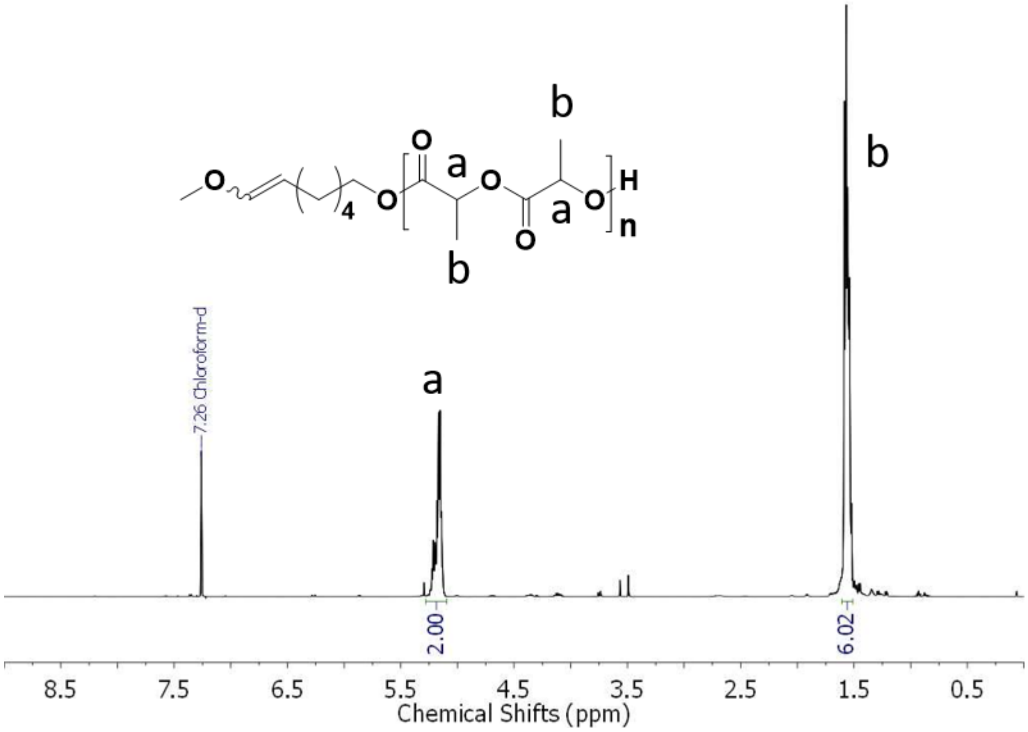


Figure S3. ^{1}H-NMR spectrum PLA macroinitiator

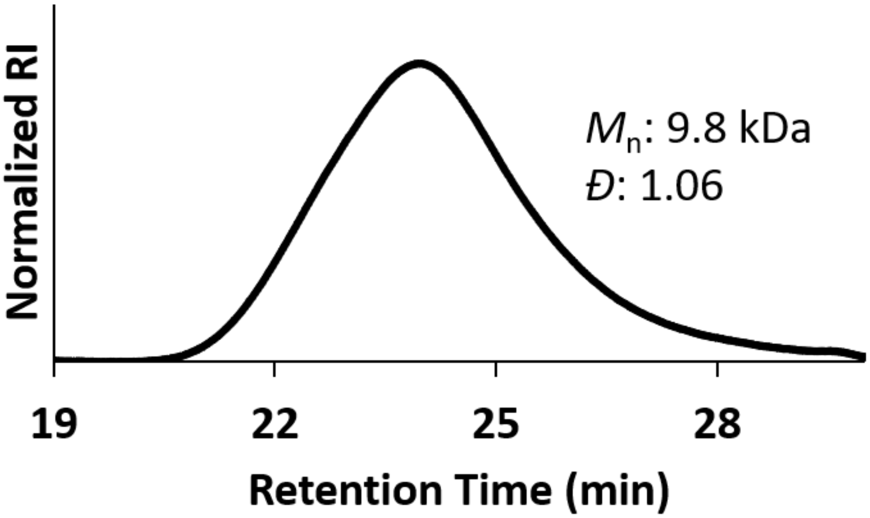


Figure S4. SEC chromatogram of PLA macroinitiator

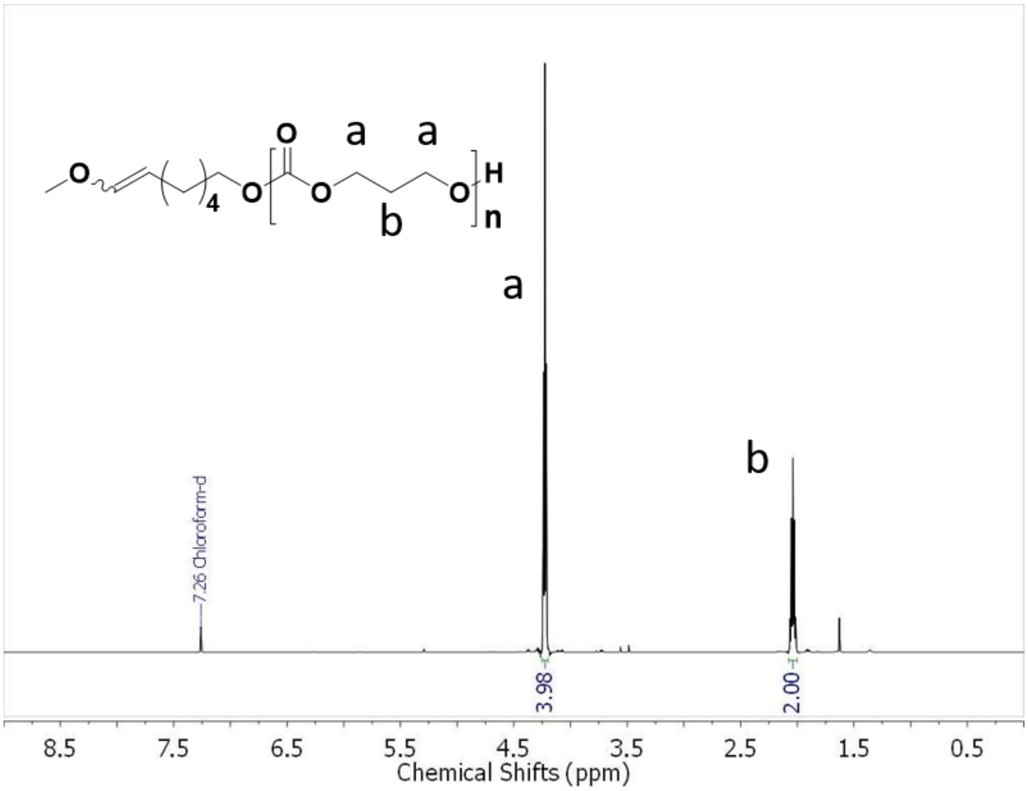


Figure S5. ^{1}H-NMR spectrum PTMC macroinitiator

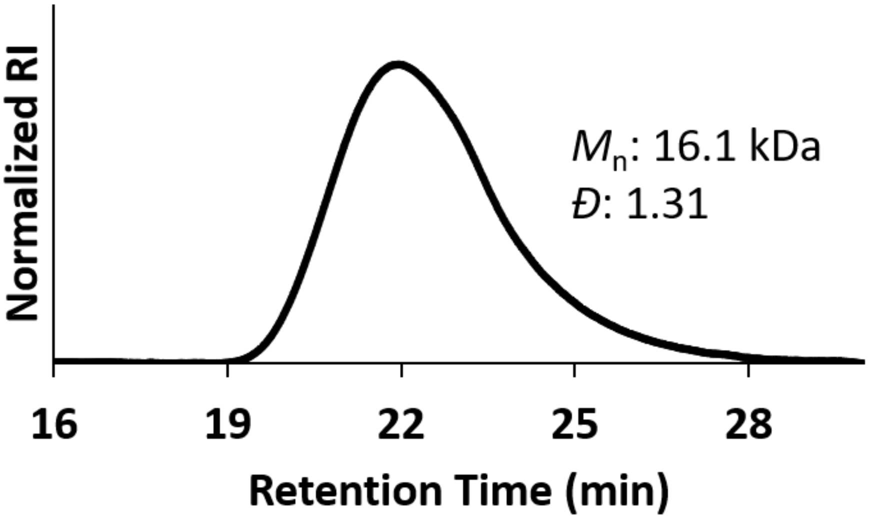


Figure S6. SEC chromatogram of PTMC macroinitiator

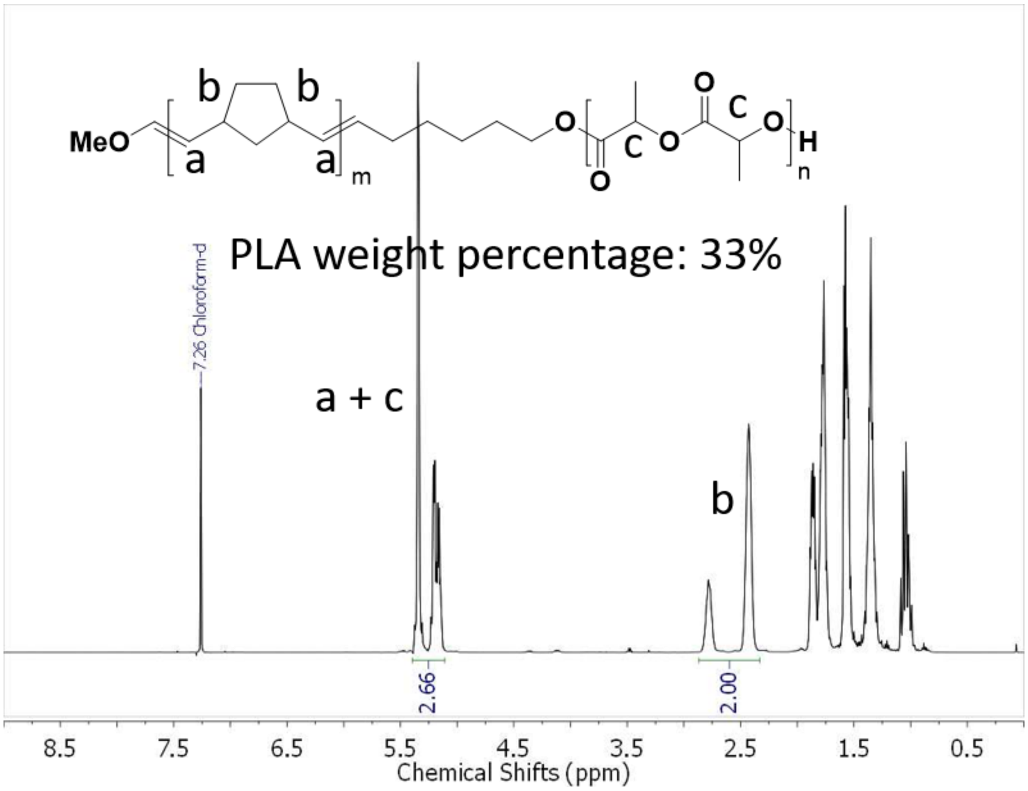


Figure S7. ^{1}H-NMR spectrum of PLA-b-PNB (entry 1 from Table 1)

