

Supporting Information:

A general model for the kinetics of self-condensing vinyl polymerization

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1. Distribution function

Looking at the eq 11 carfully, we can fine that it has following tentative solution:

$$P_{n,m} = M_0 Q_{n,m} (1-x) x^{n+m-1} e^{-nx/\alpha} \quad (\text{A1})$$

Where $Q_{n,m}$ is the constant needing to be determined. Substituting eq A1 into Eq.(11) leads:

$$Q_{n,m} = \frac{n}{2\alpha(n+m-1)} \sum_{i,j} Q_{i,j} Q_{n-i,m-j} \quad (\text{A2})$$

It can be known from eq 11 and the initial conditions that:

$$Q_{1,0} = \alpha, \quad Q_{0,1} = 1 - \alpha \quad (\text{A3})$$

Combining eq A2 with eq A3 and taking a direct summation gives rise to

$$Q_{n,m} = \alpha \frac{n^{n+m-1}}{n!m!} \left(\frac{1-\alpha}{\alpha} \right)^m \quad (\text{A4})$$

In summary, the solution of eq 11 is

$$P_{n,m} = \alpha M_0 \frac{n^{n+m-1}}{n!m!} \left(\frac{1-\alpha}{\alpha} \right)^m (1-x) x^{n+m-1} e^{-nx/\alpha} \quad (\text{A5})$$

2. The second moment

Eq 13 can be rewritted by

$$P_i = \sum_{n=0}^i P_{n,i-n} = \alpha M_0 \frac{1-x}{x} \sigma^i \sum_{n=0}^i \frac{n^{i-1}}{n!(i-n)!} \eta^n \quad (\text{A6})$$

Where

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$$\sigma = \frac{1-\alpha}{\alpha}x \quad \eta = \frac{\alpha}{1-\alpha}e^{-x/\alpha} \quad (\text{A7})$$

Combining eq A6 with eqs 3 and 4 yields:

$$\sum_i \sigma^i \sum_{n=0}^i \frac{n^{i-1}}{n!(i-n)!} \eta^n = \frac{x}{\alpha} \quad (\text{A8})$$

Therefore

$$\begin{aligned} \sum_i i^2 P_i &= \alpha M_0 \frac{1-x}{x} \left(\sigma \frac{\partial}{\partial \sigma} \right)^2 \left[\sum_i \sigma^i \sum_{n=0}^i \frac{n^{i-1}}{n!(i-n)!} \eta^n \right] \\ &= \alpha M_0 \frac{1-x}{x} \left(\sigma \frac{\partial}{\partial \sigma} \right)^2 \left(\frac{x}{\alpha} \right) = M_0 \frac{\alpha + x^2 - \alpha x^2}{\alpha(1-x)^2} \end{aligned} \quad (\text{A9})$$