

## Electronic Supplementary Information

### One stone two birds: From one azlactone-functionalized monomer to a heterofunctional diblock copolymer

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#### EXPERIMENTAL SECTION

**Materials.** All the reagents used in this study were purchased from Sigma-Aldrich, unless otherwise noted: 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, 98%), *tert*-butyl hydroperoxide (tBHP, Alfa Aesar, 70 wt.% in water), benzoyl peroxide (BPO, Alfa Aesar, 97% dry wt., wet with 25% water), *N,N*-dimethyl aniline (DMA<sub>n</sub>, ≥ 99.5%), benzylamine (99%), allylamine (98%), aluminum oxide (activated, neutral, Brockmann I), ethanol (EtOH for HPLC, Fisher Chemical), tetrahydrofuran (THF, ACS reagent, ≥ 99.0%), *N,N*-dimethylformamide (DMF, 99.8%), diethyl ether, deuterated chloroform (CDCl<sub>3</sub>, Euriso-top, 99.8 % D, 0.03% TMS), deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>, Euriso-top, 99.8% D). *N,N*-dimethyl acrylamide (DMA, Sigma-Aldrich, 99%) was passed through an aluminum oxide column, 2-vinyl-4,4-dimethylazlactone (VDM) was synthesized according to literature procedure.<sup>1</sup>

#### Analytical techniques

**NMR spectroscopy.** <sup>1</sup>H Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-400 spectrometer operating at 400.16 MHz. The chemical shifts are reported in parts per million (ppm) relative to deuterated solvent resonances.

**Size Exclusion Chromatography (SEC).** The average molar masses (number-average molar mass  $M_n$ , weight-average molar mass  $M_w$ ) and dispersity ( $\mathcal{D} = M_w/M_n$ ) were measured by SEC using DMF (with 1 g/L LiBr) as an eluent, and carried out using a system equipped with an isocratic HPLC Pump Waters 1515, an autosampler Waters 2707 plus, one guard column PL gel 5 $\mu$ m, two columns PL gel 5 $\mu$ m mixed-D (the 3 columns are placed in an oven at 60 °C), a photodiode array detector Waters 2998 and a differential refractometer Waters 2414. The instrument operated at a flow rate of 1 mL.min<sup>-1</sup> and was calibrated with narrow linear poly(methyl methacrylate) (PMMA) standards between 900 g/mol<sup>-1</sup> and 304,000 g/mol<sup>-1</sup>. Samples were dissolved in a mixture of eluent/toluene (1000/1 v/v) then filtered with PTFE 0.22  $\mu$ m filters before analysis.

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<sup>1</sup> M. E. Levere, H. T. Ho, S. Pascual and L. Fontaine, *Polym. Chem.*, 2011, **2**, 2878–2887.

*FTIR spectroscopy.* Attenuated Total Reflectance (ATR) Fourier Transform Infra-Red (FT-IR) spectra were obtained using a Nicolet avatar 370 DTGS system. Spectra were obtained at regular time intervals in the MIR region of 4000–500  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$  (640 scans) and analyzed using OPUS software.

## Procedures

### *RAFT copolymerization of VDM and DMA (step 1).*

Into a bottom flask (#1) equipped with a stirring bar and a septum were placed BPO (0.065 g, 0.2 mmol) and THF (0.5 mL). The solution was degassed by bubbling argon for 20 min while stirring. Into a bottom flask (#2) equipped with a stirring bar and a septum was introduced DMA<sub>n</sub> (0.024 g, 0.2 mmol) with ethanol (0.5 ml) and the solution was degassed by bubbling argon for 20 min while stirring. Into a round bottom flask (#3) were introduced DDMAT (0.183 g, 0.5 mmol), VDM (0.353 g, 2.52 mmol) and DMA (2.150 g, 21 mmol) with ethanol (4 mL) and DMF (0.5 mL) used as internal standard. Then the solution was degassed by bubbling argon for 30 min while stirring. The mixtures (#1) and (#2) were injected with a degassed syringe in the round bottom flask (#3). The final mixture was placed in a regulated bath at 25 °C while stirring during 6h. Samples were withdrawn at  $t = 0$  and  $t = 6$  h and analyzed by  $^1\text{H}$  NMR to determine monomers conversion, by FTIR spectroscopy to assess azlactone stability, and by SEC. The final product (named P(DMA-*stat*-VDM)-TTC) was employed for post-polymerization modification using benzylamine without purification.

Monomers conversion by  $^1\text{H}$  NMR: > 99% for VDM and 93.6 % for DMA.

SEC analysis:  $M_w = 3,300$  g/mol,  $M_n = 2,500$  g/mol,  $\bar{D} = 1.3$ .