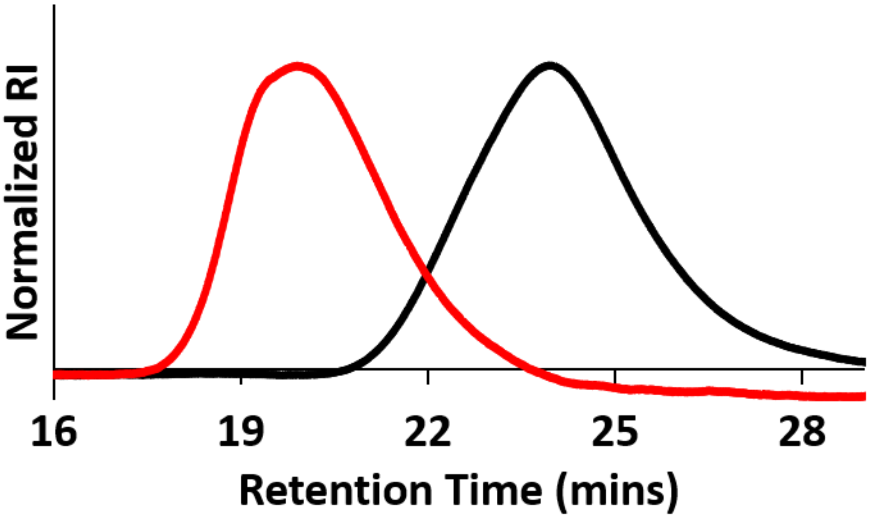


Figure S8. SEC chromatograms of PLA-b-PNB (entry 1 from Table 1, red line) and corresponding macroinitiator (black line)

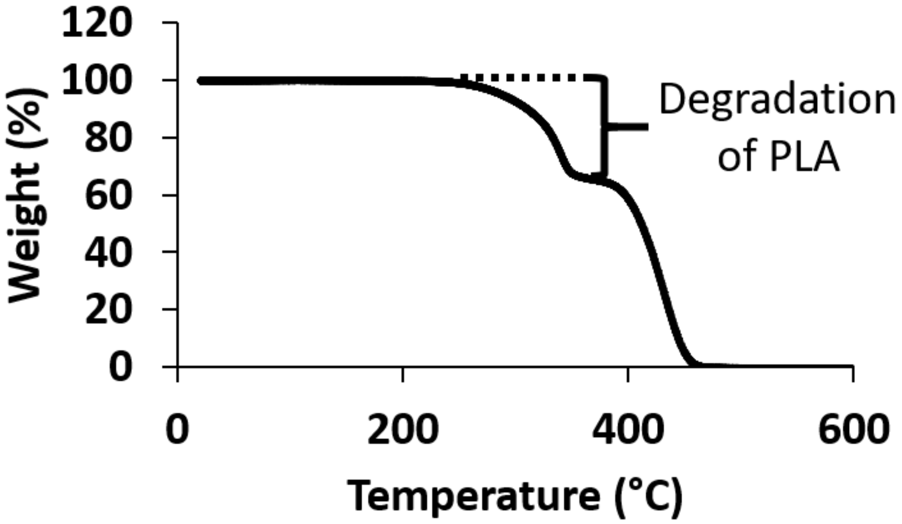


Figure S9. Thermogravimetric analysis of PLA-b-PNB (entry 1 from Table 1). The weight percentage of PLA block is around 33%.

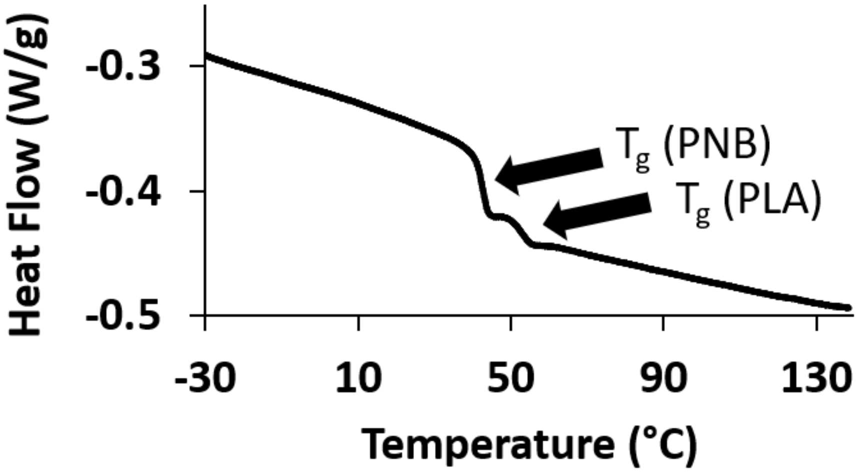


Figure S10. DSC (Exo up) of PLA-b-PNB (entry 1 from Table 1)

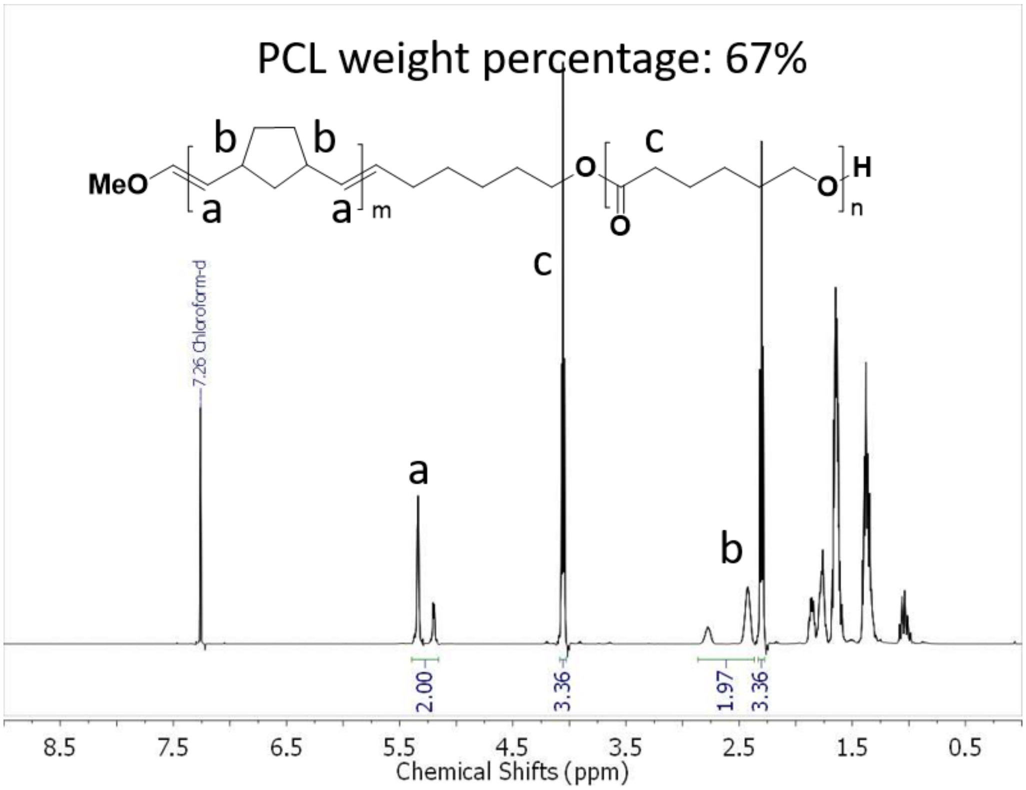


Figure S11. ^{1}H-NMR spectrum of PCL-b-PNB (entry 2 from Table 1)

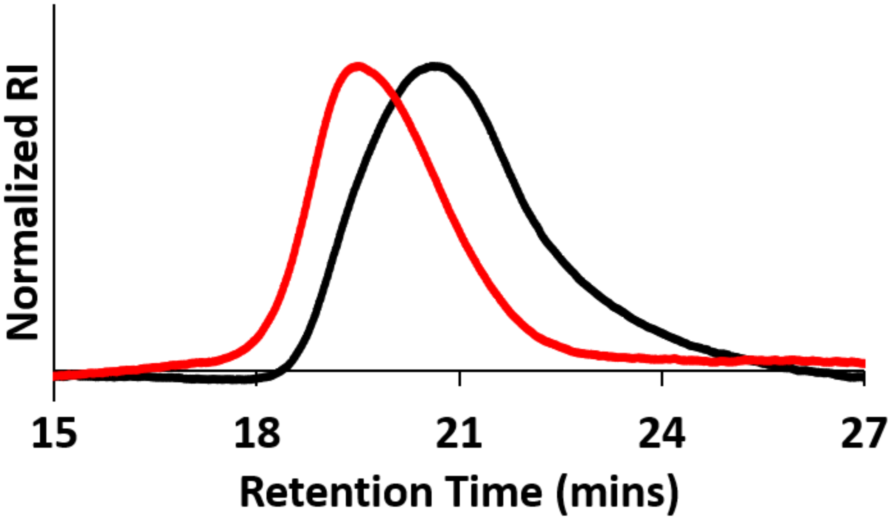


Figure S12. SEC chromatograms of PCL-b-PNB (entry 2 from Table 1, red line) and corresponding macroinitiator (black line)

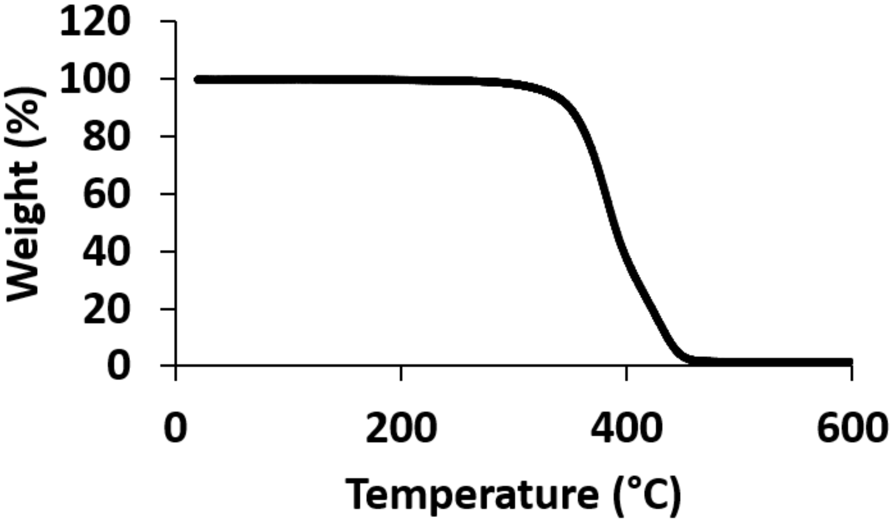


Figure S13. Thermogravimetric analysis of PCL-b-PNB (entry 2 from Table 1)

