

### Supporting Information. Derivation of Pseudo-steady State Model.

The pseudo-steady state model is developed by simplifying the comprehensive model (reproduced as eqs A1-A5 below). The pseudo-steady state model is useful for the validating the comprehensive model.

$$\frac{d[STR \bullet]}{dt} = k_a'[STR - DTC] - k_{t,rev}[STR \bullet][DTC \bullet] - k_t[STR \bullet]^2 \quad (A1)$$

$$\frac{d[STR - DTC]}{dt} = -k_a'[STR - DTC] + k_{t,rev}[STR \bullet][DTC \bullet] \quad (A2)$$

$$\frac{d[DTC \bullet]}{dt} = k_{a,TED}[TED] - k_{t,TED}[DTC \bullet]^2 + k_a'[STR - DTC] - k_{t,rev}[STR \bullet][DTC \bullet] \quad (A3)$$

$$\frac{d[TED]}{dt} = -k_{a,TED}[TED] + k_{t,TED}[DTC \bullet]^2 \quad (A4)$$

$$\frac{dT}{dt} = k'k_p[STR \bullet][M] \quad (A5)$$

Applying the assumption of no irreversible termination reactions simplifies eq A1 to yield eq A6:

$$\frac{d[STR \bullet]}{dt} = k_a'[STR - DTC] - k_{t,rev}[STR \bullet][DTC \bullet] \quad (A6)$$

Making a pseudo-steady state assumption for the surface-tethered carbon radicals (eq A2) yields eq A7:

$$[STR - DTC]_s = \frac{k_{t,rev}[STR\bullet]_s[DTC\bullet]_s}{k'_a} \quad (A7)$$

where  $[STR - DTC]_s$  is the concentration of surface-tethered radicals reversibly-terminated by dithiocarbamyl radicals at pseudo-steady state,  $[STR\bullet]_s$  is the concentration of surface-tethered radicals at pseudo-steady state and  $[DTC\bullet]_s$  is the concentration of dithiocarbamyl radicals at pseudo-steady state.

A mole balance for reversibly deactivated surface-tethered species yields eq A8 for  $[STR - DTC]_s$ .

$$[STR - DTC]_s = [STR - DTC]_0 - [STR\bullet]_s \quad (A8)$$

Substituting eq A8 into eq A7 and simplifying yields

$$[STR\bullet]_s = \frac{f_1 k_a [STR - DTC]_0}{f_1 k_a + [DTC\bullet]_s} \quad (A9)$$

The pseudo-steady state concentration of dithiocarbamyl radicals can be obtained by applying pseudo-steady state analysis to eq A3. In cases where TED is in excess, the contribution of  $DTC\bullet$  radicals generated from low-area flat substrates is negligible

compared to DTC• radicals generated from photolytic cleavage of free TED molecules in the solution. This simplifies eq A3 to the following:

$$\frac{d[DTC \bullet]}{dt} = k'_{a,TED} [TED] - k_{t,TED} [DTC \bullet]^2 \quad (A10)$$

Again applying the pseudo-steady state approximation to eq A10 provides the pseudo-steady state concentration of dithiocarbamyl radicals:

$$[DTC \bullet]_s = \sqrt{\frac{k'_{a,TED} [TED]_s}{k_{t,TED}}} \quad (A11)$$

Substituting this expression for  $[DTC \bullet]_s$  into eq A9 and replacing  $[TED]_s$  by  $[TED]_0$  (initial concentration of TED) yields eq A12, which expresses the pseudo-steady state concentration of surface-tethered radicals during the initial stages of SI-PMP in the presence of excess TED.

$$[STR \bullet]_s = \frac{k'_a [STR - DTC]_0}{k'_a + \sqrt{\frac{k'_{a,TED} [TED]_0}{k_{t,TED}}}} \quad (A12)$$

This expression for  $[STR \bullet]_s$  can be substituted in eq A5 to obtain the (maximum) growth rate of the PMMA layers.

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