### *Post-polymerization modification of P(DMA-*stat*-VDM)-TTC with benzylamine (step 2, PPM1).*

Benzylamine (0.267 g, 2.5 mmol) was added in the solution of copolymer P(DMA-*stat*-VDM)-TTC (2.5 g, 2.5 mmol in azlactone units) previously synthesized (step 1). The solution was subsequently stirred at 25 °C for 2h. After post-polymerization modification, a sample was withdrawn for FT-IR and SEC analysis and the rest of mixture was stored in refrigerator for the next step.

SEC analysis:  $M_w = 4,200$  g/mol,  $M_n = 3,000$  g/mol,  $\bar{D} = 1.4$ .

### *Extension of P(DMA-*stat*-VDM/benzylamine)-TTC by RAFT polymerization of VDM and DMA (step 3).*

To the previous reaction mixture (from step 2) was added VDM (0.353 g, 2.52 mmol), DMA (2.150 g, 21 mmol) and ethanol (4 mL) and then degassed by bubbling argon during 30 min while stirring (flask #1). In another flask (#2) equipped with a stirring bar and a septum were placed BPO (0.065 g, 0.2 mmol) and THF (0.5 mL). The solution was degassed by bubbling argon for 20 min while stirring. Into a bottom flask (#3) equipped with a stirring bar and a septum DMA<sub>n</sub> (0.024 g, 0.2 mmol) was introduced with ethanol (0.5 mL) and degassed by bubbling argon for 20 min while stirring. The mixtures (#2) and (#3) were injected with a degassed syringe in the round bottom flask (#1) and a sample was withdrawn ( $t = 0$ ). The final mixture was placed in a bath regulated at 25 °C while stirring during 6 h. After 6 h, a sample was withdrawn and the rest of mixture was kept for post-polymerization modification.

Samples withdrawn at  $t = 0$  and  $t = 6$  h were analyzed by NMR  $^1\text{H}$  spectroscopy to determine monomers conversion. The withdrawn sample at  $t = 6$  h was used for FT-IR and SEC analyses.

Monomers conversion by  $^1\text{H}$  NMR analysis:  $> 99\%$  for VDM and  $90\%$  for DMA.

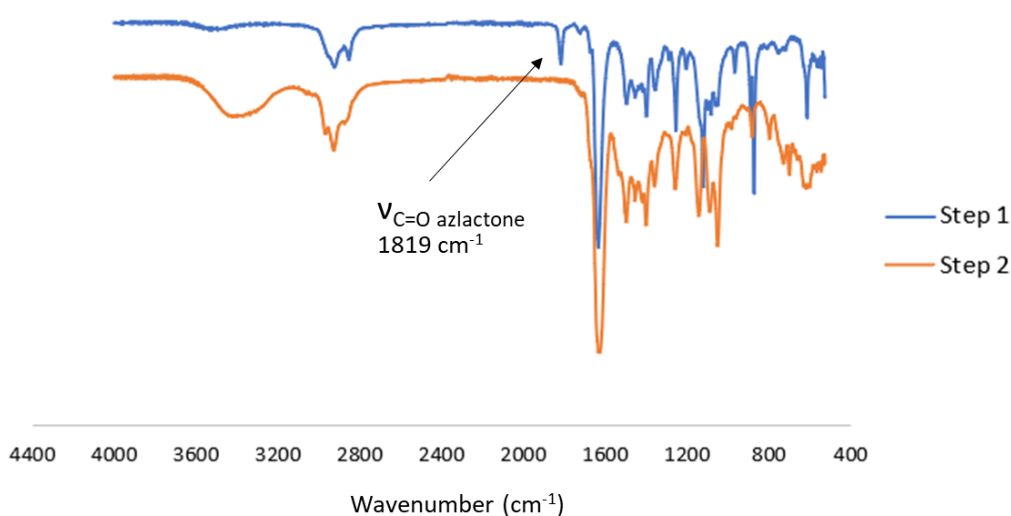
SEC analysis:  $M_w = 8,200$  g/mol,  $M_n = 6,000$  g/mol,  $\mathcal{D} = 1.4$ .

*Post-polymerization modification of P((DMA-stat-VDM/benzylamine)-b-P(DMA-stat-VDM))-TTC with allylamine (step 4, PPM2).*