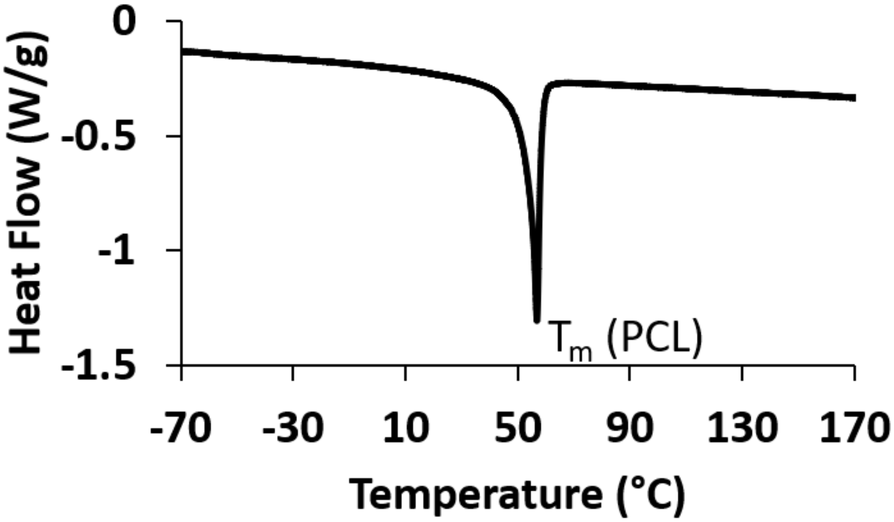


Figure S14. DSC (Exo up) of PLA-b-PNB (entry 2 from Table 1)

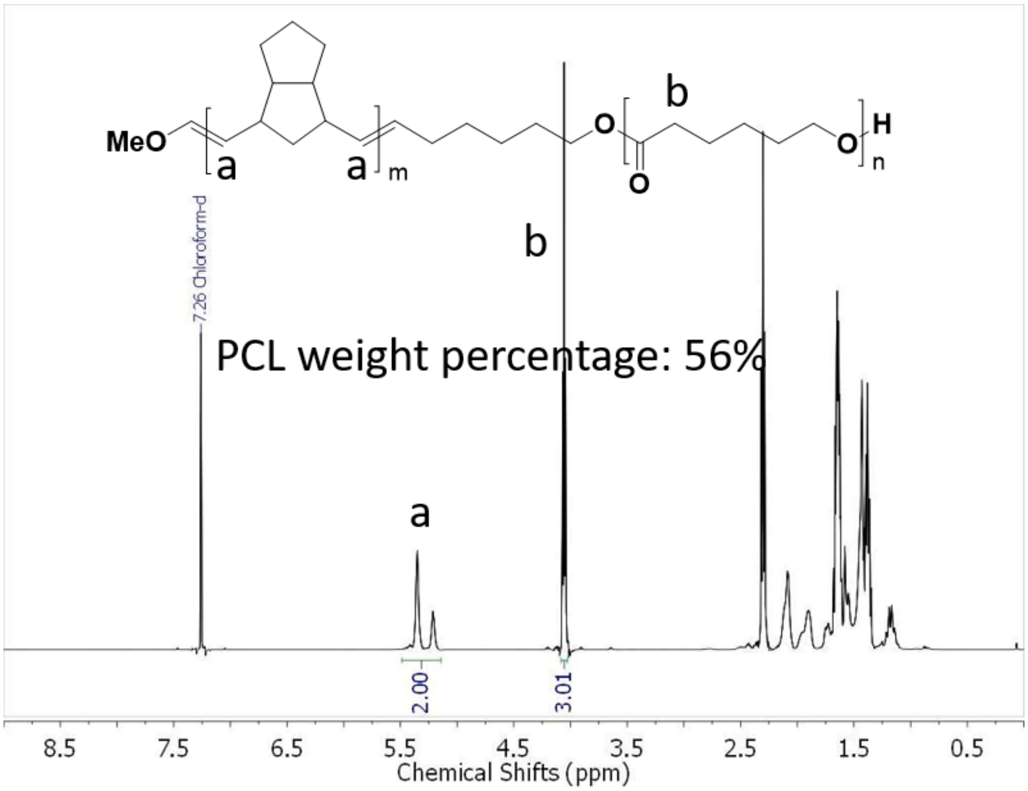


Figure S15. ^{1}H-NMR spectrum of PCL-b-PDCPD-H2 (entry 3 from Table 1)

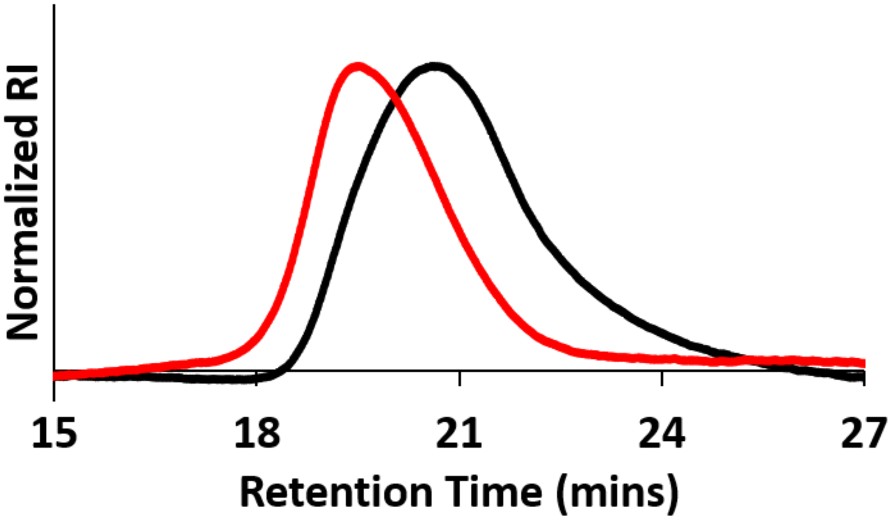


Figure S16. SEC chromatograms of PCL-b-PDCPD-H2 (entry 3 from Table 1, red line) and corresponding macroinitiator (black line)

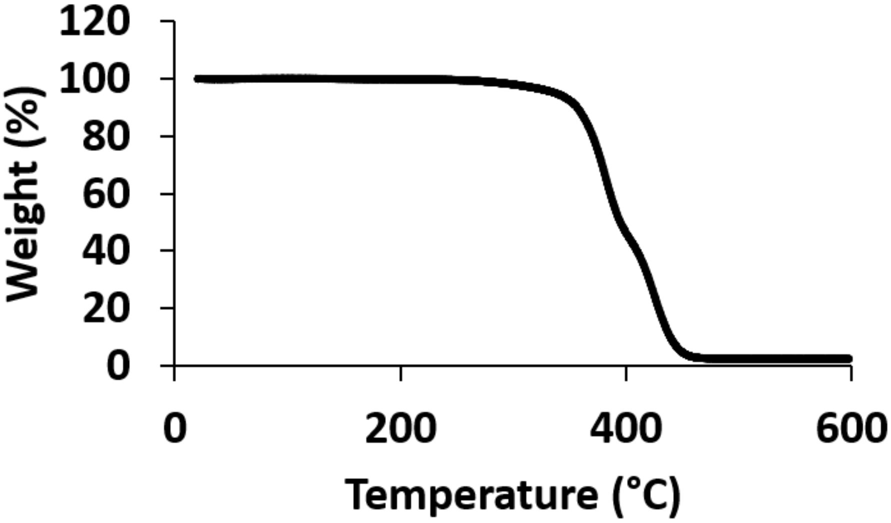


Figure S17. Thermogravimetric analysis of PCL-b-PDCPD-H2 (entry 3 from Table 1)

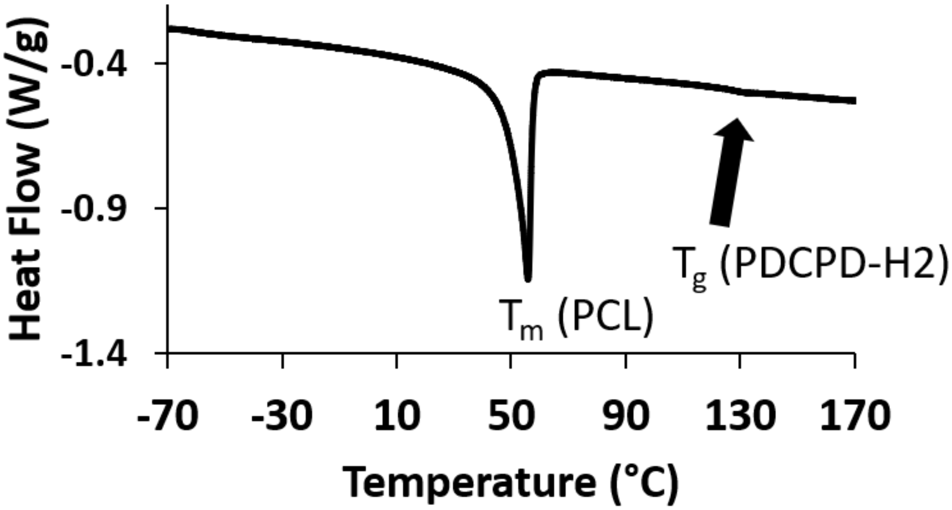


Figure S18. DSC (Exo up) of PLA-b-PDCPD-H2 (entry 3 from Table 1)

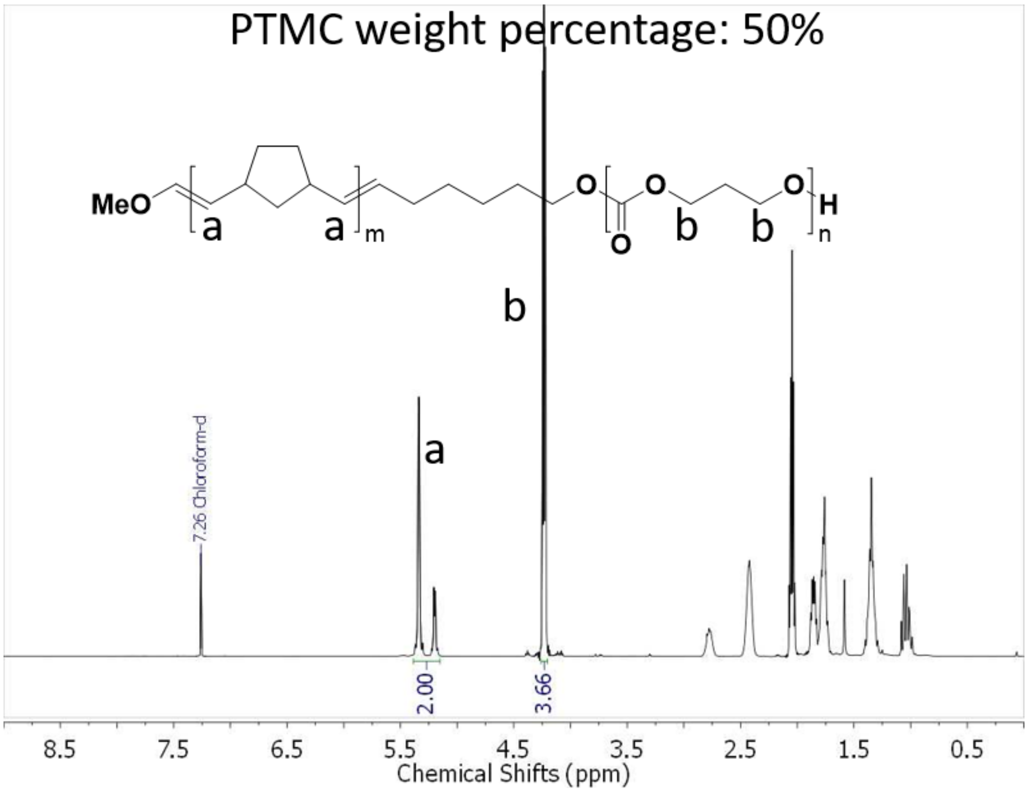


Figure S19. ^{1}H-NMR spectrum of PTMC-b-PNB (entry 4 from Table 1)

