# Supporting information

## Contents

# 1 Flory-Schulz distributions in presence of chain transfer agent

The derivation presented here follows that of Flory,[1,2,3] but takes also the effect of chain transfer into account.

## 1.1 Mole and weight fractions in radical chain polymerization

Consider a short period $\Delta t$ early in the reaction, during which the reactant composition doesn't significantly change. During this time several reactions take place: new active centers are generated by the initiator, monomer is added to the propagating centers, and active centers are destroyed by coupling with other active centers or by chain transfer reactions, which immediately regenerate the center but stop the previous chain growth. Rate of these reactions are given by the well known rate equations

$$
\begin{aligned}
R_i &= 2k_i f[\mathrm{I}] && (1)\\
R_p &= -\frac{d[\mathrm{M}]}{dt} = k_p[\mathrm{M}][\mathrm{M}\cdot] && (2)\\
R_{tr} &= -\frac{d[\mathrm{CTA}]}{dt} = k_{tr}[\mathrm{CTA}][\mathrm{M}\cdot] && (3)\\
R_c &= 2k_c[\mathrm{M}\cdot][\mathrm{M}\cdot] && (4)
\end{aligned}
$$

Here $i$, $p$, $tr$ and $c$ stand for initiation, propagation, transfer and chain coupling, respectively. [I], [M], [M·] and [CTA] indicate the initiator, monomer, propagating radical and transfer agent concentrations, $k$ are the corresponding rate constants and $f$ the initiator efficiency. Assuming steady-state conditions, i.e.,

$$\frac{d[\mathrm{M}\cdot]}{dt} = R_i - R_c = 0 \qquad (5)$$

the number of events during the time Δt are given by

$$
\begin{aligned}
N_i = N_c &= R_c\Delta t && (6)\\
N_p &= R_p\Delta t && (7)\\
N_{tr} &= R_{tr}\Delta t && (8)
\end{aligned}
$$

In the case that one could reach to the reactor after $\Delta t$ and take a closer look at the chains formed, five different types of molecules would be found. These are shown in Supporting Table 1. Type 1 molecules are initiated by an initiator fragment and

*Supporting Table 1:* Structure of species formed in radical chain polymerization in the presence of chain transfer agent. I denotes an initiator fragment, CT a reinitiating chain transfer agent fragment, A the atom or fragment transferred and *x* the number units in the chain, including the initiating fragments.

| Designation | Structure | Chain length | No. of kinetic chains |
|---|---|---|---|
| 1 | $\mathrm{I{-}M_{x-1}{-}A}$ | x | 1 |
| 2 | $\mathrm{CT{-}M_{x-1}{-}A}$ | x | 1 |
| 3 | $\mathrm{I{-}M_{x-2}{-}I}$ | x | 2 |
| 4 | $\mathrm{I{-}M_{x-2}{-}CT}$ | x | 2 |
| 5 | $\mathrm{CT{-}M_{x-2}{-}CT}$ | x | 2 |

terminated by a chain transfer reaction whereas type 2 molecules are initiated by a chain transfer agent fragment and terminated by a chain transfer reaction. The transfer reaction can be depicted as

