Supporting Information

Quantifying synergy for mixed end-scission and random-scission catalysts in polymer upcycling

Ziqiu Chen[1], Emmanuel Ejiogu[1], and Baron Peters[1, 2]

[1] *Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61820, USA.*

[2] *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61820, USA.*

**Corresponding author, Email: baronp@illinois.edu*

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Section SI-1: Supplementary plots for maximum synergy at different *Mn*(0)/Δ*n*

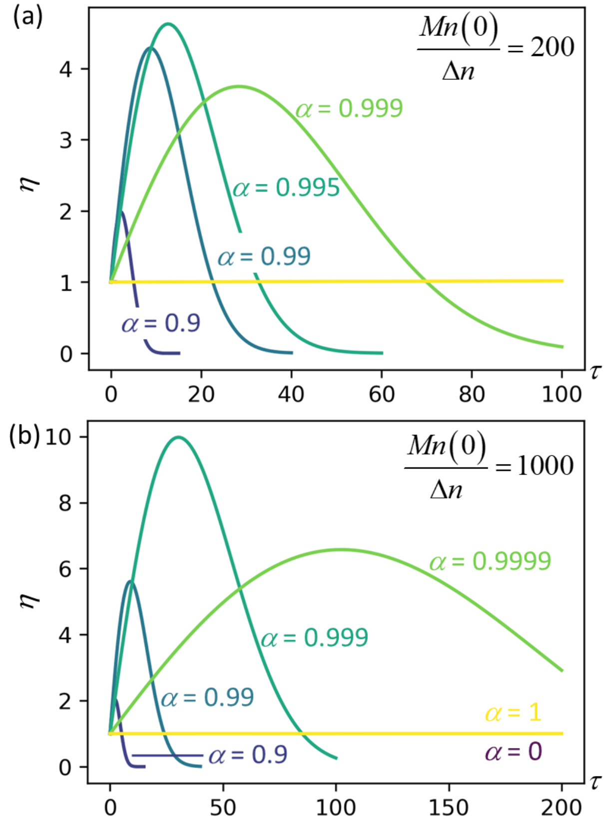

Figure SI-1. Synergistic acceleration vs. dimensionless time at different values with (a) *Mn*(0)/Δ*n* = 200; (b) *Mn*(0)/Δ*n* = 1000.

As we can see in **Figure SI-1**, for $M_n(0)/\Delta n = 200$ and $M_n(0)/\Delta n = 1000$, the maximum synergy appears at $\alpha = 0.995$ and $\alpha = 0.999$ respectively. Both of the α value appears to be $1 - \Delta n/M_n(0)$.

Section SI-2: Analytical Solution for Population Balance Model

Here we provide an analytical solution to the differential equation obtained in our population balance model using the technique employed by Ziff and McGrady, 1985:

$$\frac{\partial \rho}{\partial \tau} + \frac{\partial}{\partial N}[(1-\alpha)\rho] = -\alpha N \rho + 2\alpha \int_N^\infty \rho(N', \tau) dN' \qquad \text{(SI-1)}$$

First we guess a solution of the form: $\rho(N, \tau) = A(\tau) e^{B(\tau) \cdot N}$. Inserting this expression in (SI-1) above forces the expressions for $A(\tau)$ and $B(\tau)$ to be of the form:

$$A(\tau) = \exp\left\{ 2\ln(1+\alpha\frac{\tau}{s}) + (1-\alpha)(\alpha\frac{\tau^2}{2} + s\tau) \right\} \qquad \text{(SI-2)}$$

$$B(\tau) = -(\alpha\tau + s) \qquad \text{(SI-3)}$$

In the above, $A(0) = 1$ and $B(0) = -s$. Due to the linearity of the differential equation (SI-1), one could write down any sum or integral of the guessed expression and still get another solution. Therefore, the expression below is also a solution.

$$\rho(N, \tau) = \int_0^\infty f(s) \cdot A(\tau) e^{B(\tau) N} ds \qquad \text{(SI-4)}$$

