- FULL INITIATION $-\!-$

Activation:
$$Q = \frac{h\nu, k_l}{k_{-l}}$$
 $^3Q = \frac{\mathbf{k_l}}{\mathbf{k_{-l}}} \approx 1e8 - 1e10 \quad c^{-1}$

Quenching:

$${}^{3}Q + DH \xrightarrow{k_{diff}} [{}^{3}Q, DH] \xrightarrow{k_{qE}} [Q^{\bullet-}, DH^{\bullet+}]_{s} \xrightarrow{k_{H+}} [QH^{\bullet}, D^{\bullet}]_{s} \xrightarrow{k_{diff}} QH^{\bullet} + D^{\bullet}$$

$$\begin{array}{c} \mathbf{k_{qE}} \approx 1e8 - 1e10 & M^{-1}c^{-1} \\ \mathbf{k_{-qE}} \approx 1e7 - 1e9 & c^{-1} \\ \mathbf{k_{H+}} \approx 1e8 - 1e10 & c^{-1} \\ \mathbf{k_{diff}} \approx 1e8 - 1e9 & c^{-1} \end{array}$$

$$^3Q + QHH \xrightarrow{k_{qH}} 2QH^{\bullet} \xrightarrow{k_{dQ}} Q + QHH \xrightarrow{k_{\mathbf{qH}}} \approx 1e5 - 1e9 \xrightarrow{M^{-1}c^{-1}} \frac{\mathbf{k_{redQ}}}{\mathbf{k_{dQ}}} \approx 1e3 \xrightarrow{M^{-1}c^{-1}} \frac{M^{-1}c^{-1}}{\mathbf{k_{dQ}}}$$

$$^{3}Q+QHD \xrightarrow{k_{qQD}} QH^{\bullet}+QD^{\bullet} \quad \mathbf{k_{qQD}} \approx ? \quad M^{-1}c^{-1}$$

$$QH^{\bullet} + D^{\bullet} \xrightarrow{k_r} QHD \xrightarrow{k_p} QHH + \text{N-prod} \xrightarrow{\mathbf{k_r}} \approx 1\text{e}7 - 1\text{e}9 \xrightarrow{M^{-1}c^{-1}} \mathbf{k_p} \approx 1\text{e}-5 - 1\text{e}-3 \xrightarrow{c^{-1}}$$

$$2D^{\bullet} \xrightarrow{k_{TD-rec}} \text{D-D} \qquad \qquad \mathbf{k_{rD-rec}} \approx 1e10 \quad M^{-1}c^{-1}$$
 $2D^{\bullet} \xrightarrow{k_{TD-dis}} \text{DH + N-prod} \xrightarrow{\mathbf{k_{rD-dis}}} \approx 1e9 \quad M^{-1}c^{-1}$

$$Q+D^{\bullet}$$
 k_{D} QD^{\bullet} k_{D} $\approx ?(1)$ $M^{-1}c^{-1}$ k_{-D} $\approx (0.05)$ c^{-1}

Photolysis: ${}^3Q \xrightarrow{k_{Ph}} \text{prod} \quad \mathbf{k_{Ph}} \approx 1\text{e-}4 - 1\text{e-}3 \quad c^{-1}$

———— SIMPLE SYSTEM –

Activation: $Q \xrightarrow{h\nu, k_l} {}^3Q \quad \mathbf{k_l} \approx 1e8 - 1e10 \quad c^{-1}$

Quenching:
$${}^3Q+DH \xrightarrow{k_{diff}} QH^{\bullet}+D^{\bullet} \xrightarrow{k_r} \operatorname{prod} \begin{array}{c} \mathbf{k_{diff}} \approx 1e8 - 1e10 & M^{-1}c^{-1} \\ \mathbf{k_r} \approx 1e7 - 1e9 & M^{-1}c^{-1} \end{array}$$