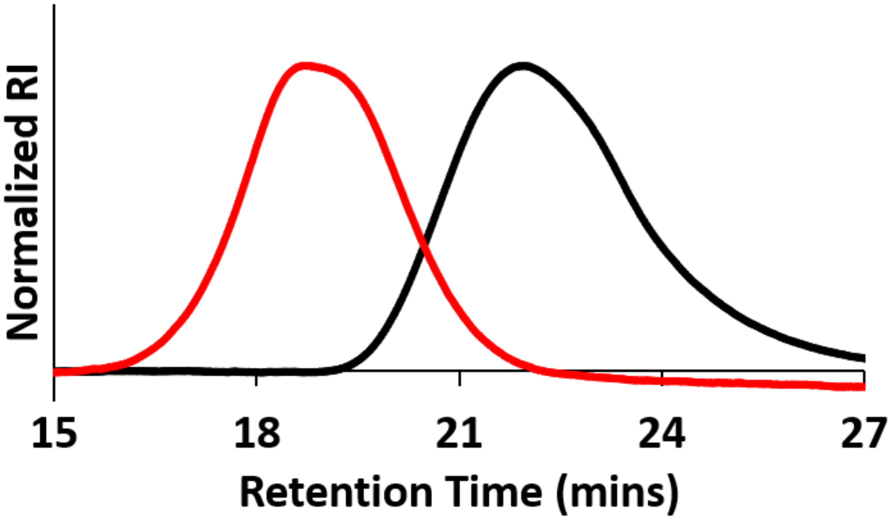


Figure S20. SEC chromatograms of PTMC-b-PNB (entry 4 from Table 1, red line) and corresponding macroinitiator (black line)

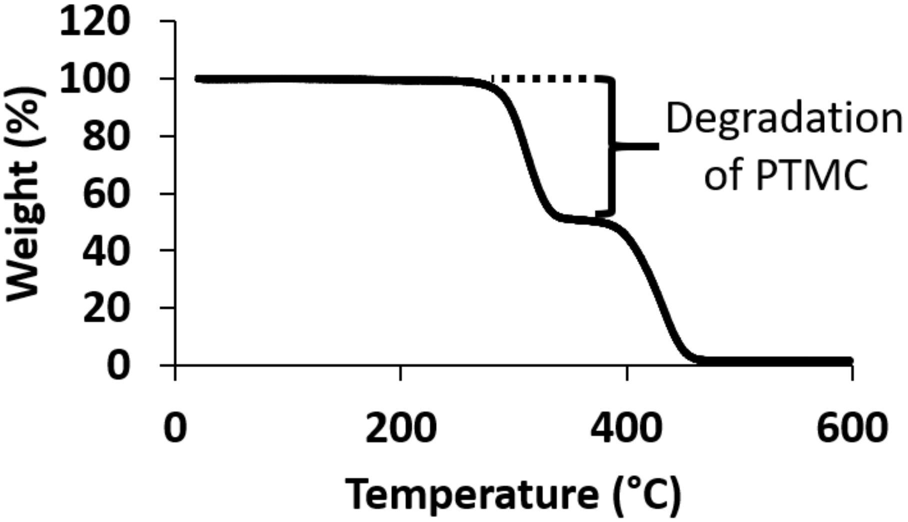


Figure S21. Thermogravimetric analysis of PTMC-b-PNB (entry 4 from Table 1). The weight percentage of PTMC block is around 50%.

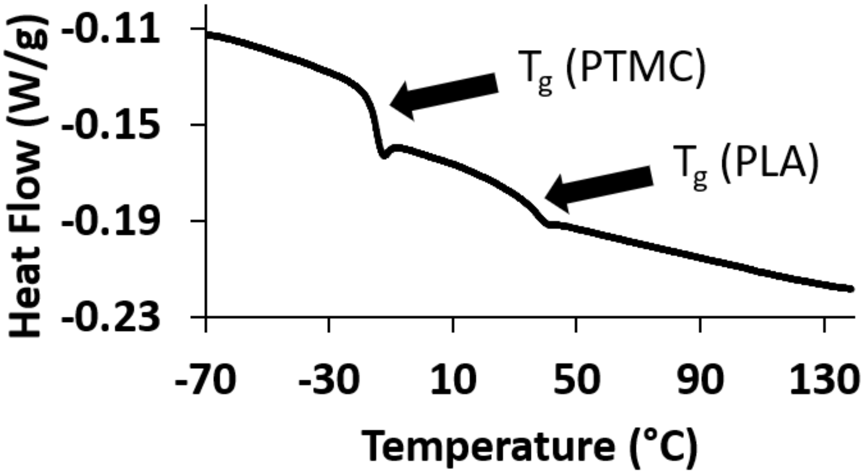


Figure S22. DSC (Exo up) of PTMC-b-PNB (entry 4 from Table 1)

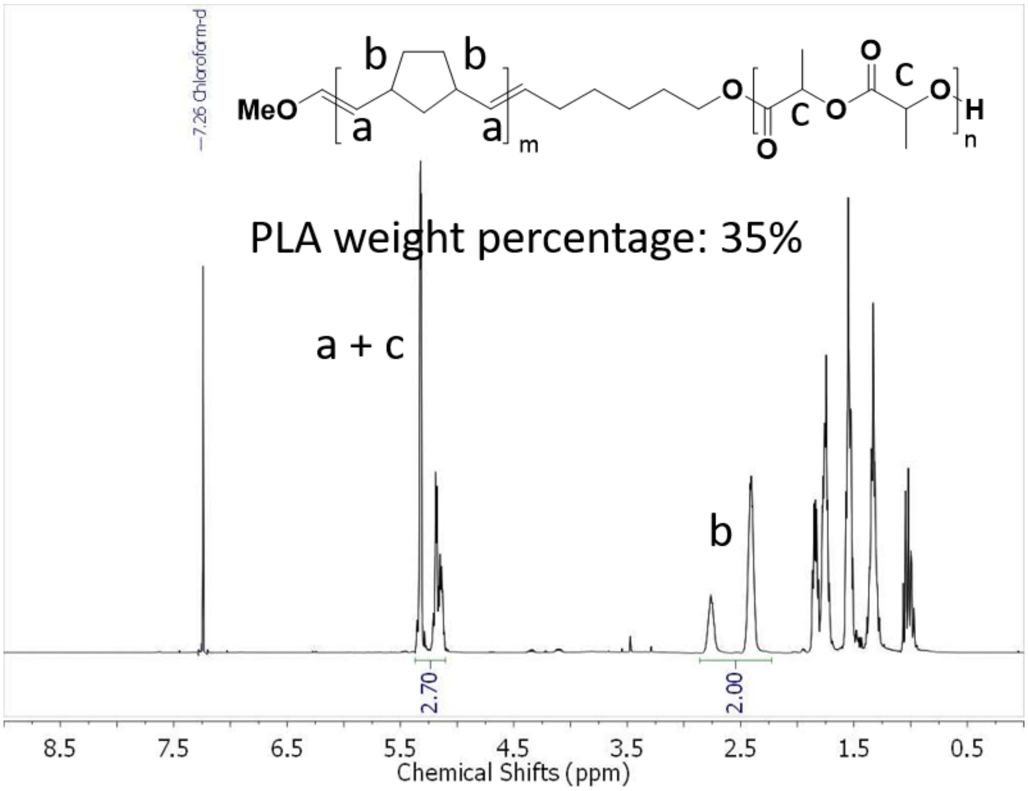


Figure S23. ^{1}H-NMR spectrum of PLA-b-PNB (entry 1 from Table 2)

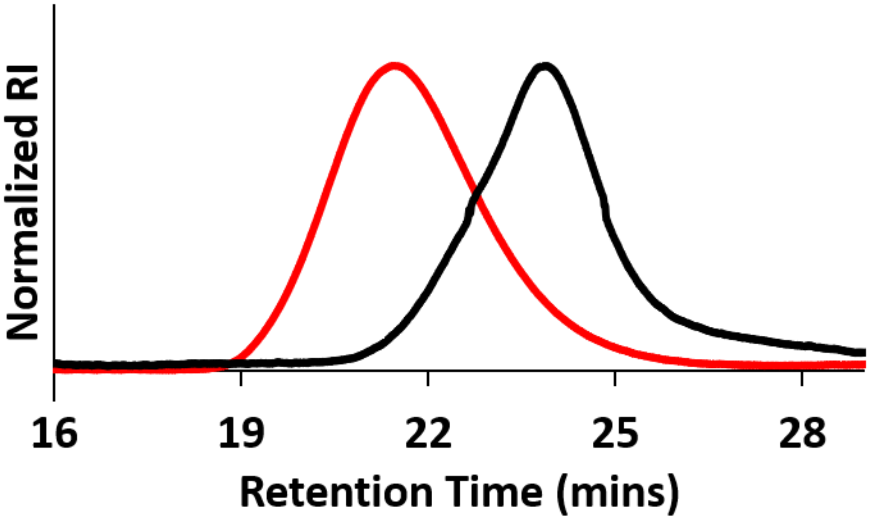


Figure S24. SEC chromatograms of PLA-b-PNB (entry 1 from Table 2, red line) and corresponding macroinitiators (black line)

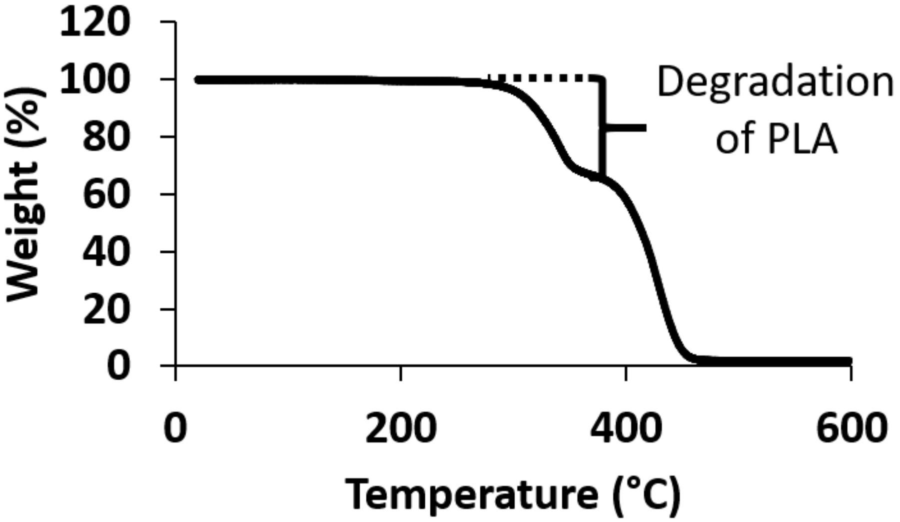


Figure S25. Thermogravimetric analysis of PLA-b-PNB (entry 1 from Table 2). The weight percentage of PLA block is around 34%.

