Supporting information

Reversible oligomerization of 3-aryl-2-cyanothioacrylamides *via* $[2_s + 4_s]$ cycloaddition to substituted 3,4-dihydro-2*H*-thiopyrans

Julia Kötteritzsch, Stefan Bode, Ilknur Yildirim, Christine Weber, Martin D. Hager*, Ulrich S. Schubert*

Figure S1. ^1H NMR spectrum of **3a2** and the dimeric species in CDCl_3 .

Figure S2. ESI-TOF mass spectrum of **3b4** with peak assignment and exemplary overlays of the measured and calculated isotopic patterns (tetrameric and hexameric species).

Figure S3. Kinetic study of the equilibrium of **3b4** at 25 °C in $(\text{CD}_3)_2\text{CO}$ after dissolving and after 16 d in solution.

Figure S4. Kinetic study of the equilibrium of compound **3b4** at 50 °C in $(\text{CD}_3)_2\text{CO}$ after 15 min and after 16 h in solution.

Figure S5. Kinetic study of the equilibrium of compound **3b4** at 70 °C in DMSO after dissolving and after 30 min in solution.

Fi

Figure S6. Concentration study of **3b5** in CH_2Cl_2 .

Figure S7. 2D spectrum of **3b5** with RID and DAD (at 300 and 350 nm).

Figure S8. SEC traces of **3b5** before and after heating to 100 °C.

Figure S9. SEC traces of **3b5** before and after addition of 0.5 eq. ZnCl₂ per functional unit thioamide (c = 20 mg/mL).

Figure S10. ^1H NMR spectrum of polymer **P1** in CD_2Cl_2 .

Figure S11. UV/Vis spectra of initiator **3b3** and polymer **P1** (left) and 3D plot of SEC measurement of **P1** with DAD (right).