

## *Supporting Information*

### **Organocatalytic and Chemoselective Polymerization of Multivinyl-Functionalized $\gamma$ -Butyrolactones**

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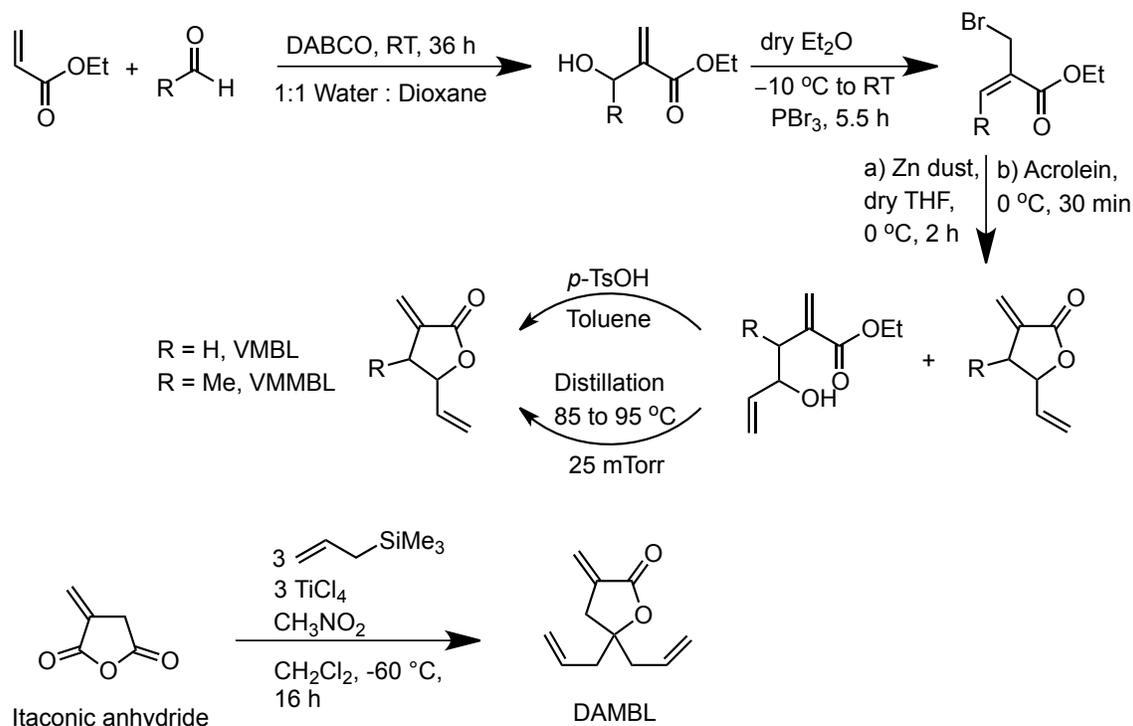
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#### **Part A. Experimental Details**

**Materials, Reagents, and Methods.** All syntheses and manipulations of air- and moisture-sensitive reagents and materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an inert gas (Ar or N<sub>2</sub>)-filled glovebox. NMR-scale reactions were conducted in Teflon-valve-sealed J. Young-type NMR tubes. HPLC-grade organic solvents were first sparged extensively with N<sub>2</sub> during filling 20 L solvent reservoirs and then dried by passage through activated alumina (for Et<sub>2</sub>O, THF, and CH<sub>2</sub>Cl<sub>2</sub>) followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. HPLC-grade DMF was degassed and dried over CaH<sub>2</sub> overnight, followed by vacuum distillation (CaH<sub>2</sub> was removed before distillation), and this procedure repeated twice before use. Benzene-*d*<sub>6</sub> and toluene-*d*<sub>8</sub> were dried over sodium/potassium alloy and vacuum-distilled or filtered, whereas CD<sub>2</sub>Cl<sub>2</sub>, CDCl<sub>3</sub>, CF<sub>3</sub>COOD, and DMSO-*d*<sub>6</sub> were dried over activated Davison 4 Å molecular sieves. NMR spectra were recorded on a Varian Inova 300 (300 MHz, <sup>1</sup>H; 75 MHz, <sup>13</sup>C), 400, or 500 MHz spectrometer. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C spectra were referenced to internal solvent resonances and are reported as parts per million relative to SiMe<sub>4</sub>.

Itaconic anhydride, 1,4-diazabicyclo[2.2.2]octane, acetaldehyde, dioxane, nitromethane, and acrolein were purchased from Alfa Aesar Chemical Co. Allyl magnesium bromide, allyl(trimethyl)silane, titanium(IV) chloride, and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from Acros Organics Chemical Co. Ethyl acrylate, zinc dust, phosphorus tribromide, formaldehyde (37 wt. % in H<sub>2</sub>O),  $\alpha,\alpha'$ -azobisisobutyronitrile (AIBN), 4-*tert*-butylbenzylmercaptan, 1-adamantanethiol, and 2,2,6,6-tetramethylpiperidine (TMP) were purchased from Sigma-Aldrich Chemical Co. Monomers ( $\gamma$ -vinyl- $\alpha$ -

methylene- $\gamma$ -butyrolactone (VMBL),<sup>1</sup>  $\gamma$ -vinyl- $\beta$ -methyl- $\alpha$ -methylene- $\gamma$ -butyrolactone (VMMBL),<sup>1</sup> and  $\gamma$ -diallyl- $\alpha$ -methylene- $\gamma$ -butyrolactone (DAMBL)<sup>2</sup> were prepared according to literature procedures, except for VMMBL which was prepared using the adopted procedure with acetaldehyde as the starting material instead of formaldehyde, Scheme S1.



**Scheme S1.** Synthetic routes to three monomers VMBL, VMMBL, and DAMBL.

These three monomers were first degassed and dried over  $\text{CaH}_2$  overnight, followed by filtration in the glovebox; the purified monomers were stored inside a glovebox freezer at  $-30 \text{ }^\circ\text{C}$ . Butylated hydroxytoluene (BHT-H, 2,6-di-*tert*-butyl-4-methylphenol) was purchased from Alfa Aesar Chemical Co. and recrystallized from hexanes prior to use. NHC catalyst 1,3-di-*tert*-butylimidazolin-2-ylidene ( $I^t\text{Bu}$ ) was purchased from Strem Chemical Co., while 1,3-di-isopropyl-4,5-dimethylimidazolin-2-ylidene ( $I^i\text{Pr}$ ) was prepared according to a literature procedure.<sup>3</sup> All other above commercial reagents were used as received.

