Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Dynamic Polythioesters via Ring-Opening Polymerization of 1,4-thiazine-2,5-diones

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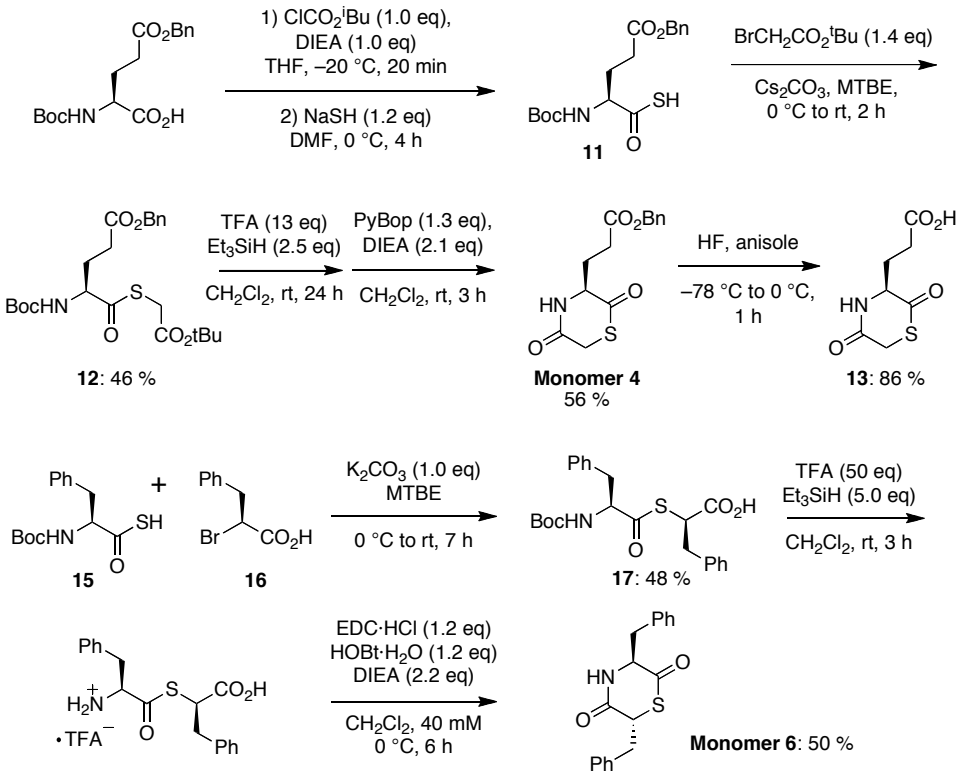
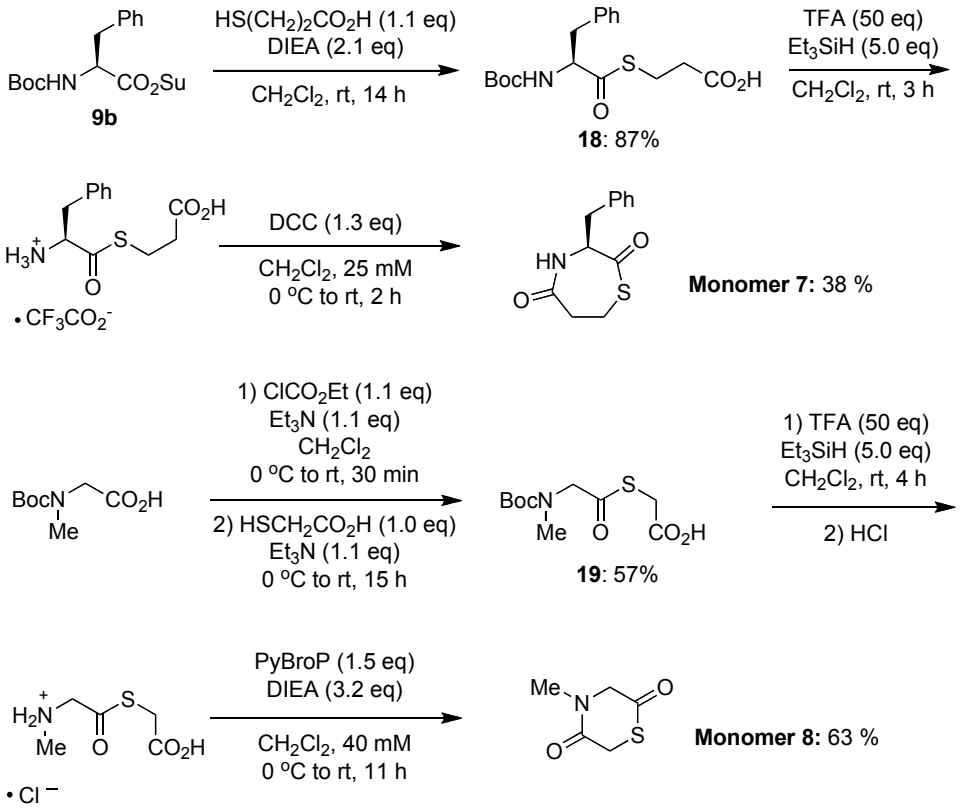
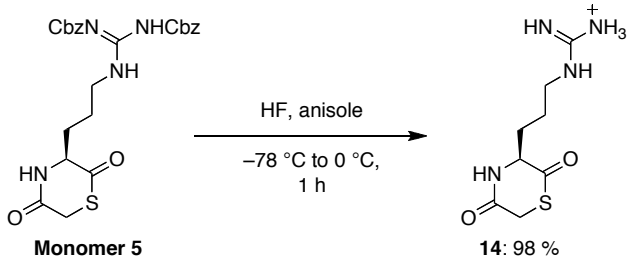