This becomes,

$$\rho(N, \tau) = \int_0^\infty f(s) \cdot \left(1 + \alpha\frac{\tau}{s}\right)^2 \cdot \exp\left\{(1-\alpha)(\alpha\frac{\tau^2}{2} + s\tau)\right\} \cdot \exp\left\{-(\alpha\tau + s)N\right\} ds \qquad \text{(SI-5)}$$

With some rearrangement and introduction of a new variable $M = N - (1-\alpha)\tau$, we get

$$\rho(M + (1-\alpha)\tau, \tau) = \exp\left\{-\alpha\tau\left[M + (1-\alpha)\frac{\tau}{2}\right]\right\} \int_0^\infty f(s) \cdot \left(1+\alpha\frac{\tau}{s}\right)^2 e^{-sM} \qquad \text{(SI-6)}$$

We now define a new functional form: $\tilde{\rho}(M, \tau) = \rho(M + (1-\alpha)\tau, \tau)$. This gives,

$$\tilde{\rho}(M, \tau) = \exp\left\{-\alpha\tau\left[M + (1-\alpha)\frac{\tau}{2}\right]\right\} \int_0^\infty f(s) \cdot \left(1+\alpha\frac{\tau}{s}\right)^2 e^{-sM} \qquad \text{(SI-7)}$$

Hence, setting τ to 0, we obtain,

$$\tilde{\rho}(M, 0) = \int_0^\infty f(s) \cdot e^{-sM} ds \qquad \text{(SI-8)}$$

It is clear from the above expression that $\tilde{\rho}(M, 0)$ is the Laplace transform of $f(s)$. Hence, using the properties of the Laplace transform and the fact that the area under the initial distribution $\tilde{\rho}(M, 0)$ should not diverge:

$$\int_M^\infty \tilde{\rho}(y, 0) dy = \int_0^\infty \frac{1}{s} f(s) \cdot e^{-sM} ds \qquad \text{(SI-9)}$$

$$\int_M^\infty (y - M)\tilde{\rho}(y, 0) dy = \int_0^\infty \frac{1}{s^2} f(s) \cdot e^{-sM} ds \qquad \text{(SI-10)}$$

If we expand the expression, $\left(1 + \alpha\frac{\tau}{s}\right)^2$, while making use of the laplace properties, we get:

$$\tilde{\rho}(M,\tau) = \exp\left\{-\alpha\tau\left[M + (1-\alpha)\frac{\tau}{2}\right]\right\}\left\{\tilde{\rho}(M,0) + \int_M^\infty \tilde{\rho}(y,0)\{2\alpha\tau + (\alpha\tau)^2(y-M)dy\}\right\} \quad \text{(SI-11)}$$

Now we can revert back to our original variable N and functional form $\rho(N,\tau)$ using $M = N - (1-\alpha)\tau$ and $\tilde{\rho}(M,\tau) = \rho(M + (1-\alpha)\tau, \tau)$ to get a general solution. It should be noted that a change of variable has been done on the integral: $y = z - (1-\alpha)\tau$.

$$\rho(N,\tau) = \zeta(N,\tau)\cdot\left\{\rho(N + [1-\alpha]\tau, 0) + \int_N^\infty \rho(z + [1-\alpha]\tau, 0)\cdot\{2\alpha\tau + (\alpha\tau)^2(z-N)\}\,dz\right\} \quad \text{(SI-12)}$$

where,

$$\zeta(N,\tau) = \exp\left\{-\alpha\tau\left[N - (1-\alpha)\frac{\tau}{2}\right]\right\} \quad \text{(SI-13)}$$

If the initial distribution is a delta function, say, $\delta(N-L)$, we obtain the solution below.

$$\rho(N,\tau) = \begin{cases} \zeta(N,\tau) & \text{if} \quad N = L - (1-\alpha)\tau \\ \zeta(N,\tau)\left\{2\alpha\tau + (\alpha\tau)^2(L - (1-\alpha)\tau - N)\right\} & \text{if} \quad 0 < N < L - (1-\alpha)\tau \\ 0 & \text{otherwise} \end{cases} \quad \text{(SI-14)}$$

