Supporting Information

High-Load, ROMP-Generated Oligomeric *Bis*-Acid Chlorides: Design of Soluble and Insoluble Nucleophile Scavengers

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Experimental Section

General Methods. All reactions were carried out under argon in oven-dried or flame-dried glassware unless stated otherwise. CH₂Cl₂ was purified by passage through the Solv-Tek purification system employing activated Al₂O₃. Thin layer chromatography was performed on silica gel 60F₂₅₄ plates (EM-5717, Merck). ¹H NMR spectra were recorded in CDCl₃ (unless stated otherwise) on a Bruker DRX-400 spectrometer operating at 400 MHz; or a Bruker Avance-500 spectrometer operating at 500 MHz and referenced to residual solvent protons. Capillary gas chromatography was performed on a Hewlett-Packard HP 6890 gas chromatograph.

ROMP Procedure for the generation of the oligomeric *bis*-acid chlorides (OBACs)

²⁰⁰OBAC₁₀₀ (2a): In a round-bottom flask, trans-bicyclo[2.2.1]hept-5-ene-2,3-dicarbonyl dichloride (1) (3.6 g, 16.4 mmol) was dissolved in degassed (argon) CH₂Cl₂ (164 mL). To this solution, was added the 2nd generation Grubbs metathesis catalyst (138 mg, 0.164 mmol). The reaction was refluxed under argon and monitored by TLC analysis. Once the polymerization was completed, the reaction was quenched with ethyl vinyl ether (3.0 mL) over a 30 min period. The mixture was reduced to 1/5th the original volume and added dropwise into 200 mL of dry Et₂O to induce precipitation. Subsequent filtration produced the²⁰⁰OBAC₁₀₀ 2a as a light-brown solid.

¹⁴⁰OBAC₄₀ (2b): In a round-bottom flask, trans-bicyclo[2.2.1]hept-5-ene-2,3-dicarbonyl dichloride (1) (3.0 g, 13.7 mmol) was dissolved in degassed (argon) CH₂Cl₂ (137 mL). To this solution, was added the 1st generation Grubbs metathesis catalyst (281 mg, 0.34 mmol). The reaction was refluxed under argon and monitored by TLC analysis. Once the polymerization was completed, the reaction was quenched with ethyl vinyl ether (3.0 mL) over a 30 min period. The mixture was reduced to 1/5th the original volume and added dropwise into 200 mL dry Et₂O to induce precipitation. The organic layer was decanted from the solid polymer. The polymer was washed with dry Et₂O (3x, 100 mL). An appropriate volume of DCM was added to produce stock solutions of¹⁴⁰OBAC₄₀ 2b.
General Procedure for Scavenging
In a small pyrex pressure tube, was added benzoyl chloride (1 equiv.) dropwise to a solution of base (5 equiv.) and the nucleophile (2 equiv.) in CH$_2$Cl$_2$ (0.5M) at RT. Reaction progress was monitored by GC analysis. Once complete, the OBAC reagent (40- or 100-mer, 1 equiv. for amines, and 2 equiv. for alcohols and thiols) was added (1GOBAC$_{40}$ was added as a stock solution while 2GOBAC$_{100}$ was added directly as a solid). Reaction temperatures varied on the nature of the nucleophilic species: amines (RT) alcohols and thiols (reflux). When utilizing 2GOBAC$_{100}$, the "scavenged" reaction mixture was directly diluted with EtOAc (5 mL) and filtered (SiO$_2$). When utilizing 1GOBAC$_{40}$ optimal results were obtained by concentrating the "scavenged" reaction mixture under reduced pressure first, then diluting with EtOAc (5 mL) and filtering (SiO$_2$). Both methods afforded the desired benzoylated products in high yields and purities. Purity levels were determined by GC and $^1$H NMR spectroscopy.