$$\mathrm{M_n\cdot\ + CTA \longrightarrow M_n{-}A + CT\cdot}$$

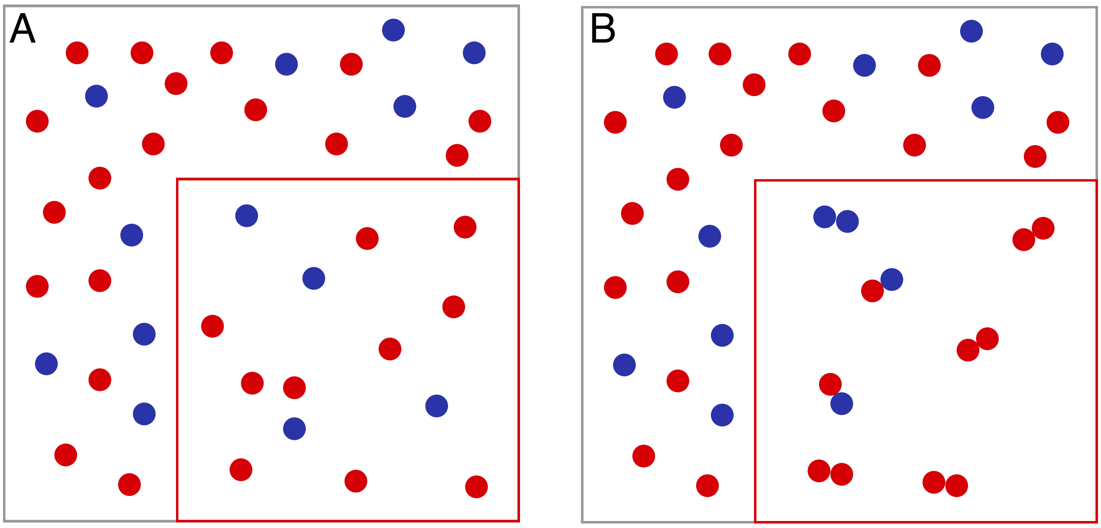
where a chain transfer agent CTA transfers an atom or fragment A to the active n-mer $\mathrm{M_n\cdot}$ terminating the chain growth and becomes an active fragment $\mathrm{CT\cdot}$, which can start a new chain growth.

Type 3 to 5 molecules are the molecules that are formed by coupling of chains initiated by initiator or chain transfer agent fragments. Type 3 to 5 molecules are each formed from two kinetic chains, which were started either by a chain transfer agent fragment or an initiator fragment. Fractions of kinetic chains and their combination are depicted in Supporting Figure 1.

Let us take a closer look into the mole fractions of each type of molecules in Supporting Table 1. In the limit of large number of molecules the mole fraction of each type corresponds to the probability that such a molecule is formed, which furthermore corresponds to the probability that we pick one type of molecule from the mixture of all formed molecules at random. The number of kinetic chains formed during $\Delta t$ equals the number of growing radicals destroyed. This is given by

$$N_v = N_c + N_{tr} \tag{9}$$

This, however, is not the total number molecules formed during $\Delta t$, which we need to determine the probabilities. The total number of molecules is given by



*Supporting Figure 1:* Kinetic chains formed in polymerization during $\Delta t$. Red and blue circles denote kinetic chains started by a transfer agent fraction and an initiator fragment, respectively. Red square marks the fraction of kinetic chains that are terminated by coupling. **A**: All kinetic chains. **B**: The actual molecules obtained.

$$N = \frac{N_c}{2} + N_{tr} \tag{10}$$

because for a molecule to form, one radical has to be destroyed by transfer or two radicals by combination. If we reach into a reactor depicted in Supporting Figure 1 B, the probabilities to obtain a transfer terminated molecule and a combined molecules are

$$n_{tr} = \frac{N_{tr}}{N_{tr} + N_c/2} = \frac{2p_{tr}}{1 + p_{tr}} \tag{11}$$

$$n_c = \frac{N_c/2}{N_{tr} + N_c/2} = \frac{1 - p_{tr}}{1 + p_{tr}} \tag{12}$$

respectively. Here $p_{tr}$ is the fraction of all radicals destroyed by transfer.

$$p_{tr} = \frac{N_{tr}}{N_{tr} + N_c} \tag{13}$$

Every chain transfer reaction not only destroys a radical but also creates a new one. Therefore any chain can be started by an initiator fragment or a chain transfer agent fragment. Probability that a chain is started by a transfer agent fragment is the fraction of transfer events $p_{i,tr}$ from all events that generate an active center

$$p_{i,tr} = \frac{N_{tr}}{N_{tr} + N_i} \tag{14}$$

where subindex $i$ stands for initiation. Under steady-state kinetics the number of radicals created and destroyed by initiation and combination, however, are the same and therefore the mole fractions of kinetic chains started by transfer agent fragment and initiator fragment $p_i$ are

$$\begin{aligned} p_{i,tr} &= \frac{N_{tr}}{N_{tr} + N_c} = p_{tr} && (15) \\ p_i &= 1 - p_{i,tr} = 1 - p_{tr} && (16) \end{aligned}$$

Because Equations 15 and 16 apply to all the kinetic chains in general, the fractions of kinetic chains started by transfer and initiator are the same for the both populations of transfer terminated (outside the red box) and combined (inside the red box) molecules in Supporting Figure 1.