Radicals:

$$2QH^{\bullet} \xrightarrow{k_{dQ}} Q + QHH \qquad \mathbf{k_{dQ}} \approx 1e9 \quad M^{-1}c^{-1}$$

$$2D^{\bullet} \xrightarrow{k_{rD-rec}} \text{D-D} \qquad \qquad \mathbf{k_{rD-rec}} \approx 1e10 \quad M^{-1}c^{-1}$$

$$2D^{\bullet} \xrightarrow{k_{rD-dis}} \text{DH + N-prod} \xrightarrow{\mathbf{k_{rD-dis}}} \approx 1e9 \quad M^{-1}c^{-1}$$

—— FULL POLIMERIZATION –

 $D^{\bullet} + M \xrightarrow{k_{init}} \sim P_1^{\bullet}$ $M^{-1}c^{-1}$ Initiation: $\mathbf{k_{init}}$ Propagation: $\sim P_n^{\bullet} + M \xrightarrow{k_{prop}} \sim P_{n+1}^{\bullet}$ $M^{\bullet} + M \xrightarrow{k_{prop}} \sim P_2^{\bullet}$ k_{prop} $\approx 1e2 - 1e4 \quad M^{-1}c^{-1}$

 $\sim P_n^{\bullet} + \text{Sol} \xrightarrow{k_{trans-sol}} Sol^{\bullet} + \sim P_n$ $k_{trans-sol} \approx 5$ $M^{-1}c^{-1}$ $\sim P_n^{\bullet} + M \xrightarrow{k_{trans-m}} M^{\bullet} + \sim P_n$ $\mathbf{k_{trans-m}} \approx 1e\text{-}3 - 1 \qquad M^{-1}c^{-1}$

Inhibition: $\sim P_n^{\bullet} + Z \xrightarrow{k_{inh}} Z^{\bullet} + \sim P_n$ $\mathbf{k_{inh}}$ $\approx 1e2 - 1e3$ $M^{-1}c^{-1}$ Termination: $\sim P_n^{\bullet} \xrightarrow{k_{ter-lin}} \sim P_n$ $\mathbf{k_{ter-lin}}$ $\sim P_n$ $\mathbf{k_{ter-lin}}$ $\sim P_n$ $\mathbf{k_{ter-rec}}$ $\approx ?$ c^{-1} $\sim P_n^{\bullet} + \sim P_k^{\bullet} \xrightarrow{k_{ter-disp}} \sim P_n - P_k \sim$ $\mathbf{k_{ter-rec}}$ $\approx 1e7 - 1e8$ $M^{-1}c^{-1}$ $\sim P_n^{\bullet} + \sim P_k^{\bullet} \xrightarrow{k_{ter-disp}} \sim P_{n-1} = CH_2 + \sim P_{k-1} - CH_3$ $\mathbf{k_{ter-disp}}$ \approx $M^{-1}c^{-1}$

SIMPLE POLIMERIZATION ——

	$D^{\bullet} + M \xrightarrow{k_{init}} \sim P^{\bullet}$	$\mathbf{k_{init}}$	$\approx M^{-1}c^{-1}$
Propagation:	$\sim P_n^{\bullet} + M \xrightarrow{k_{prop}} \sim P_{n+1}^{\bullet}$	$\mathbf{k_{prop}}$	$\approx M^{-1}c^{-1}$
	$M^{\bullet} + M \xrightarrow{k_{prop}} \sim P_2^{\bullet}$		
	$\sim P_n^{\bullet} + Z \xrightarrow{k_{inh}} Z^{\bullet} + \sim P_n$	$\mathbf{k_{inh}}$	$\approx M^{-1}c^{-1}$
Termination:	$\sim P_n^{\bullet} \xrightarrow{k_{ter-lin}} \sim P_n$	$\mathbf{k_{ter-l}}$	$\approx M^{-1}c^{-1}$
	$\sim P_n^{\bullet} + \sim P_k^{\bullet} \xrightarrow{k_{ter-rec}} \sim P_n - P_k \sim$		
	$\sim P_n^{\bullet} + \sim P_k^{\bullet} \xrightarrow{k_{ter-disp}} \sim P_{n-1} = CH_2 + \sim P_{k-1} - CH_3$	$k_{\rm ter-disp}$	$\approx M^{-1}c^{-1}$