**General Polymerization Procedures.** Polymerizations were performed in 20 mL oven-dried glass reactors inside the glovebox under ambient conditions (~23 °C). For polymerizations of VMBL, a predetermined volume of I'Bu stock solution in DMF (5.00 mmol, 0.60 mL, 3.36  $\mu$ mol for a run with 600 equiv. VMBL relative to I'Bu) was diluted with DMF to a total volume of 4.5 mL. The polymerization was started by rapid addition of a DMF solution of I'Bu into the pre-weighed VMBL (0.25 g, 2.01 mmol  $\gamma$ -VMBL, 600 equiv relative to I'Bu) containing reactor under vigorous stirring. The amount of monomer was fixed for all polymerizations, whereas the amount of the NHC catalyst was adjusted according to the [VMBL]/[I'Bu] ratio specified in the text. The polymerization of VMML and DAMBL was performed in the same fashion. In all cases, after the measured time interval, a 0.2 mL aliquot was taken from the reaction mixture *via* syringe and quickly quenched into a 1.5 mL septum cap sealed vial containing 0.6 mL of “undried” CDCl<sub>3</sub> stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by <sup>1</sup>H NMR to obtain monomer conversion data. The remaining bulk polymerization reaction was immediately quenched after the removal of the last aliquot by addition of 5 mL of 5% HCl-acidified methanol and precipitated into 100 mL of MeOH. The quenched mixture was stirred for 6 h, and the polymer produced was filtered and obtained as white powdery solid. The isolated polymer was washed with MeOH, pentanes, and dried in a vacuum oven at room temperature overnight to a constant weight.

**PVMBL.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  5.92 (b.s, 1H, -CH=CH<sub>2</sub>), 5.41–5.29 (b.m, 2H, -CH=CH<sub>2</sub>), 4.95 (b.s, 1H, OCH), 2.25 (b.s, 4H, CH<sub>2</sub>, main-chain and lactone ring). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>, 25 °C): 178.6 (C=O), 135.3 (CH=), 118.7 (=CH<sub>2</sub>), 77.6 (OCH), 46.3 (quaternary carbon), (CH<sub>2</sub>'s of main-chain and lactone ring; broad and obscured resonances due to overlapping with DMSO-*d*<sub>6</sub> not included).

**PVMML.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  6.33–5.77 (b.m, 1H, -CH=CH<sub>2</sub>), 5.38 (b.s, 2H, -CH=CH<sub>2</sub>), 4.87 (b.s, 1H, OCH), 3.58 (b.s, 1H, CH), 2.64–2.11 (b.s, 2H, CH<sub>2</sub>, main-chain), 0.98 (b.m, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>, 25 °C): 178.8 (C=O), 134.0 (CH=), 119.6 (=CH<sub>2</sub>), 82.1 (OCH), 46.6 (quaternary carbon), (CH<sub>2</sub> of main-chain and CH of lactone ring; broad and obscured resonances due to overlapping of DMSO-*d*<sub>6</sub> not included), 8.50 (CH<sub>3</sub>).

**PDAMBL.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta$  5.72 (b.s, 2H,  $-\text{CH}=\text{CH}_2$ ), 5.17 (b.s, 4H,  $-\text{CH}=\text{CH}_2$ ), 2.55–1.87 (b.m, 8H,  $\text{CH}_2$ , main-chain, lactone ring, and allyl).

**Post-Functionalization via the Thiol-Ene “Click” Reaction.** In a typical reaction by photoinitiation, 50 mg of PVMBL was dissolved in 5 mL of degassed  $\text{CHCl}_3$  inside a glovebox. The obtained homogeneous solution was charged in a 20 mL reactor containing a magnetic stirrer, 0.2 equiv of DMPA, and 5-10 equiv of a thiol as specified. Subsequently the capped reactor was removed from the glovebox, and placed in a photoreactor (Luzchem, LZC-4 photoreactor with a horizontal UVA lamp configuration, radiation centered at 350 nm) where it was stirred at room temperature for 5–10 h as specified in the text. An aliquot (0.1 mL) of the solution was withdrawn and quenched into 1.5 mL vials containing 0.6 mL of  $\text{CDCl}_3$  for conversion measurement by  $^1\text{H}$  NMR. The remaining mixture was precipitated into 150 mL of methanol and stirred over night; the off-white product was filtered, washed with methanol, and dried in a vacuum oven at 50 °C to a constant weight. For thermoinitiation, the above procedure was used with the following conditions: PVMBL (50 mg),  $\text{CHCl}_3$  (5 mL), AIBN (0.5 equiv), thiol (5–10 equiv), and at 60°C for 24 h (conventional heating with a thermoshaker).

**PVMBL-SR1.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta$  4.64 (b.s, 1H,  $\text{OCH}$ ), 2.66 (b.m, 2H,  $\text{SCH}_2\text{CH}_2$ ), 2.34–1.69 (b.m, 21H,  $\text{CH}_2$ –main-chain and lactone ring,  $\text{SCH}_2\text{CH}_2$ ,  $\text{CH}$ -adamantane,  $\text{CH}_2$ -adamantane).