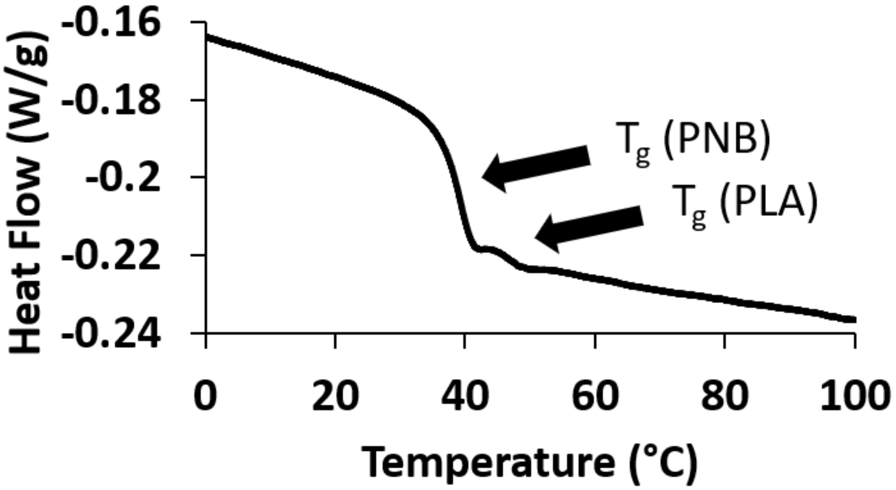


Figure S26. DSC (Exo up) of PTMC-b-PNB (entry 1 from Table 2)

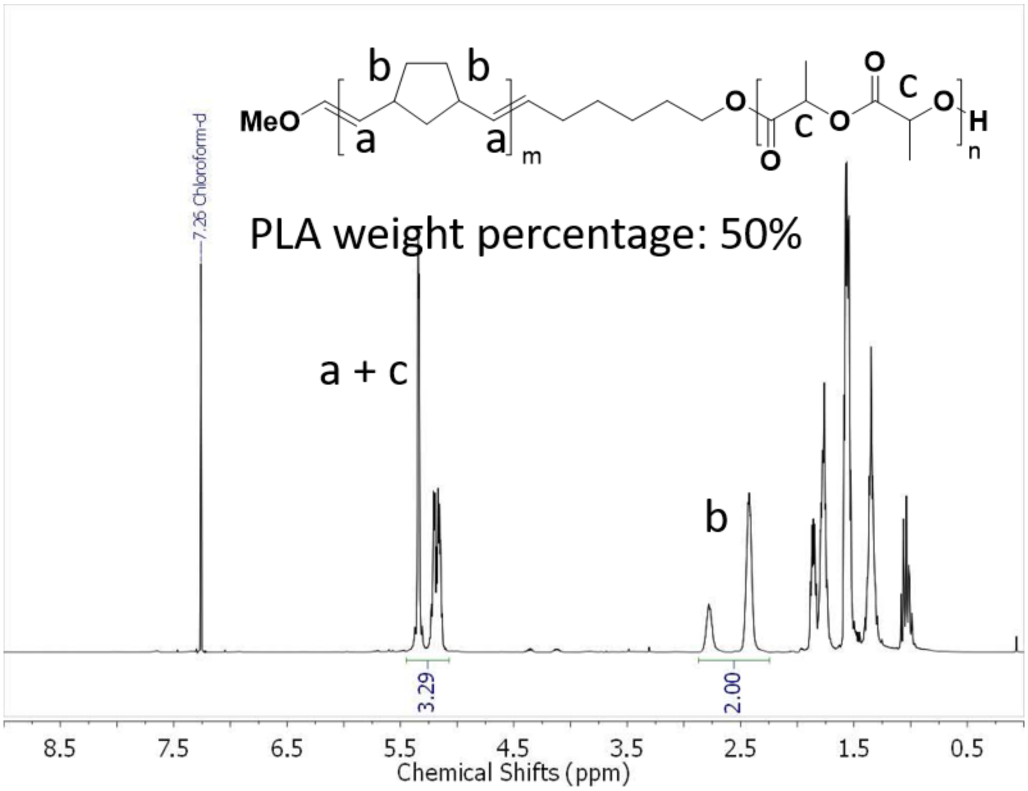


Figure S27. ^{1}H-NMR spectrum of PLA-b-PNB (entry 2 from Table 2)

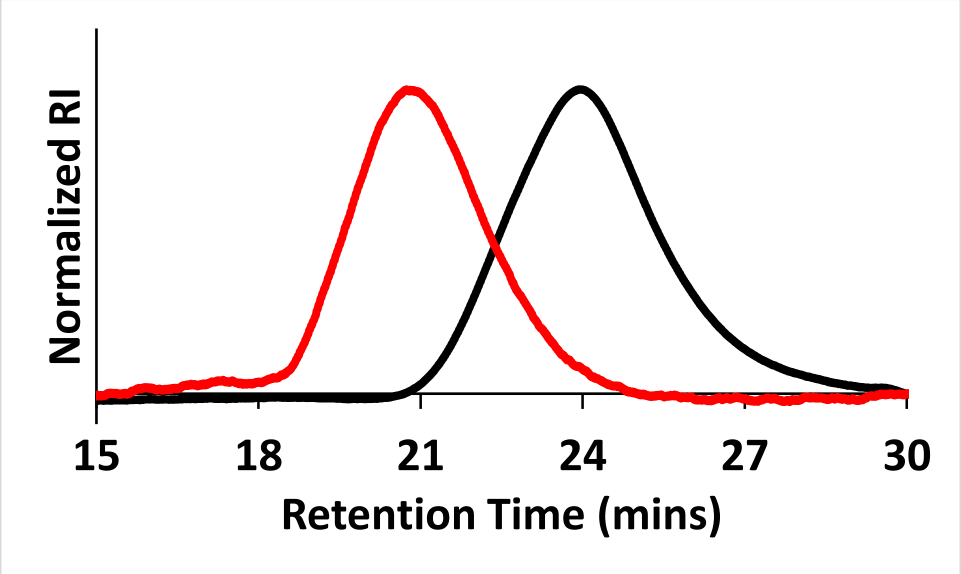


Figure S28. SEC chromatograms of PLA-b-PNB (entry 2 from Table 2, red line) and corresponding macroinitiator (black line)

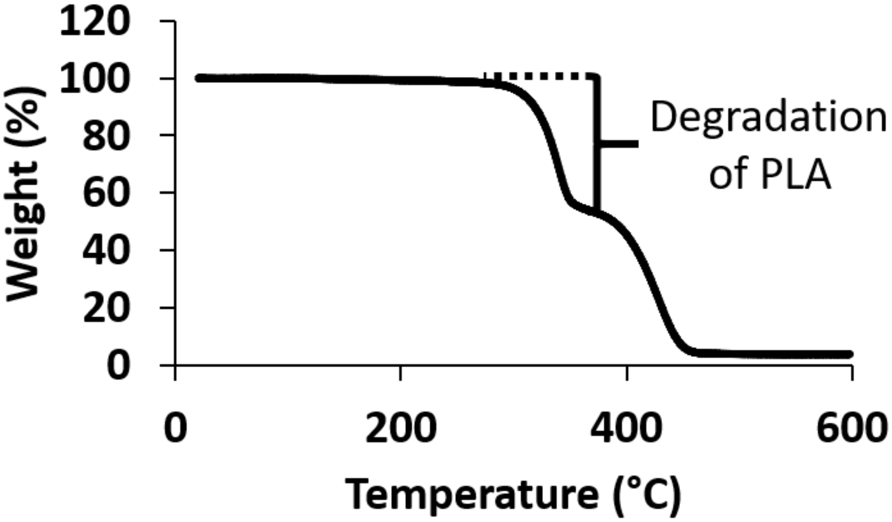


Figure S29. Thermogravimetric analysis of PLA-b-PNB (entry 2 from Table 2). The weight percentage of PLA block is around 47%.

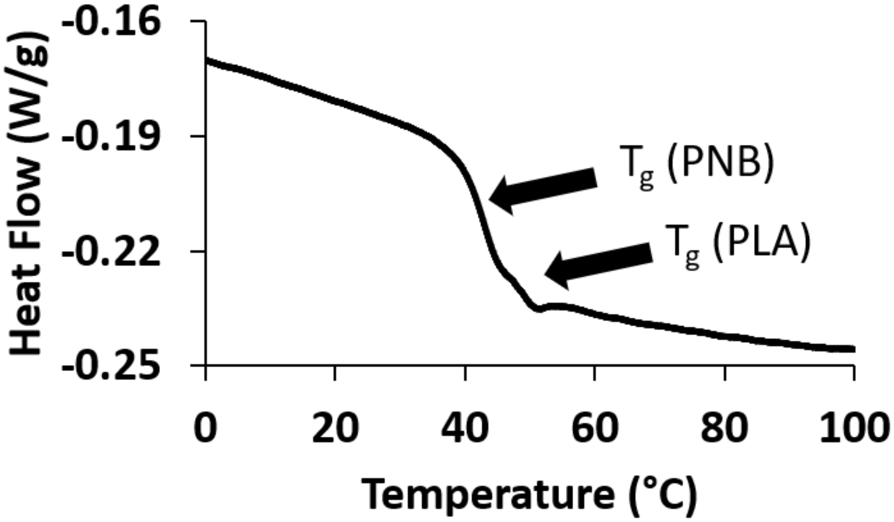


Figure S30. DSC (Exo up) of PTMC-b-PNB (entry 2 from Table 2)

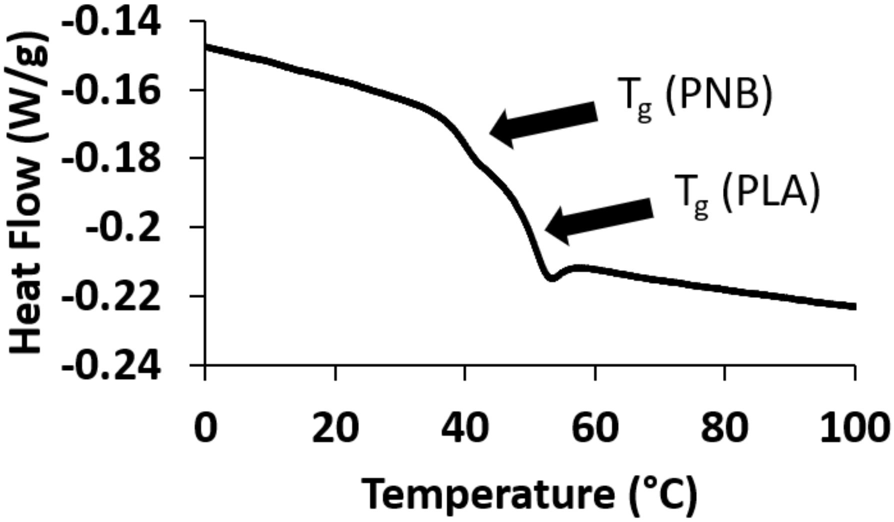


Figure S31. DSC of PTMC-b-PNB (entry 3 from Table 2)