Also, starting with an initial Gaussian distribution $\mathcal{N}(\mu,\sigma^2)$ with mean μ and standard deviation σ, the evolution of the distribution will be:

$$\rho(N,\tau) = \frac{\zeta(N,\tau)}{\sigma\sqrt{2\pi}}\cdot\left\{(1 + (\alpha\tau\sigma)^2)\exp\{-\overline{N}^2\} + (2\alpha\tau\sigma - (\alpha\tau\sigma)^2\overline{N})\cdot\sqrt{\frac{\pi}{2}}(1 - \text{erf}\{\overline{N}\})\right\} \quad \text{(SI-15)}$$

where,

$$\overline{N} = \frac{1}{\sqrt{2}}\cdot\frac{N - (\mu - (1-\alpha)\tau}{\sigma} \quad \text{(SI-16)}$$

$$\text{erf}\,\overline{N} = \frac{2}{\sqrt{\pi}}\int_0^{\overline{N}} e^{-u^2}du \quad \text{(SI-17)}$$

Plotting equation (SI-15) for different values of α, $\mu = 1$ and $\sigma = 0.075$, we get **Figure SI-2**

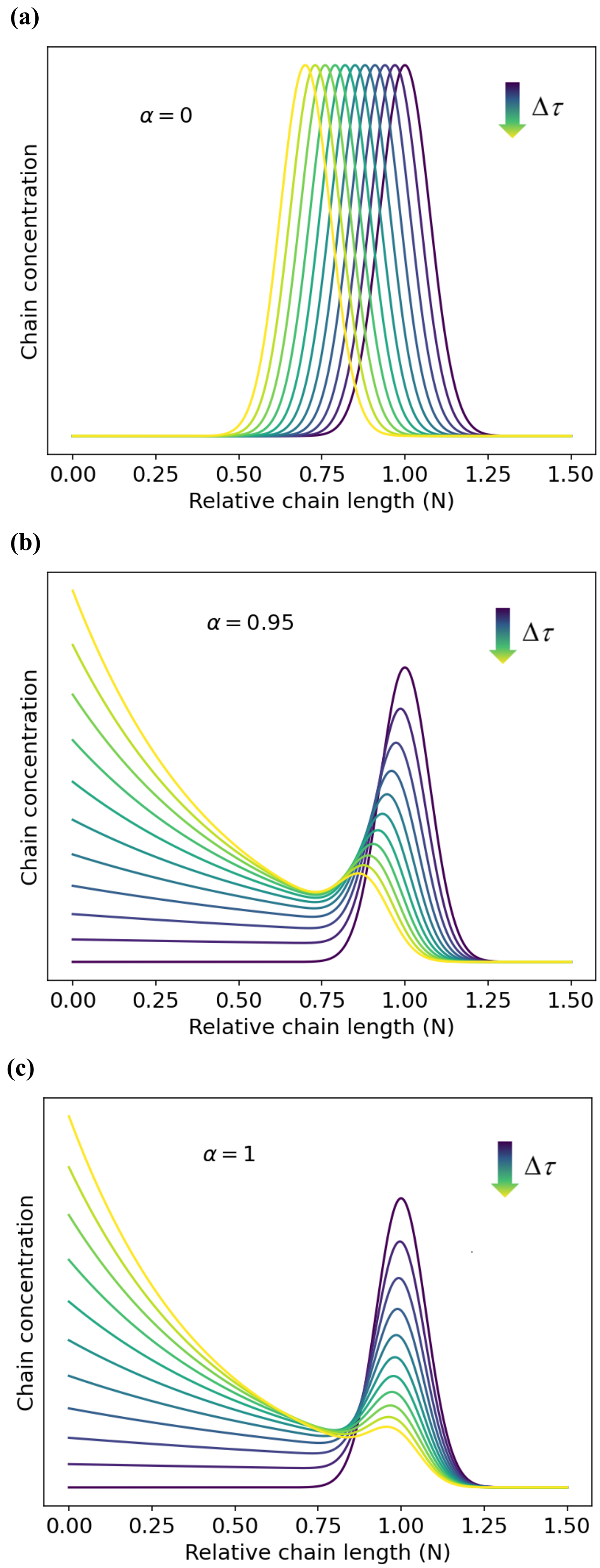

Figure SI-2: **The graphs (a), (b), and (c) show the evolution of the distribution for different values of α: 0, 0.95 and 1 respectively**