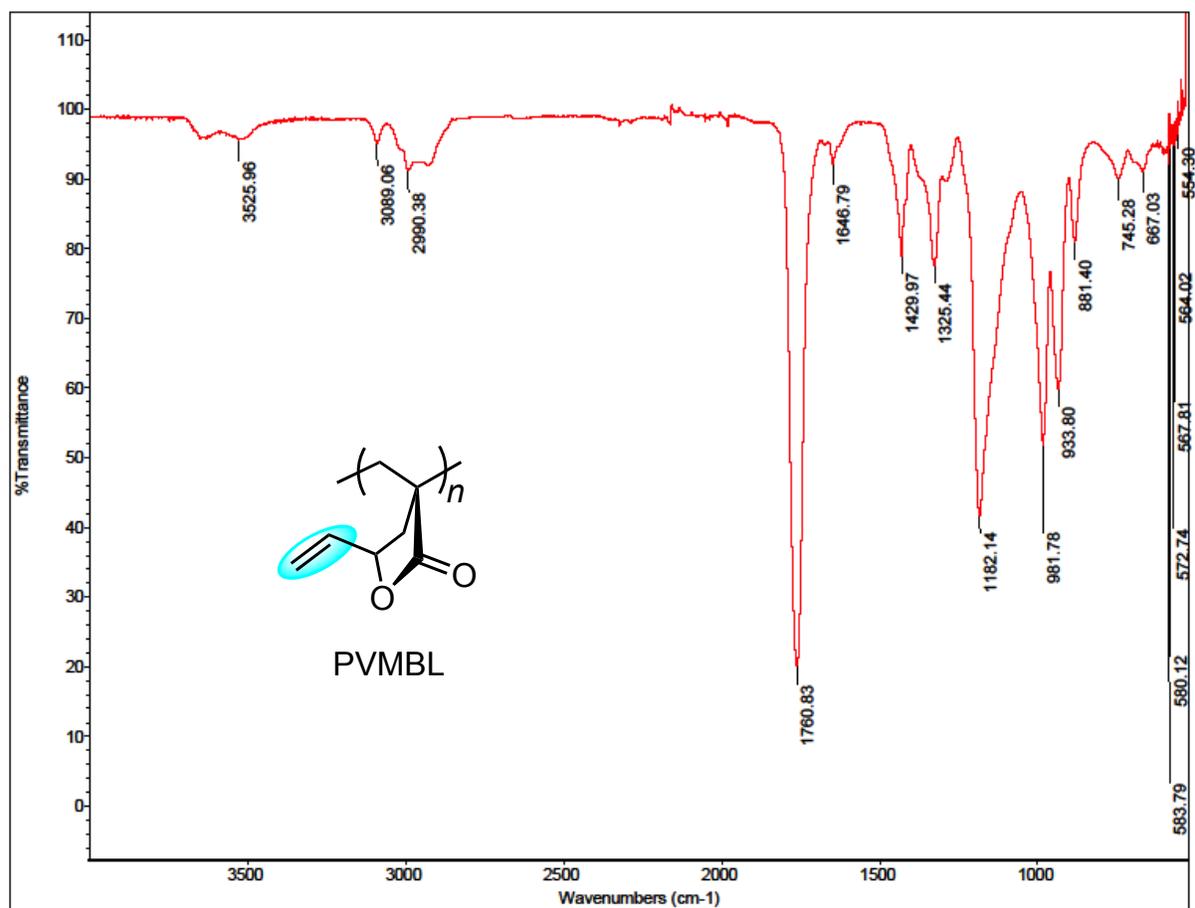
**PVMBL-SR2.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta$  7.29 (b.s, 2H, Ar H), 7.19 (b.s, 2H, Ar H), 4.61 (s, 1H,  $\text{OCH}$ ), 3.64 (b.s, 2H,  $\text{SCH}_2\text{Ar}$ ), 2.56 (b.s, 2H,  $\text{SCH}_2\text{CH}_2$ ), 2.33–1.69 (b.m, 6H,  $\text{CH}_2$ –main-chain and lactone ring,  $\text{SCH}_2\text{CH}_2$ ), 1.27 (s, 9H,  $t\text{Bu}$ ).

**Polymer Characterization.** Polymer number-average molecular weights ( $M_n$ ) and molecular weight distributions ( $D = M_w/M_n$ ) were measured by gel permeation chromatography (GPC) analyses carried out at 40 °C and a flow rate of 1.0 mL  $\text{min}^{-1}$ , with DMF as the eluent, on a Waters University 1500 GPC instrument equipped with four PLgel 5  $\mu\text{m}$  mixed-C columns (Polymer Laboratories; linear

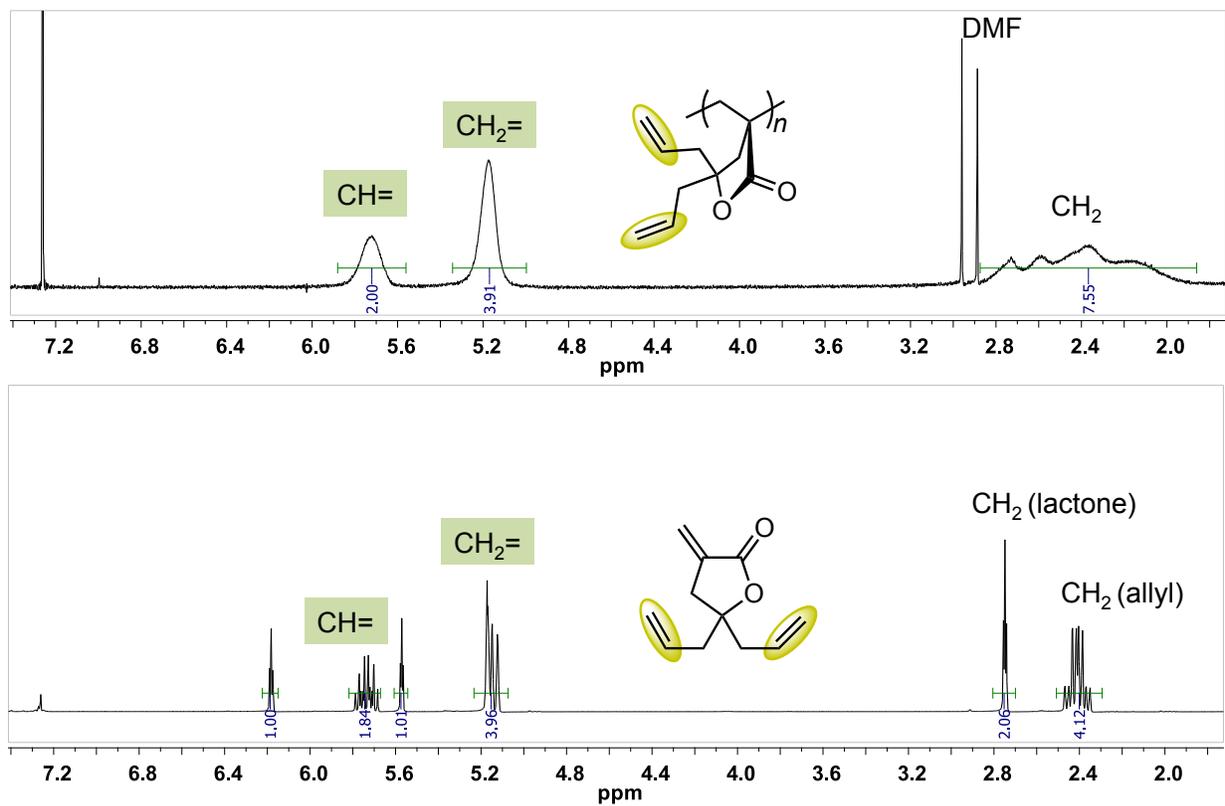
range of molecular weight = 200–2,000,000) and calibrated using 10 PMMA standards. Chromatograms were processed with Waters Empower software (version 2002).

Glass transition temperatures ( $T_g$ ) of the polymers were measured by differential scanning calorimetry (DSC) on a Q20 DSC, TA Instruments. Samples were first heated to a temperature below the polymer curing and decomposition onset temperatures at 10 °C/min, cooled to –50 °C at 10 °C/min, and then reheated to 450 °C at 10 °C/min. All  $T_g$  values were obtained from the second heating scan, after removing the thermal history, and are reported as half-height midpoints. Maximum rate decomposition temperatures ( $T_{max}$ ) and decomposition onset temperatures ( $T_{onset}$ ) of the polymers were measured by thermal gravimetric analysis (TGA) on a Q50 TGA Thermogravimetric Analyzer, TA Instrument. Polymer samples were heated from 20 °C to 700 °C at a rate of 10 °C/min. Values of  $T_{max}$  were obtained from derivative (wt %/°C) vs temperature (°C), while  $T_{onset}$  values (initial and end temperatures) were obtained from wt % vs temperature (°C) plots.