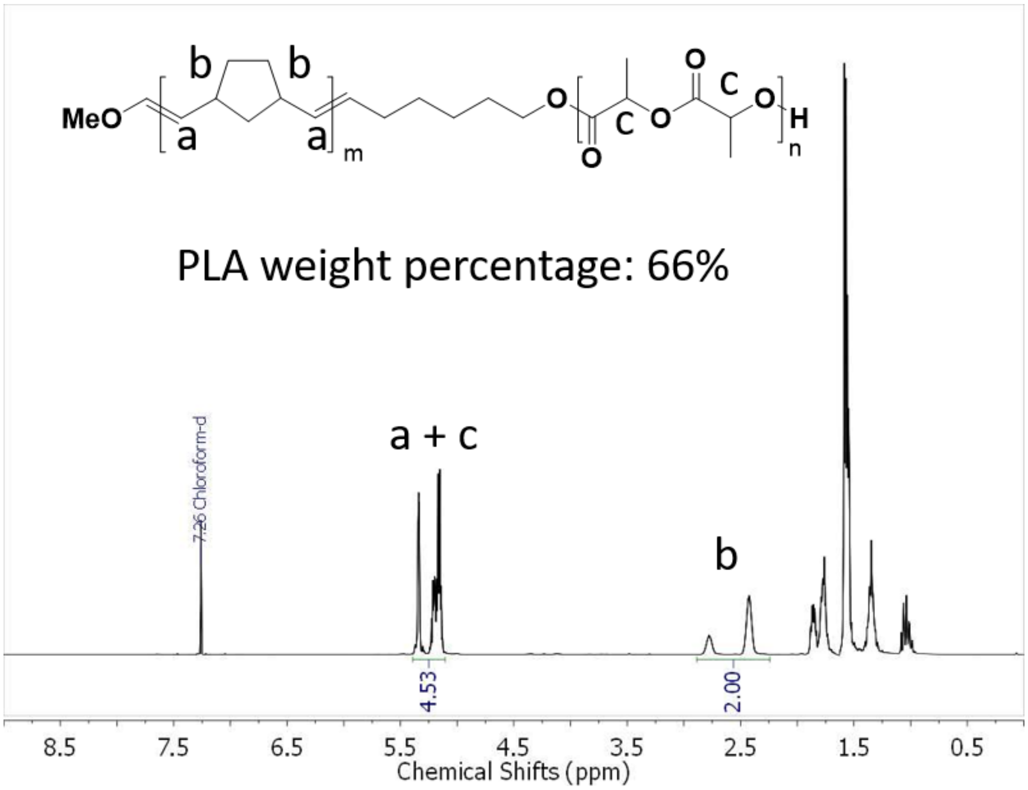


Figure S32. ^{1}H-NMR spectrum of PLA-b-PNB (entry 4 from Table 2)

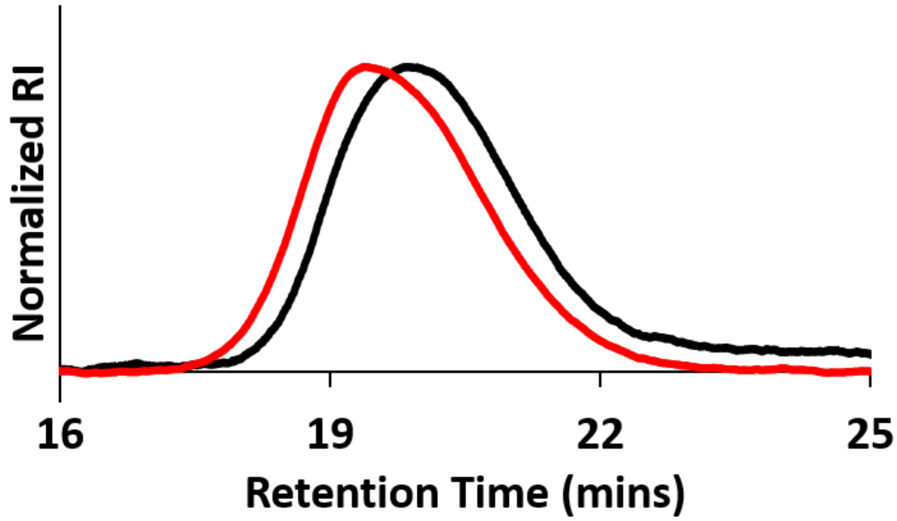


Figure S33. SEC chromatograms of PLA-b-PNB (entry 4 from Table 2, red line) and corresponding macroinitiator (black line)

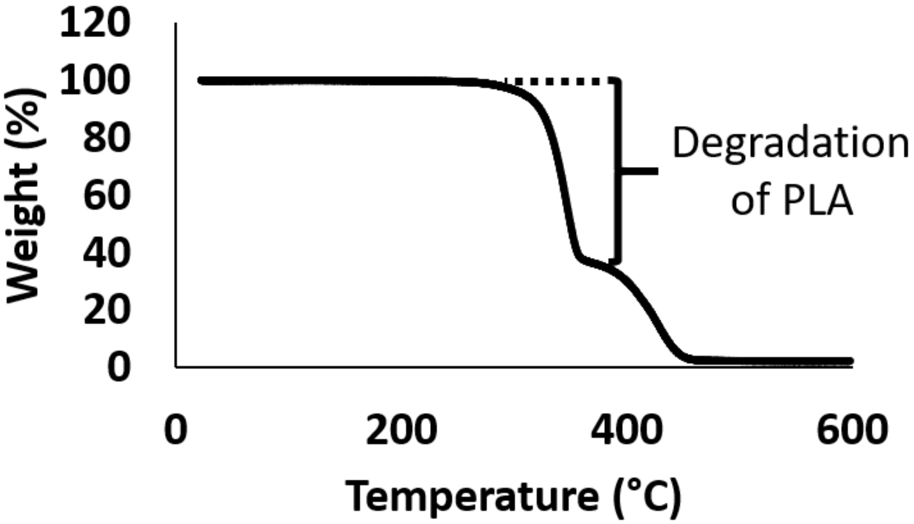


Figure S34. Thermogravimetric analysis of PLA-b-PNB (entry 4 from Table 2). The weight percentage of PLA block is around 64%.

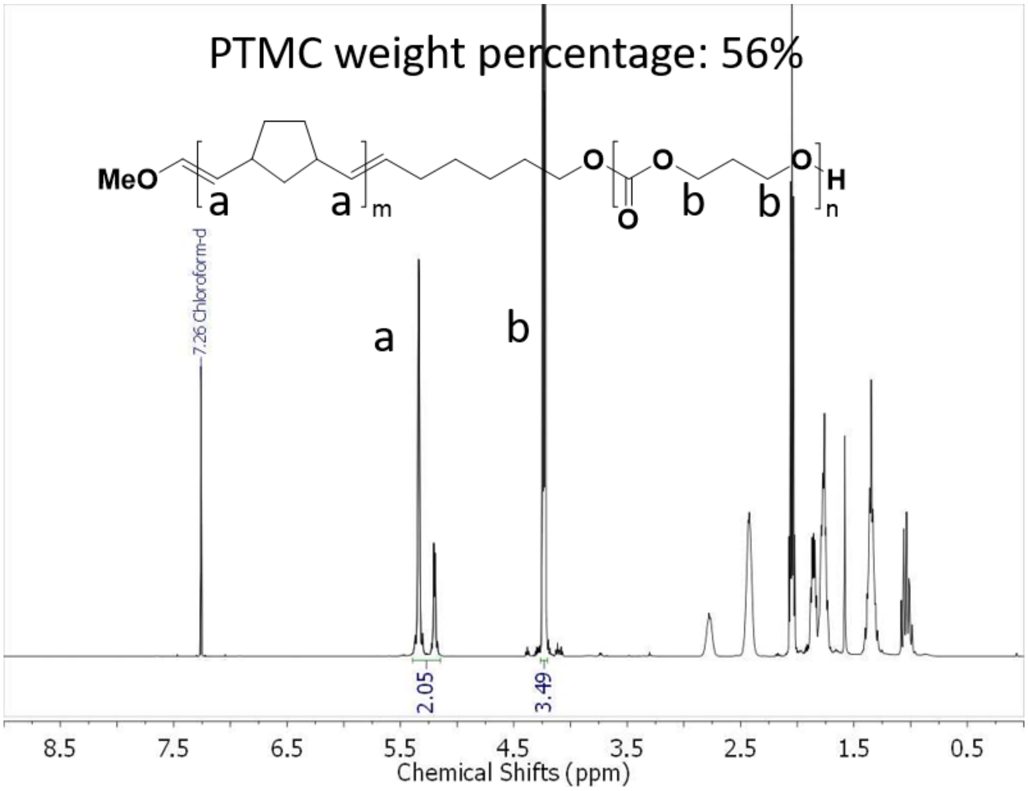


Figure S35. ^{1}H-NMR spectrum of PTMC-b-PNB (entry 5 from Table 2)

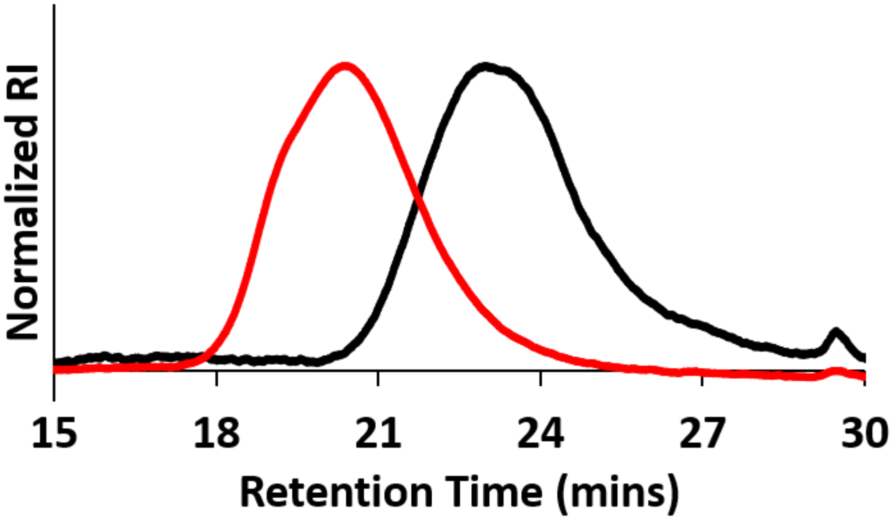


Figure S36. SEC chromatograms of PTMC-b-PNB (entry 5 from Table 2, red line) and corresponding macroinitiator (black line)

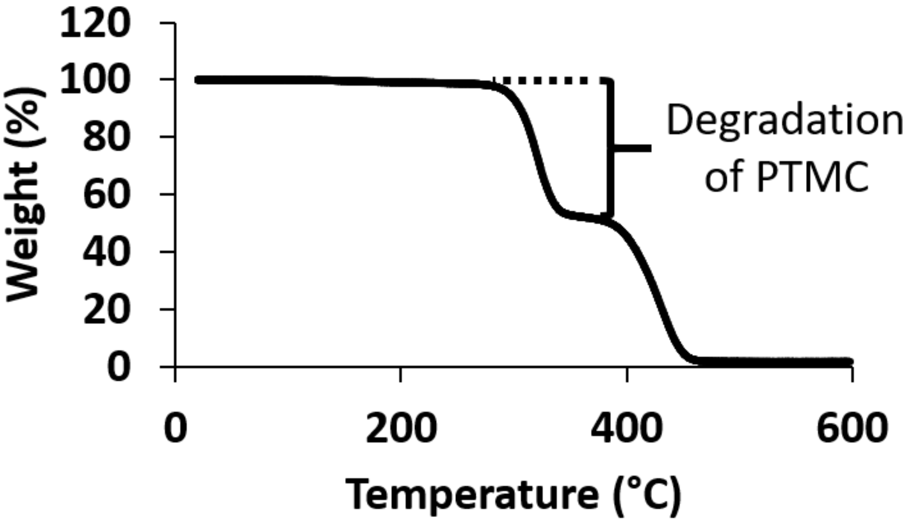


Figure S37. Thermogravimetric analysis of PLA-b-PNB (entry 5 from Table 2). The weight percentage of PTMC block is around 50%.