Scheme S1. Synthesis and deprotection of monomers **4** and **6**.



Scheme S2. Synthesis of monomers **7** and **8**.



Scheme S3. Deprotection of monomer **5**.

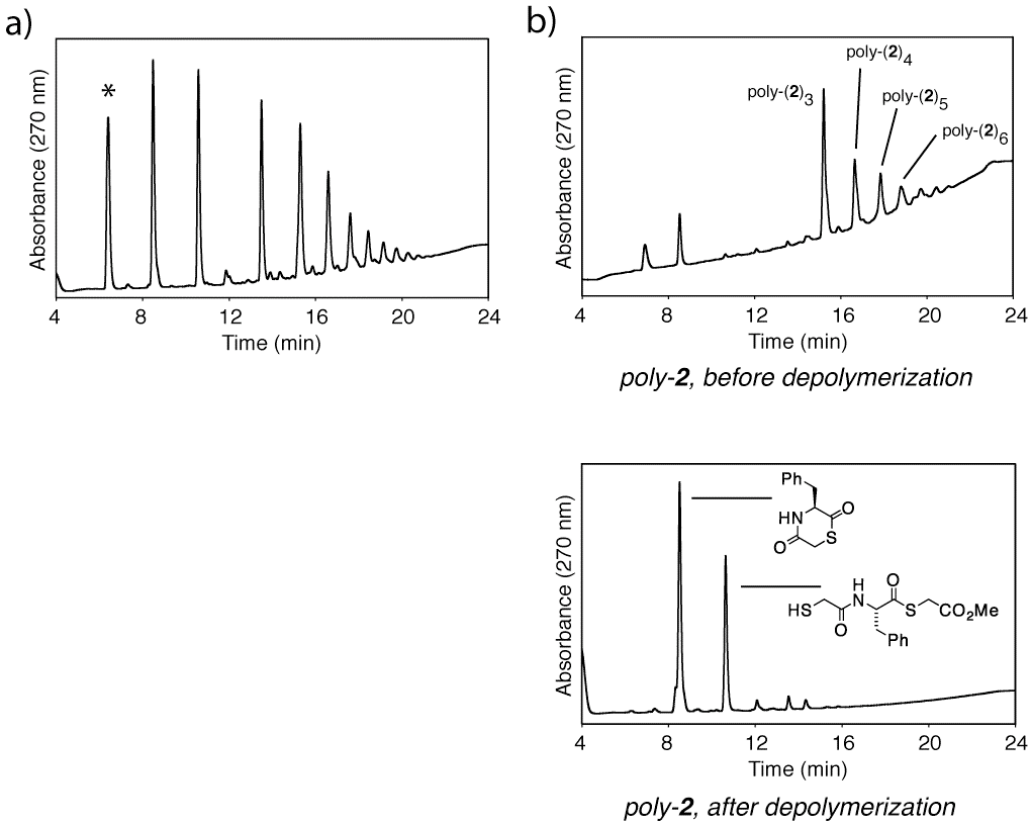


Figure S1. HPLC spectra demonstrating polymer formation and depolymerization. a) HPLC spectra of a 5 min time point for a reaction employing monomer **2** in DCM (200 mM), 10 eq DIEA, and 1.0 eq $HSCH_2CO_2Me$ as initiator (note that only short oligomers are observed in the spectrum since longer polymers are insoluble in the HPLC solvent). The peak labeled "❋" corresponds to acetanilide, the internal concentration standard. b) Experiment demonstrating the reversibility of the 1,4-thiazine-2,5-dione polymerization. A sample of poly-**2** (prepared as in Table 1, entry 2) was dissolved in DMF and sampled for HPLC analysis (top). The DMF solution was then treated with a large excess of DIEA and $HSCH_2CO_2Me$. After a period of five minutes, HPLC analysis indicated the polymer was cleanly depolymerized to yield cyclic monomer **2** and the ring-opened monomeric derivative in a ~2:1 ratio, respectively (bottom), supporting the reversibility of the polymerization reaction.