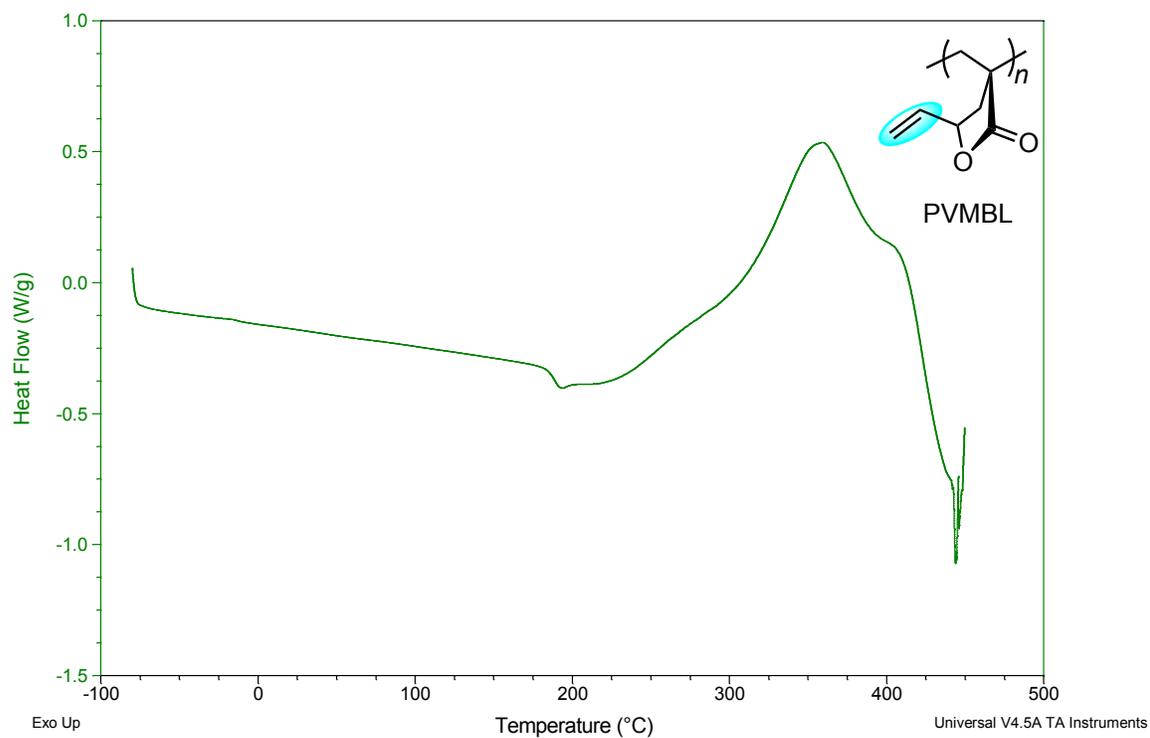
## Part B. Additional Figures



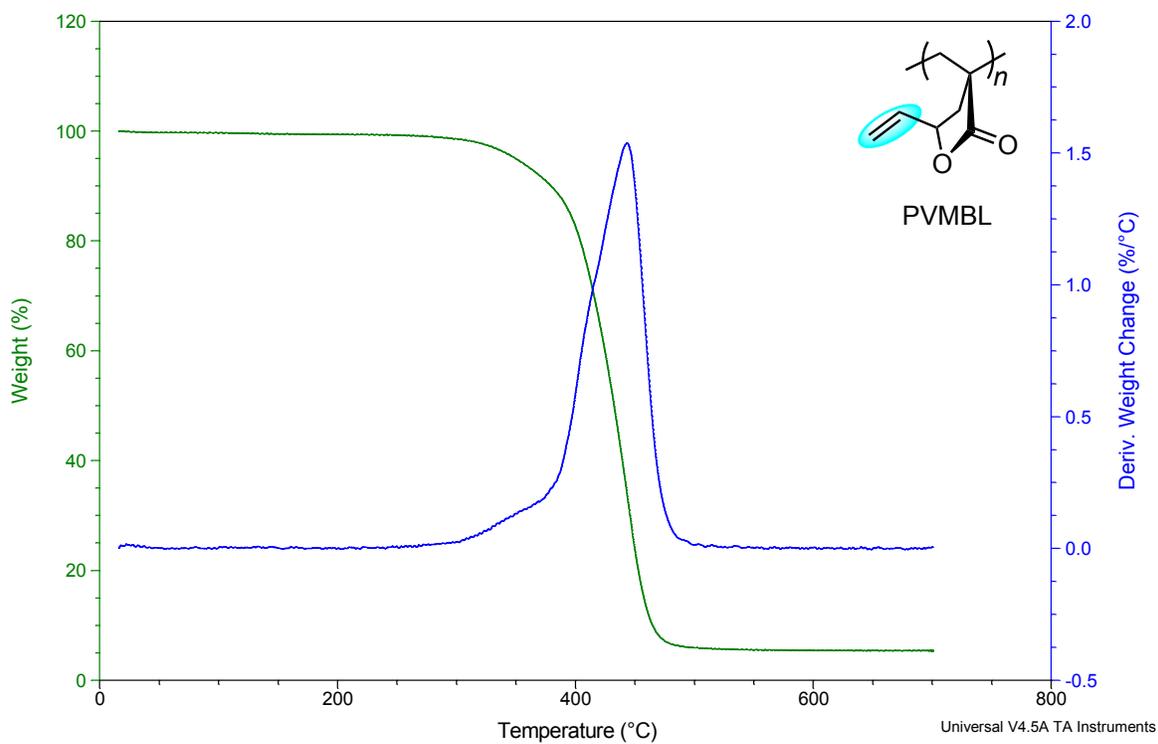
**Figure S1.** FT-IR spectrum of PVMBL (entry 1, Table 1).



