## **Supplementary Information**

# The effect of Z-group modification on the RAFT polymerization of Nvinylpyrrolidone controlled by "switchable" N-pyridyl-functional dithiocarbamates

Sarah J. Stace, Graeme Moad, Christopher M. Fellows and Daniel J. Keddie\*

### Preparation of poly(*N*-vinylpyrrolindone) using RAFT agents 4-9 at 60 °C.

A solution containing a RAFT agent (4-9) (0.150 mmol, see Table S1 for amounts), NVP (3.33 g, 30.0 mmol), AIBN (6.2 mg,  $3.7 \times 10^{-2}$  mmol) and 1,4-dioxane to a volume of 5 mL was prepared in a volumetric flask. The reaction mixture was divided in five and transferred to schlenk tubes which were degassed by three repeated freeze–evacuate–thaw cycles and sealed. The solutions were heated at 60 °C for 3, 5, 10, 17 or 25 h (s)

RAFT agent	R'	Amount (mg)
4	CH <sub>3</sub>	33.5
5	4-MeOPh	47.3
6	Ph	42.8
7	4-FPh	45.5
8	4-Py	43.0
9	4-CNPh	46.6

Table S1. Amount (mg) of RAFT agent used in NVP polymerization

# Chain Extension of poly(*N*-vinylpyrrolidone) macro-RAFT agents with *N*-Vinylpyrrolidone

Synthesis of poly(N-vinylpyrrolidone) macro-RAFT agent, PNVP-5

A solution containing RAFT agent **5** ( 47.3 mg, 0.149 mmol), NVP (2.66 g, 24.0 mmol), AIBN (6.2 mg,  $3.7 \times 10^{-2}$  mmol) and 1,4-dioxane to a volume of 5 mL was prepared in a volumetric flask. The solution was then transferred into a Schlenk tube and degassed via sparging with N<sub>2</sub> for 15 mins in an ice bath. The solution was heated at 60 °C. Upon removal from the oil bath the reaction was quenched with exposure to air and rapid cooling in ice. The

PNVP-5 macro-RAFT agent was isolated via three cycles of precipitation into diethyl ether and isolated via filtration.

### Chain extension of poly(N-vinylpyrrolidone) macro-RAFT agent (PNVP-5) with NVP

A solution containing PNVP-5 macro-RAFT (1.06 g, 0.150 mmol), NVP (3.40 g, 30.5 mmol) AIBN (6.2 mg,  $3.7 \times 10^{-2}$  mmol) and 1,4-dioxane to a volume of 5 mL was prepared in a volumetric flask. The solution was transferred into a Schlenk tube and degassed via sparging with N<sub>2</sub> for 15 mins in an ice bath. The reaction was then heated at 60 °C. Upon removal from the oil bath the reaction was quenched with exposure to air and rapid cooling in ice. The chain extended polymer was isolated via three cycles of precipitation into an 8 fold volume of diethyl ether and isolated by filtration.

#### Preparation of poly(N-isopropylacrylamide) macro-RAFT agent with 4

### Preparation of poly(N-isopropylacrylamide) macro-RAFT agent with 4 at 60 °C

A stock solution containing 4 (33.4 mg,  $1.50 \times 10^{-1}$  mmol), NIPAM (3.50 g, 30.9 mmol), TsOH (30.1 mg,  $1.58 \times 10^{-1}$  mol) AIBN (8.6 mg,  $5.3 \times 10^{-2}$  mmol) and 1,4-dioxane to a volume of 5 mL was prepared in a volumetric flask. The reaction mixture was transferred to a Schlenk tube and degassed by sparging with nitrogen for fifteen minutes at a reduced temperature. Upon removal from the oil bath the reaction was quenched with exposure to air and rapid cooling in ice. The PNIPAM-4 macro-RAFT agent was isolated via three cycles of precipitation into an 8 fold volume of diethyl ether and isolated by filtration.



**Figure S1:** Evolution of number average molar mass  $(M_n)$  in polystyrene equivalents with monomer conversion for polymerization of NVP in the presence of RAFT agents 4 ( $\blacksquare$ ),5 ( $\bigcirc$ ),6 ( $\blacktriangle$ ),7 ( $\bigtriangledown$ ) and 8 ( $\bigcirc$ ). Dashed line illustrates theoretical linear evolution of  $M_n$  with conversion.



**Figure S2:** Evolution of molar mass dispersity (*D*) with monomer conversion for polymerization of NVP in the presence of RAFT agents 4 ( $\blacksquare$ ),5 ( $\bigcirc$ ), 6 ( $\blacktriangle$ ), 7 ( $\bigtriangledown$ ) and 8 ( $\bigcirc$ ).

8.5