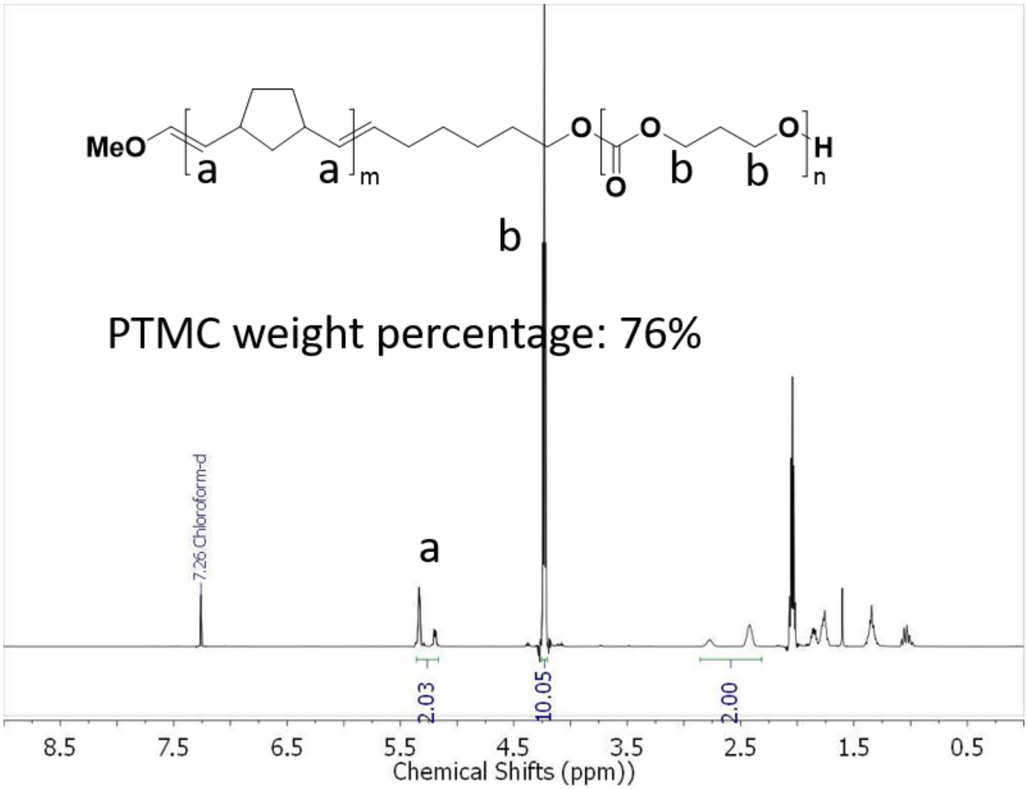


Figure S38. ^{1}H-NMR spectrum of PTMC-b-PNB (entry 6 from Table 2)

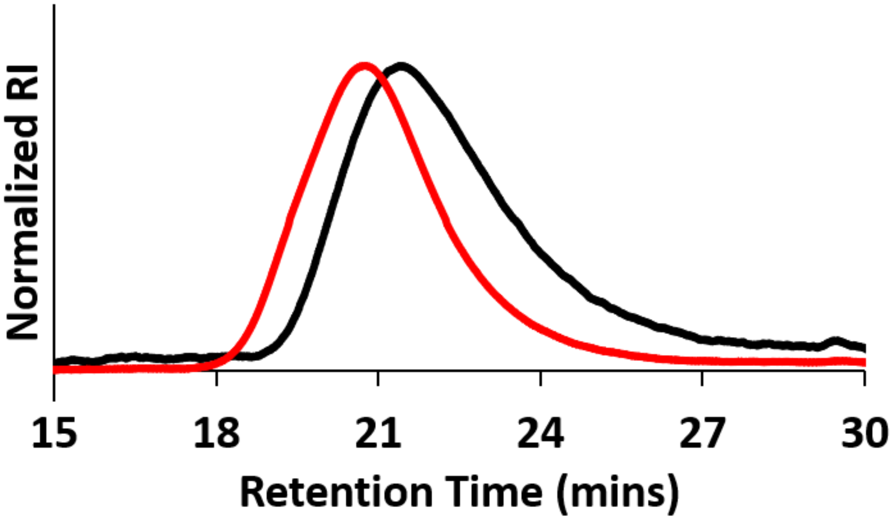


Figure S39. SEC chromatograms of PTMC-b-PNB (entry 6 from Table 2, red line) and corresponding macroinitiator (black line)

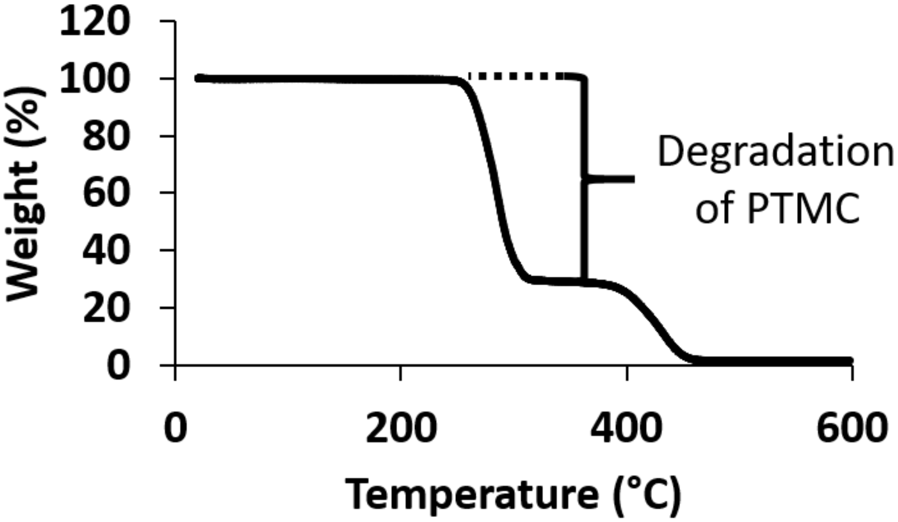


Figure S40. Thermogravimetric analysis of PTMC-b-PNB (entry 6 from Table 2). The weight percentage of PTMC block is around 71%.

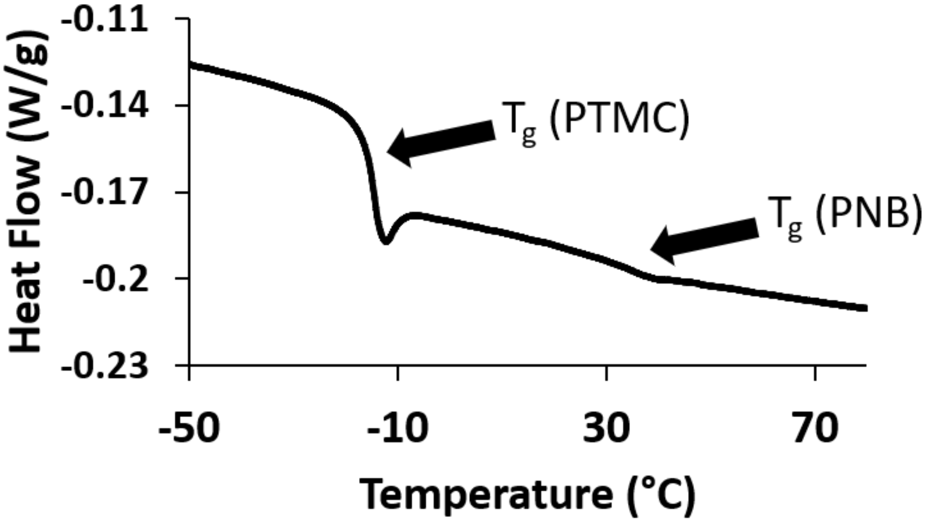


Figure S41. DSC (Exo up) of PTMC-b-PNB (entry 6 from Table 2)

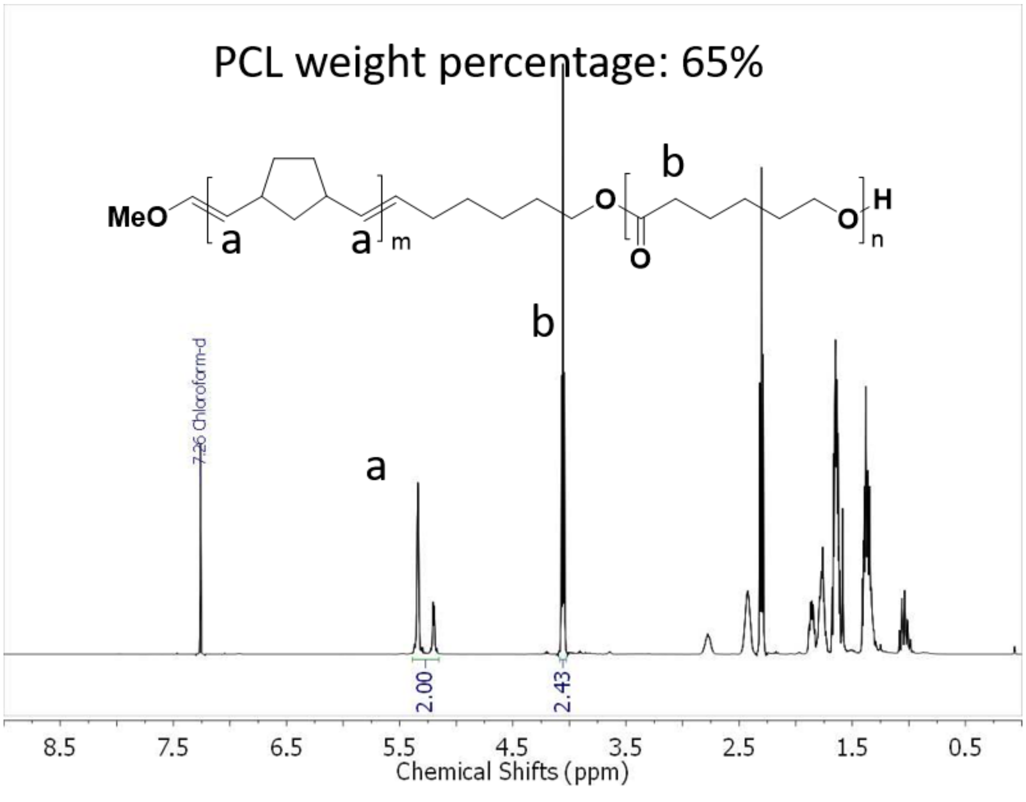


Figure S42. ^{1}H-NMR spectrum of PTMC-b-PNB (entry 7 from Table 2)