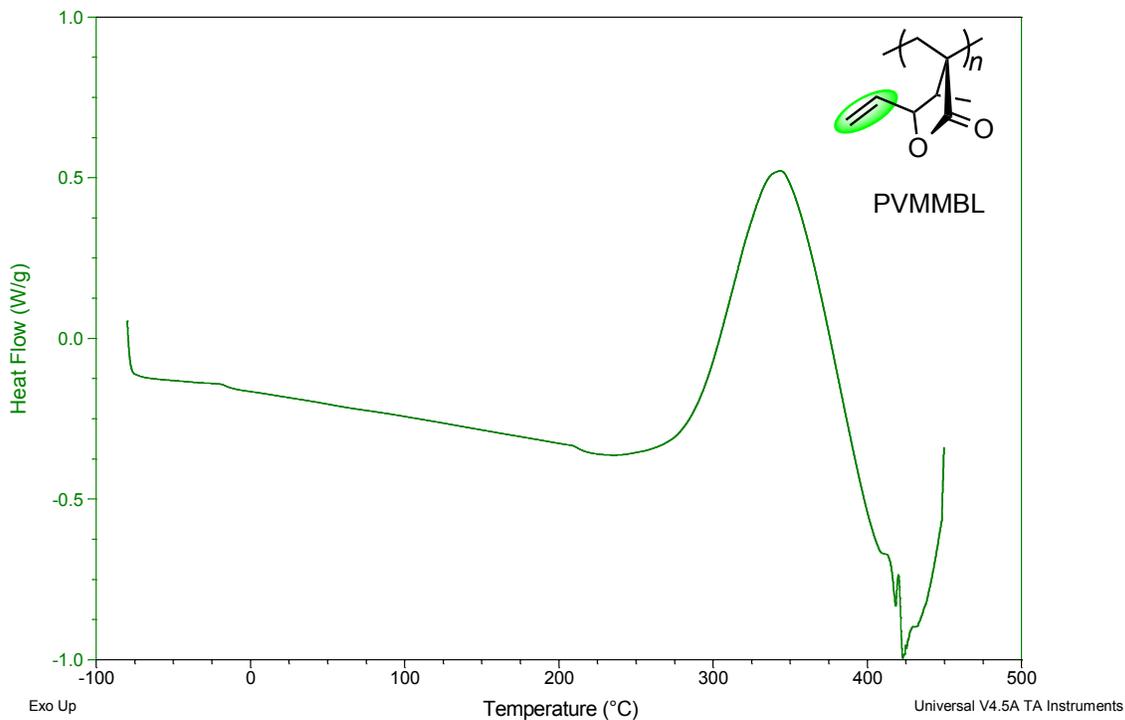
**Figure S2.** Overlay of <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectra of the monomer DAMBL and PDAMBL (entry 8, Table 1).



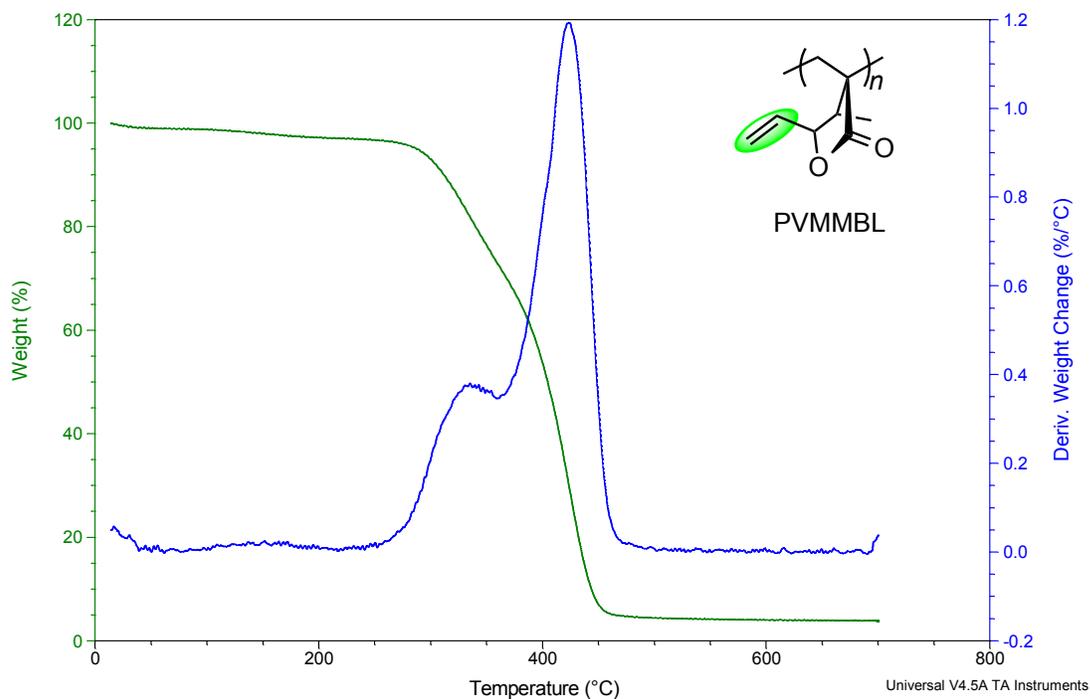
**Figure S3.** DSC trace of PVMBL (entry 1, Table 1).



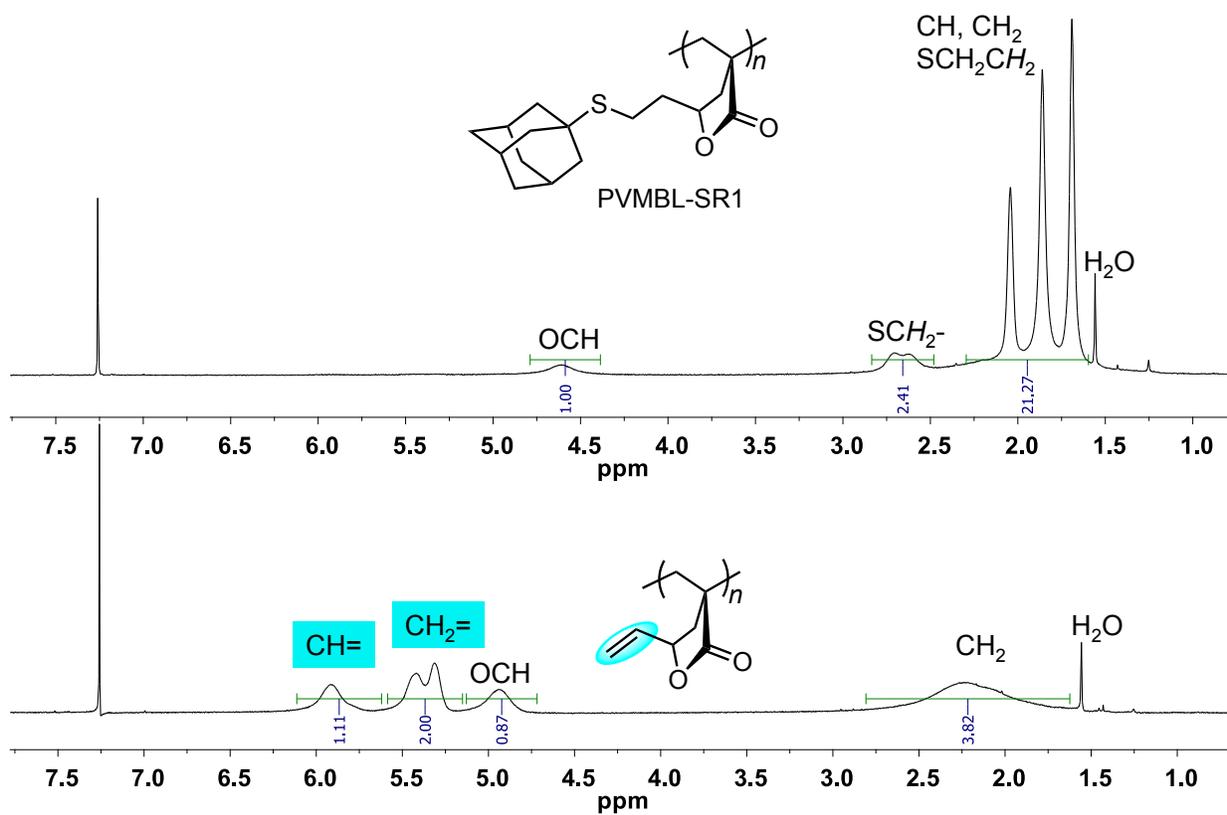
**Figure S4.** TGA trace of PVMBL (entry 1, Table 1).