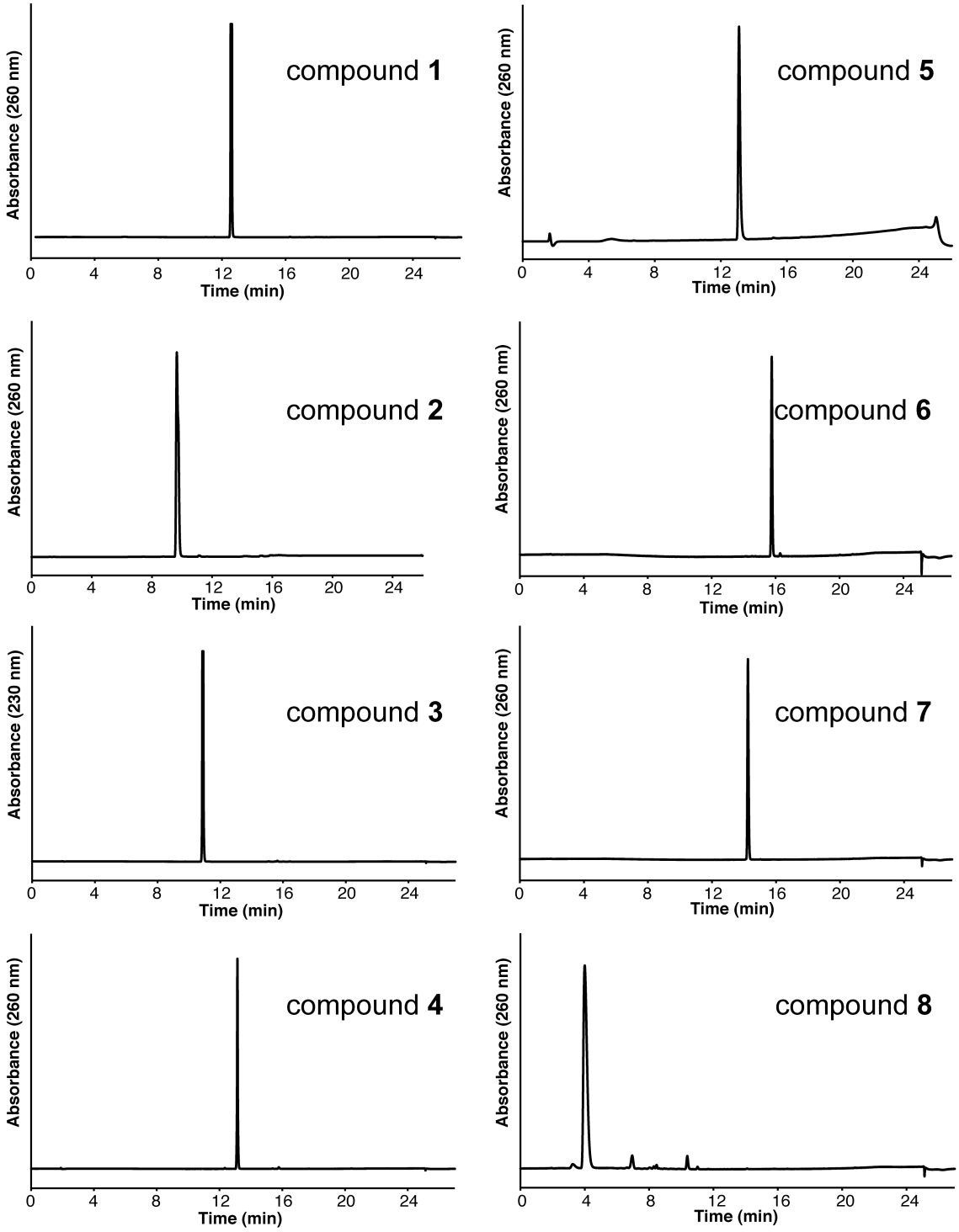


Figure S2. Analytical reverse-phase HPLC spectra demonstrating purity of 1,4-thiazine-2,5-dione monomers **1**–**8**. HPLC was performed at 260 nm or 230 nm using Phenomenex Jupiter Proteo or Zorbax 300-SB C-18 columns connected to a Hitachi D-7000 HPLC system. Solvent system (1.5 mL/min): binary gradients of solvent A (99% H_2O, 0.9% acetonitrile, 0.1% TFA) and solvent B (90% acetonitrile, 9.9% H_2O, 0.07% TFA).