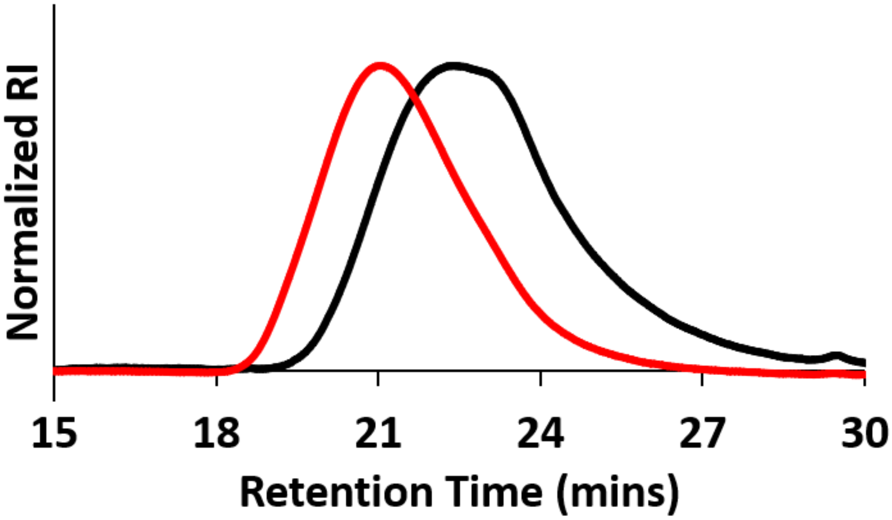


Figure S43. SEC chromatograms of PCL-b-PNB (entry 7 from Table 2, red line) and corresponding macroinitiator (black line)

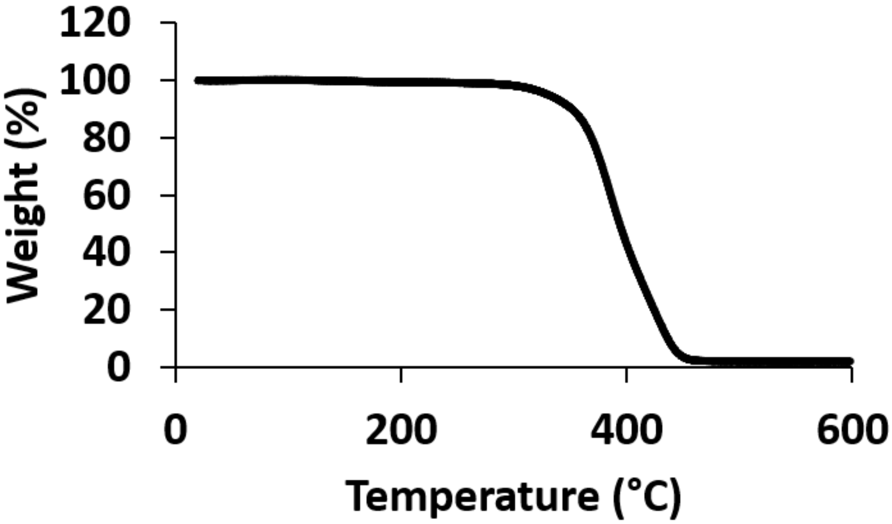


Figure S44. Thermogravimetric analysis of PCL-b-PNB (entry 7 from Table 2)

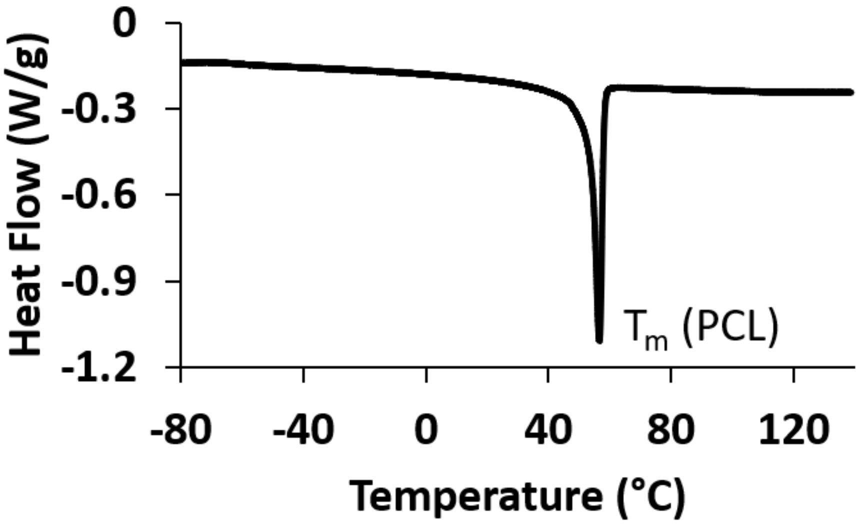


Figure S45. DSC of PCL-b-PNB (entry 7 from Table 2)

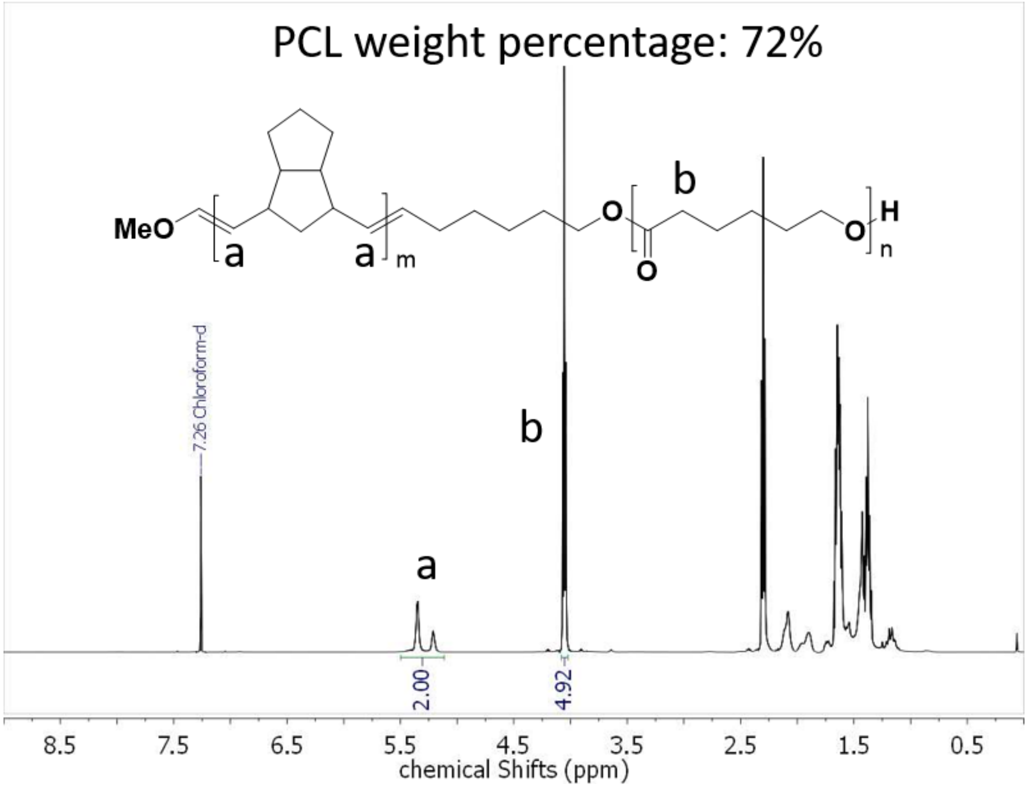


Figure S46. ^{1}H-NMR spectrum of PCL-b-PDCPD-H2 (entry 8 from Table 2)

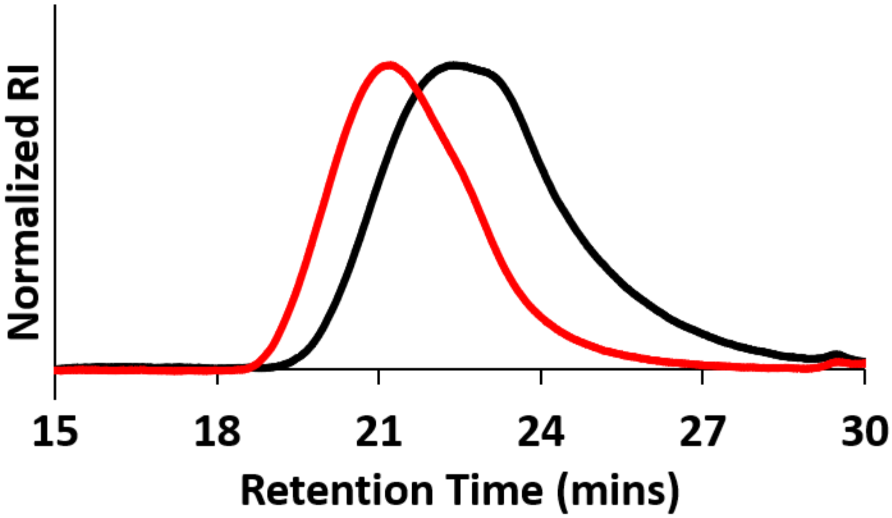


Figure S47. SEC chromatograms of PCL-b-PDCPD-H2 (entry 8 from Table 2, red line) and corresponding macroinitiator (black line)

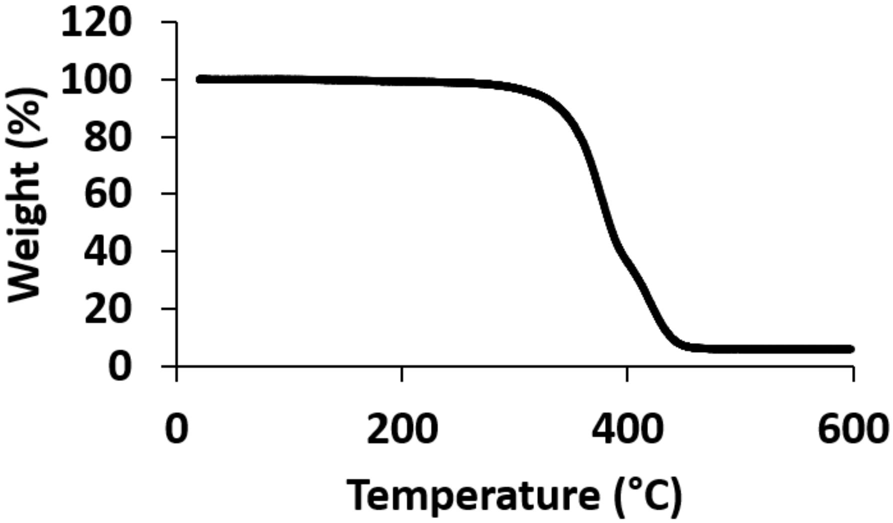


Figure S48. Thermogravimetric analysis of PCL-b-PDCPD-H2 (entry 8 from Table 2)

Notes and references

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