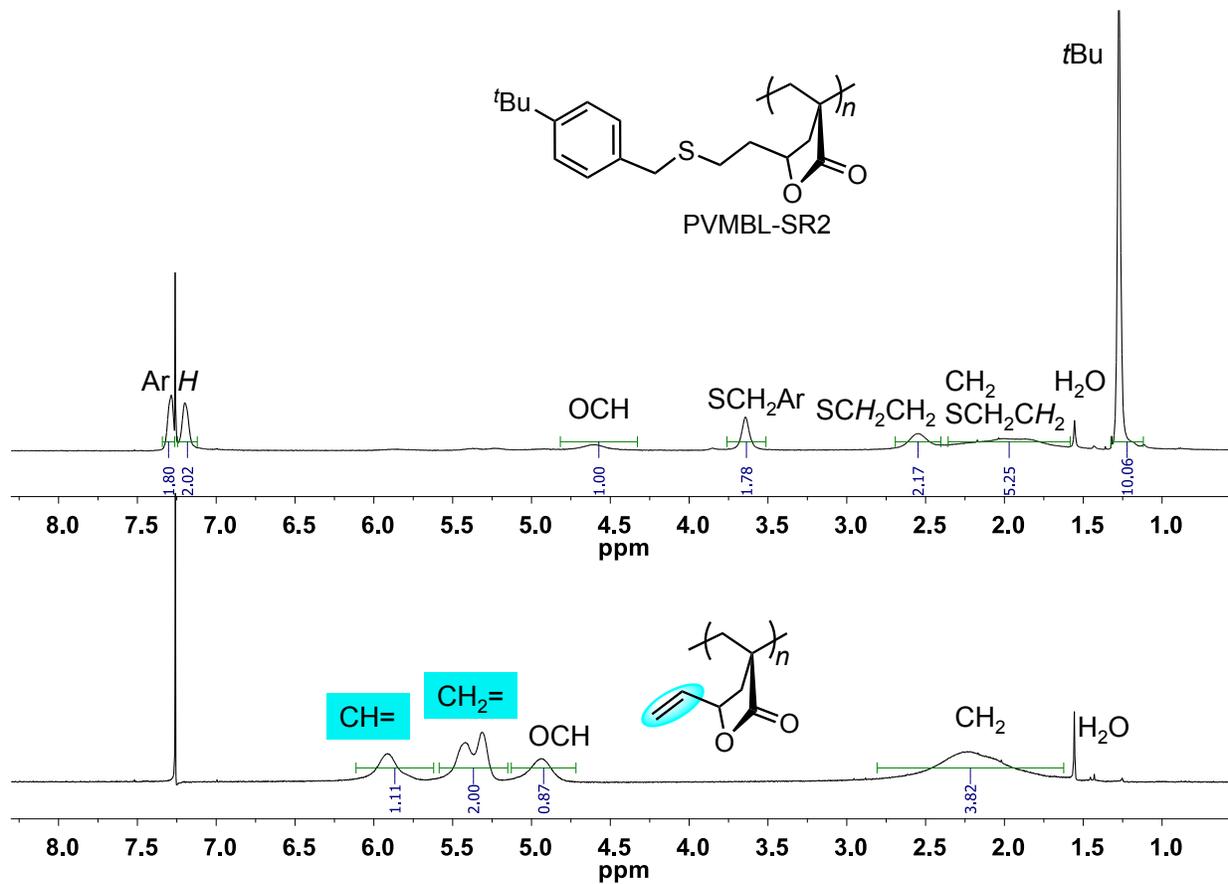
**Figure S5.** DSC trace of PVMMBL (entry 6, Table 1).



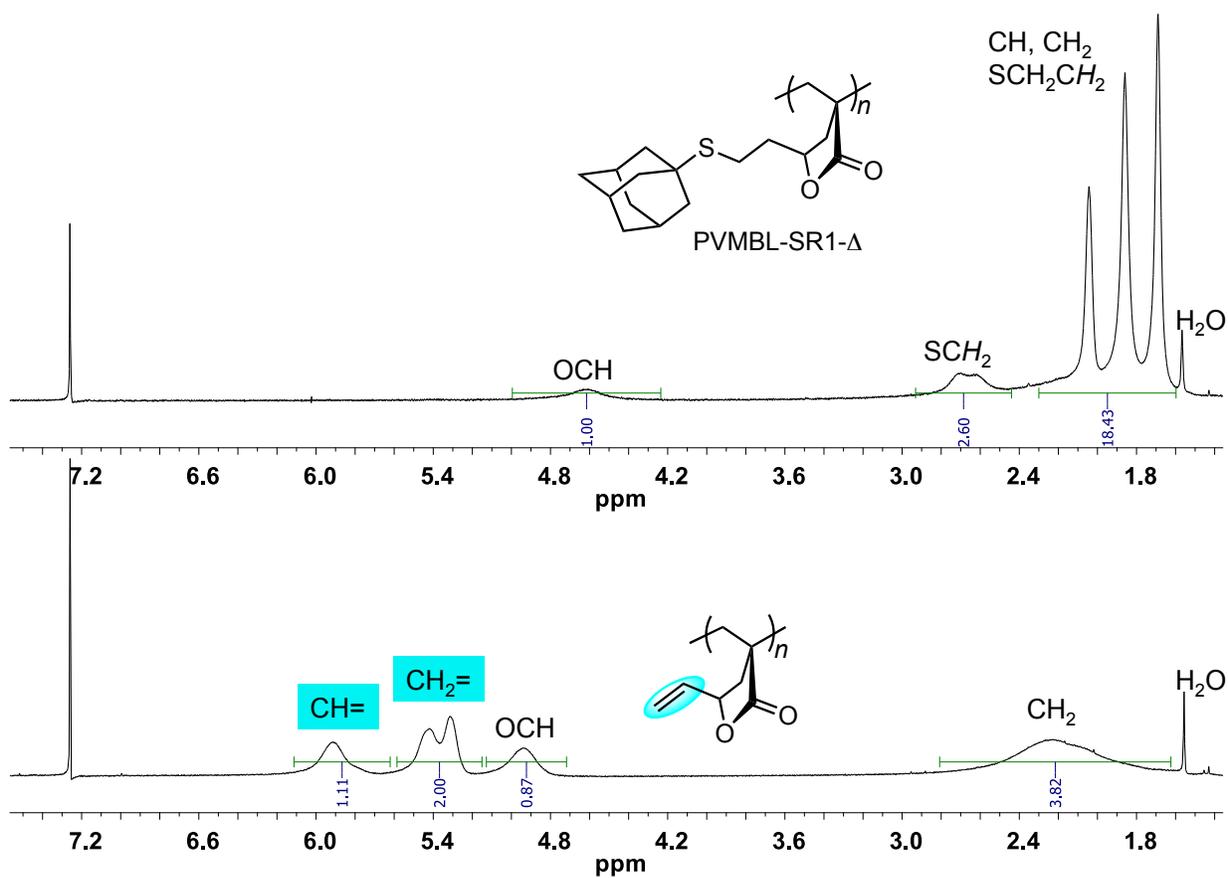
**Figure S6.** TGA trace of PVMMBL (entry 6, Table 1).