We now have the tools to calculate the probabilities for species 1 and 2 in Supporting Table 1 but species 3 to 5 require further consideration. For the combined molecules there are three end group possibilities. The probability to pick any one combination at random from $N_c/2$ possibilities is the number of ways one can build this combination from $N_c$ kinetic chains divided by the number of ways one can build any combination from $N_c$ kinetic chains. In our parlance of red (R, transfer started) and blue (B, initiator started) circles this is

$$P(RR) = \frac{\text{All the possible combinations RR from R distinct entities}}{\text{All the possible combinations of two from R} + \text{B distinct entities}}$$

$$P(BB) = \frac{\text{All the possible combinations BB from B distinct entities}}{\text{All the possible combinations of two from R} + \text{B distinct entities}}$$

$$P(RB) = \frac{\text{All the possible combinations RB from R} + \text{B distinct entities}}{\text{All the possible combinations of two from R} + \text{B distinct entities}}$$

These values are given by

$$
\begin{aligned}
P(RR) &= \frac{\binom{N_R}{2}}{\binom{N_R+N_B}{2}} = \frac{N_R(N_R-1)}{(N_R+N_B-1)(N_R+N_B)} = \frac{p_{tr}(p_{tr}N_c-1)}{N_c-1} && (17)\\
P(BB) &= \frac{\binom{N_B}{2}}{\binom{N_R+N_B}{2}} = \frac{N_B(N_B-1)}{(N_R+N_B-1)(N_R+N_B)} \\
&= \frac{(1-p_{tr})((1-p_{tr})N_c-1)}{N_c-1} && (18)\\
P(RB) &= \frac{N_R\cdot N_B}{\binom{N_R+N_B}{2}} = \frac{2N_R\cdot N_B}{(N_R+N_B-1)(N_R+N_B)} = \frac{2p_{tr}(1-p_{tr})N_c}{N_c-1} && (19)
\end{aligned}
$$

The binomial coefficient is given by

$$
\binom{n}{k} = \frac{n!}{k!(n-k)!} \tag{20}
$$

and we use the fact that $N_R + N_B = N_c$ (total number of kinetic chains ended by combination) and $N_R = p_{tr}N_c$ and $N_B = (1-p_{tr})N_c$, based on the argumentation regarding Equations 15 and 16.

The Equations 17 to 19 simplify even further when we note that

$$
\begin{aligned}
\lim_{N_c\to\infty} P(RR) &= p_{tr}^2 && (21)\\
\lim_{N_c\to\infty} P(BB) &= (1-p_{tr})^2 && (22)\\
\lim_{N_c\to\infty} P(RB) &= 2p_{tr}(1-p_{tr}) && (23)
\end{aligned}
$$

which should be applicable to the system at hand as the number of kinetic chains terminated by transfer is large as in any molecular system. The mole fractions of all the species 1 to 5 can be calculated by combining Equations 11, 12, 15, 16 and 21 - 23 in appropriate manner.

$$n_1 = \frac{2p_{tr}(1-p_{tr})}{1+ptr} \tag{24}$$

$$n_2 = \frac{2p_{tr}^2}{1+p_{tr}} \tag{25}$$

$$n_3 = \frac{(1-p_{tr})^3}{1+p_{tr}} \tag{26}$$

$$n_4 = \frac{2p_{tr}(1-p_{tr})^2}{1+p_{tr}} \tag{27}$$

$$n_5 = \frac{p_{tr}^2(1-p_{tr})}{1+p_{tr}} \tag{28}$$

Equations 24 to 28 give the mole fractions of chains with certain end groups but don't say anything about the number of units $x$ in the chain. In the case we adopt the principle of equal reactivity for simplicity, i.e., all the radicals have equal reactivity regardless of their size, then any given propagating center has a probability $p$ to add a further monomer or probability $1-p$ to terminate either by transfer or combination. The probability tree to illustrate this process is given in Supporting Figure 2.