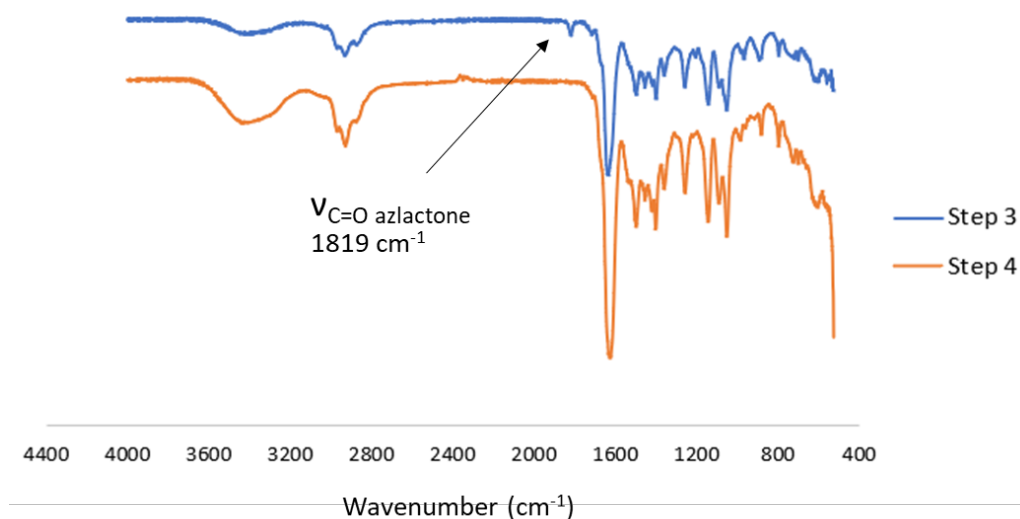
To the previous reaction mixture of P((DMA-stat-VDM/benzylamine)-b-P(DMA-stat-VDM))-TTC copolymer (step 3) (5.1 g, 2.5 mmol in azlactone units), allylamine (0.142 g, 2.5 mmol) was added and the resulting mixture was subsequently stirred at  $25\text{ }^\circ\text{C}$  for 2 h. After post-polymerization modification, the copolymer was isolated by precipitation in diethyl ether, filtration and was dried under vacuum at room temperature. The dried copolymer was analyzed by  $^1\text{H}$  NMR spectroscopy, FT-IR spectroscopy and SEC.

SEC analysis:  $M_w = 8,600$  g/mol,  $M_n = 6,300$  g/mol,  $\mathcal{D} = 1.4$ .

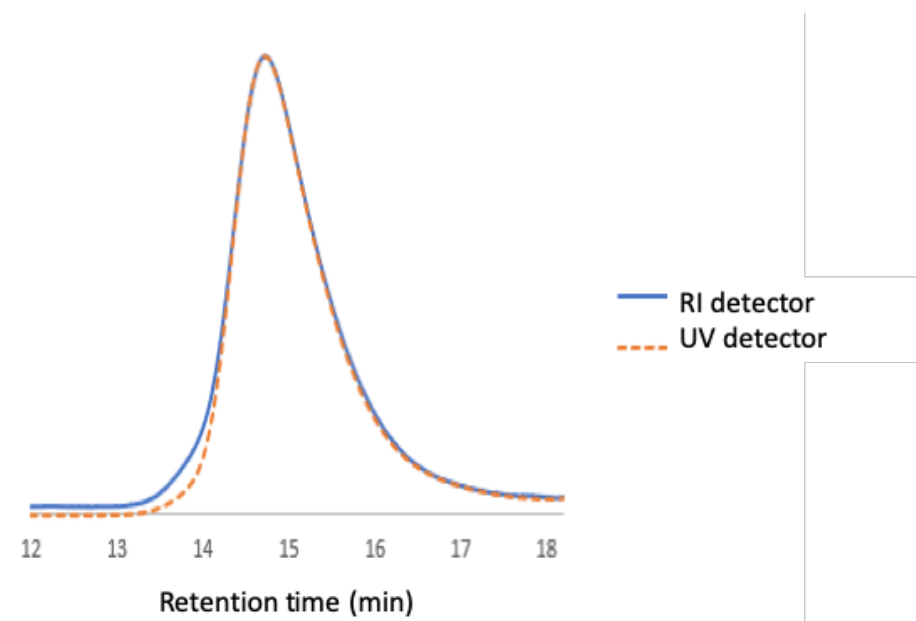
## ADDITIONAL FIGURES



**Figure S1:** Comparison of the FT-IR spectra of P(DMA-*stat*-VDM)-TTC copolymer before (blue trace) and after (orange trace) reaction with one equivalent of benzylamine (P(DMA-*stat*-VDM/benzylamine)-TTC copolymer from PPM1).



**Figure S2:** Comparison of the FT-IR spectra of P(DMA-*stat*-VDM/benzylamine)-*b*-P(DMA-*stat*-VDM)-TTC copolymer before reaction with one equivalent of allylamine (blue trace) and purified P(DMA-*stat*-VDM/benzylamine)-*b*-P(DMA-*stat*-VDM/allylamine)-TTC copolymer after PPM2 reaction (orange trace).



**Figure S3:** SEC traces using RI (blue trace) and UV detection (@309 nm, orange trace) of the final copolymer (step 4): P(DMA-*stat*-VDM/benzylamine)-*b*-P(DMA-*stat*-VDM)-TTC after PPM2 with allylamine (P(DMA-*stat*-VDM/benzylamine)-*b*-P(DMA-*stat*-VDM/allylamine)-TTC).