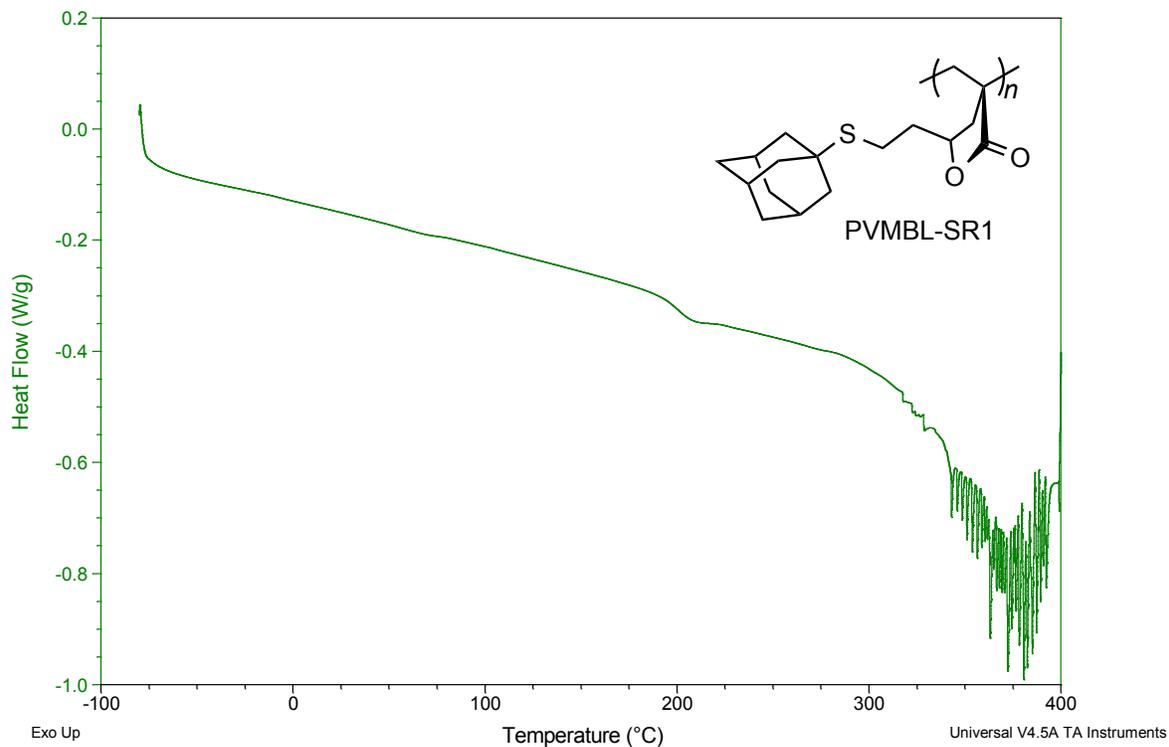
**Figure S7.** Overlay of <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectra of PVMBL and the post-functionalized polymer PVMBL-SR1 (via photoinitiation with DMPA).



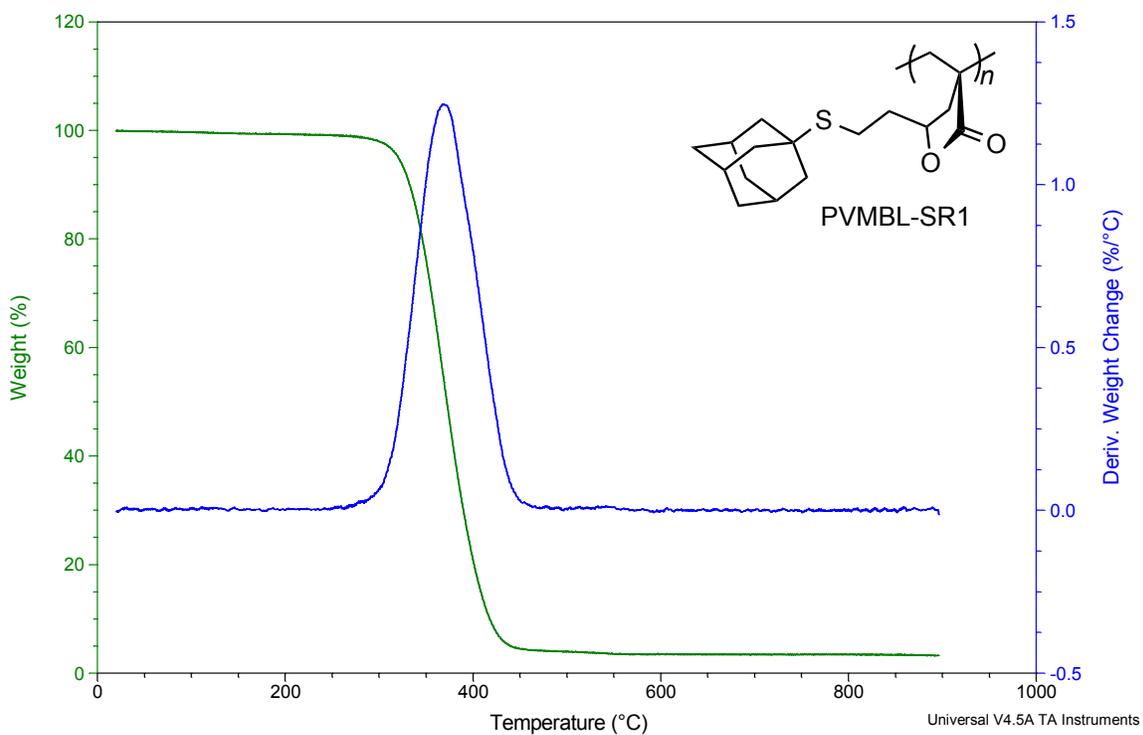
**Figure S8.** Overlay of <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectra of PVMBL and the post-functionalized polymer PVMBL-SR2 (via photoinitiation with DMPA).