The probability $p$ is given by the fraction of propagation steps of all the possible steps that the propagating center can take, i.e., propagate, terminate by transfer or combine

$$p = \frac{N_p}{N_p + N_c + N_{tr}} \tag{29}$$

The total probability for the chain propagation to stop is

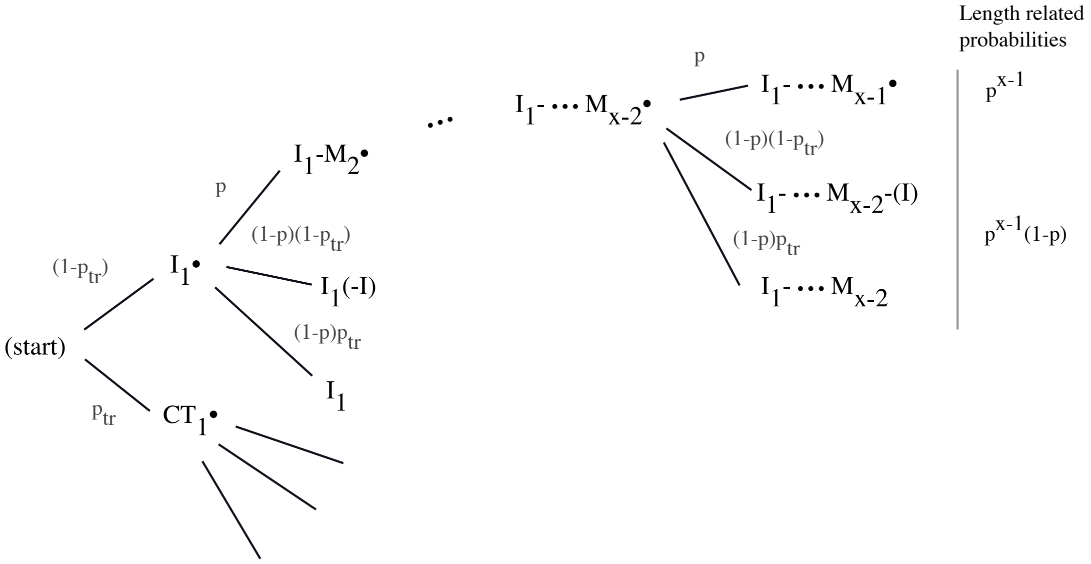
$$1 - p = \frac{N_c + N_{tr}}{N_p + N_c + N_{tr}} \tag{30}$$

and individually

$$(1-p)(1-p_{tr}) = \frac{N_c}{N_p + N_c + N_{tr}} \tag{31}$$

$$(1-p)p_{tr} = \frac{N_{tr}}{N_p + N_c + N_{tr}} \tag{32}$$

From the probability tree in Supporting Figure 2 we see that *within each population of kinetic chains* (i.e. kinetic chains with different initiation and termination modes)



*Supporting Figure 2:* Probability tree for radical chain polymerization in the presence of chain transfer agent. The probabilities that the chain is initiated by initiator or chain transfer agent fragments are $1-p_{tr}$ and $p_{tr}$, respectively. Due to assumption of equal reactivity of the propagating centers regardless of length, the probability that the propagating center adds a monomer is $p$ and the probabilites that the chain terminates by combination or transfer $(1-p)(1-p_{tr})$ and $(1-p)p_{tr}$, respectively. Within each population of kinetic chains, the probability to obtain a chain of exactly $x$ units is $p^{x-1}(1-p)$, because in a chain of $x$ units there have been $x-1$ propagation steps, each with probability p, and one termination step with probability $(1-p)$.

the probability to obtain an $x$-mer is the same $p^{x-1}(p-1)$. The difference between the populations is only the relative amounts of chains determined by the starting modes $(1-p_{tr})$ and $p_{tr}$ and the termination modes $(1-p_{tr})$ and $p_{tr}$. Therefore the length distribution in each population has the same shape and the probabilities of obtaining a kinetic $x$-mer of certain length is decoupled from its starting and termination modes.