Competition Experiments
Commercially available, polystyrene-based isocyanate resin was purchased from Argonaut Technologies. Competition experiments with this isocyanate resin were carried out in an identical fashion as described above. (1) Amine scavenging: It was found that the OBAC scavengers (40- and 100-mer, 1 equiv.) were successful in removing excess amine from a reaction mixture between 15 and 30 minutes, while the commercially available isocyanate resin was successful in a slightly shorter time ~5 minutes, however two equivalents were necessary to facilitate complete scavenging. (2) Alcohol scavenging: It was found that the OBAC scavengers (40- and 100-mer, 2 equiv.) were successful in removing excess alcohol from a reaction mixture in two hours (reflux), while the commercially available isocyanate resin (4 equiv.) in the same time frame only scavenged ~80% of the alcohol (also at reflux). (3) Thiol scavenging: It was found that the OBAC scavengers (40- and 100-mer, 2 equiv.) and commercially available isocyanate resin (4 equiv.) were equally able to scavenge the excess thiols, requiring only two hours (reflux).
Amide 5a, Table 1, using $^{2}^{1}$OBAC$_{100}$: entry 1
Amide 5a, Table 1, using $^{25}$OBAC$_{100}$: entry 2
Amide 5a, Table 1, using $^{29}$OBAC$_{100}$: entry 3
Amide 5b, Table 1, using $^{2}$OBAC$_{100}$: entry 4
Amide 5c, Table 1, using $^{2}$GBOAC$_{100}$: entry 5
Amide 5d, Table 1, using $^{2}^{2}$OBAC$_{100}$: entry 6
Amide 5d, Table 1, using $^{2}$OBAC$_{100}$: entry 7
Amide 5e, Table 1, using $^{2}\text{GOBAC}_{100}$: entry 8
Amide 5e, Table 1, using $^{2}^{6}$OBAC$_{100}$: entry 9
Amide 5f, Table 1, using $^{2}^{10}$OBAC: entry 10
Amide 5g, Table 1, using $^{2^G}{\text{OBAC}}_{100}$: *entry II*
Amide 5h, Table 1, using $^{2^G\text{OBAC}}_{\text{100}}$: entry 12
Ester 6a, Table 2, using $^{29}$OBAC$_{100}$: entry 1
Ester 6b, Table 2, using $^{26}$OBAC$_{100}$: entry 2
Ester 6c, Table 2, using $^{29}$OBAC$_{100}$: entry 3
Ester 6d, Table 2, using $^{26}$OBAC$_{100}$: entry 4
Ester 6e, Table 2, using $^{2}$$^{2}$OBAC$_{100}$: *entry 5*
Ester 6f, Table 2, using $^{2}^{10}$OBAC\textsubscript{100}: entry 6
Ester 6g, Table 2, using $^{2}$GOBAC$_{100}$: entry 7
Ester 6h, Table 2, using $^{2}$GOBAC$_{100}$: entry 8
Thioester 7a, Table 3, using $^{20}$OBAC$_{100}$: entry 1
Thioester 7b, Table 3, using $^{26}$OBAC$_{100}$: entry 2
Thioester 7c, Table 3, using $^{20}$OBAC$_{100}$: entry 3
Amide 5a, Table 4, using $^{1}$OBAC$_{40}$: entry 1
Amide 5b, Table 4, using $^{13}$OBAC$_{40}$: entry 2
Amide 5c Table 4, using $^{13}$OBAC$_{\text{40}}$: entry 3
Amide 5d, Table 4, using $^{13}$OBAC$_{40}$: entry 4
Amide 5h, Table 4, using $^{13}$OBAC$_{40}$: entry 5
Amide 5h, Table 4, using $^{13}$C{OBAC}_{40}; entry 6
Amide 5f, Table 4, using $^{1}$OBAC$_{40}$: entry 7
Ester 6a, Table 4, using $^{13}$OBAC$_{40}$: entry 8
Ester 6g, Table 4, using $^{13}$OBAC$_{40}$: entry 9
Thioester 7a, Table 4, using $^{13}$OBAC$_{40}$: entry 10