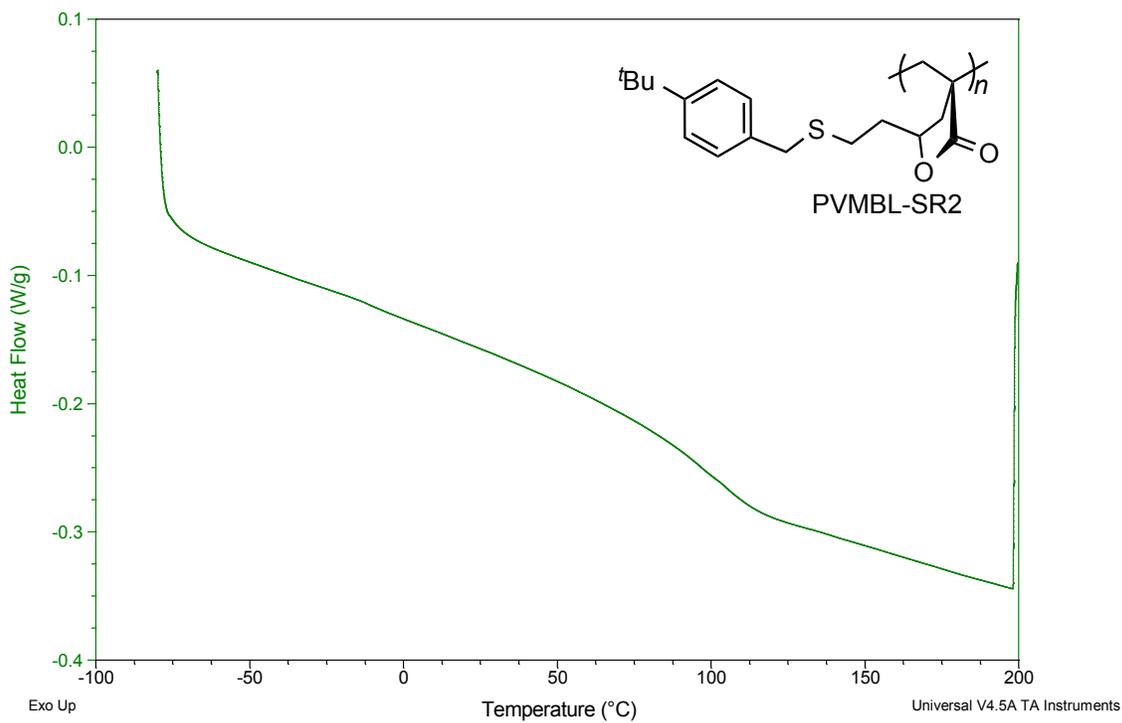
**Figure S9.** Overlay of  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 25 °C) spectra of PVMBL and the post-functionalized polymer PVMBL-SR1- $\Delta$  (via thermoinitiation with AIBN).



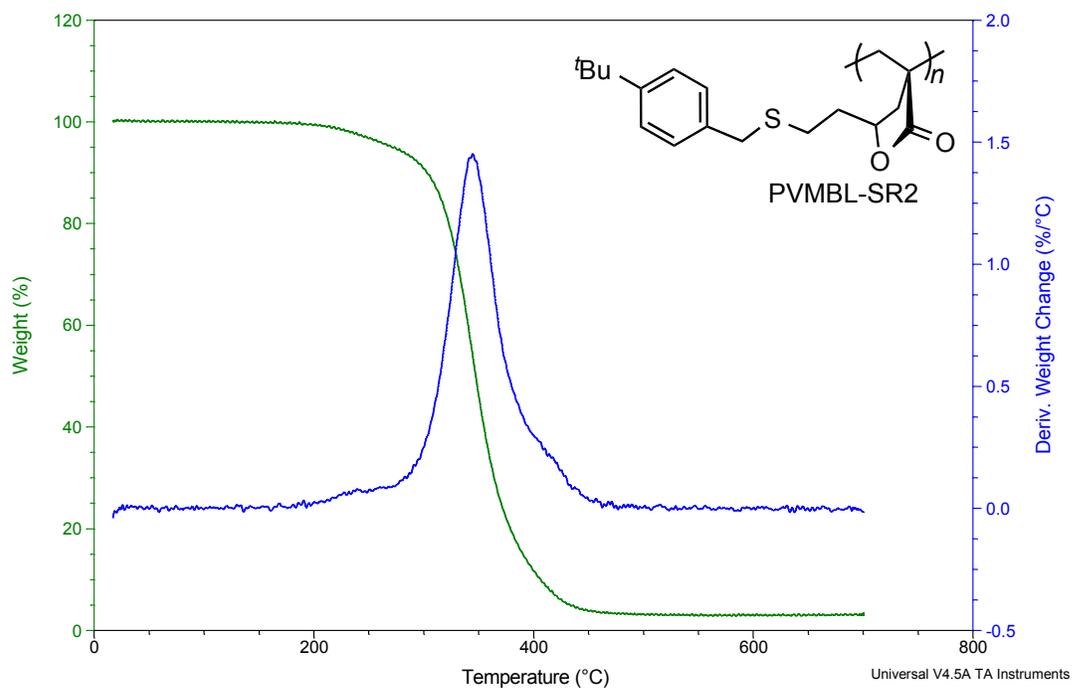
**Figure S10.** DSC trace of the post-functionalized polymer PVMBL-SR1.



**Figure S11.** TGA trace of the post-functionalized polymer PVMBL-SR1.



**Figure S12.** DSC trace of the post-functionalized polymer PVMBL-SR2.



**Figure S13.** TGA trace of the post-functionalized polymer PVMBL-SR2.

## References

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- (1) Sudhakar, G.; Satish, K.; Raghavaiah, J. *J. Org. Chem.* **2012**, *77*, 10010–10020.
- (2) (a) Michaut, M.; Santelli, M.; Parrain, J.-L. *J. Organomet. Chem.* **2000**, *606*, 93–96. (b) Pellissier, H.; Wilmouth, S.; Santelli, M. *Bull. Soc. Chim. Fr.* **1995**, *132*, 637–641.
- (3) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561–562.