The probability that a molecule that consists of one kinetic chain (species 1 and 2) has $x$ units is therefore $p^{x-1}(1-p)$. When accounting for an $x$-mer that has formed by combination, we have to recognize that the $x$-mer consists of a $y$- and $z$-mer with $y+z=x$, which can be combined in

$$\begin{array}{crcl}
1 & \mathrm{I}_1\cdot & + & \cdot\,\mathrm{M}_{z-1}\cdots\text{-}\mathrm{M}_3\text{+}\mathrm{M}_2\text{-}\mathrm{I}_1 \\
2 & \mathrm{I}_1\text{-}\mathrm{M}_2\cdot & + & \cdot\,\mathrm{M}_{z-2}\cdots\text{-}\mathrm{M}_3\text{+}\mathrm{M}_2\text{-}\mathrm{I}_1 \\
3 & \mathrm{I}_1\text{-}\mathrm{M}_2\text{-}\mathrm{M}_3\cdot & + & \cdot\,\mathrm{M}_{z-3}\cdots\text{-}\mathrm{M}_3\text{+}\mathrm{M}_2\text{-}\mathrm{I}_1 \\
\cdot & & \cdot & \\
\cdot & & \cdot & \\
\cdot & & \cdot & \\
x-3 & \mathrm{I}_1\text{-}\mathrm{M}_2\text{-}\mathrm{M}_3\text{-}\cdots\mathrm{M}_{y-3}\cdot & + & \cdot\mathrm{M}_3\text{-}\mathrm{M}_2\text{-}\mathrm{I}_1 \\
x-2 & \mathrm{I}_1\text{-}\mathrm{M}_2\text{-}\mathrm{M}_3\text{-}\cdots\mathrm{M}_{y-2}\cdot & + & \cdot\mathrm{M}_2\text{-}\mathrm{I}_1 \\
x-1 & \mathrm{I}_1\text{-}\mathrm{M}_2\text{-}\mathrm{M}_3\text{-}\cdots\mathrm{M}_{y-1}\cdot & + & \cdot\mathrm{I}_1
\end{array}$$

$(x-1)$ ways. The probability that a combined molecule has $x$ units is therefore

$$(x-1)p^{y-1}(1-p)p^{z-1}(1-p)=(x-1)p^{x-2}(1-p)^2 \tag{33}$$

Combining these results with the analysis of mole fractions of the species 1 to 5, the mole fractions of $x$-mers of all species are given by

$$n_{x,1} = \frac{2p_{tr}(1-p_{tr})}{1+p_{tr}}(1-p)p^{x-1} \tag{34}$$

$$n_{x,2} = \frac{2p_{tr}^2}{1+p_{tr}}(1-p)p^{x-1} \tag{35}$$

$$n_{x,3} = \frac{(1-p_{tr})^3}{1+p_{tr}}(1-p)^2(x-1)p^{x-2} \tag{36}$$

$$n_{x,4} = \frac{2p_{tr}(1-p_{tr})^2}{1+p_{tr}}(1-p)^2(x-1)p^{x-2} \tag{37}$$

$$n_{x,5} = \frac{p_{tr}^2(1-p_{tr})}{1+p_{tr}}(1-p)^2(x-1)p^{x-2} \tag{38}$$

The weight fractions are given by

$$w_x = \frac{xn_xN}{\sum_{x=1}^{\infty} xn_xN} = \frac{xn_x}{\sum_{x=1}^{\infty} xn_x} \tag{39}$$

where N is the total number of molecules. The sum in the denominator evaluates to

$$\begin{aligned} \sum_{x=1}^{\infty} xn_x &= \sum_{x=1}^{\infty} xn_{x,1} + \sum_{x=1}^{\infty} xn_{x,2} + \sum_{x=1}^{\infty} xn_{x,3} + \sum_{x=1}^{\infty} xn_{x,4} + \sum_{x=1}^{\infty} xn_{x,5} \\ &= \frac{2}{(1+p_{tr})(1-p)} \end{aligned} \tag{40}$$

when using sums

$$\sum_{x=1}^{\infty} xp^{x-1} = \frac{1}{(1-p)^2} \tag{41}$$

$$\sum_{x=1}^{\infty} x(x-1)p^{x-2} = \frac{2}{(1-p)^3} \tag{42}$$

to evaluate the individual sums for Equations 34 to 38. Using Equation 39 for every mole fraction of species 1 to 5 then gives

$$w_{x,1} = p_{tr}(1-p_{tr})(1-p)^2xp^{x-1} \tag{43}$$

$$w_{x,2} = p_{tr}^2(1-p)^2xp^{x-1} \tag{44}$$

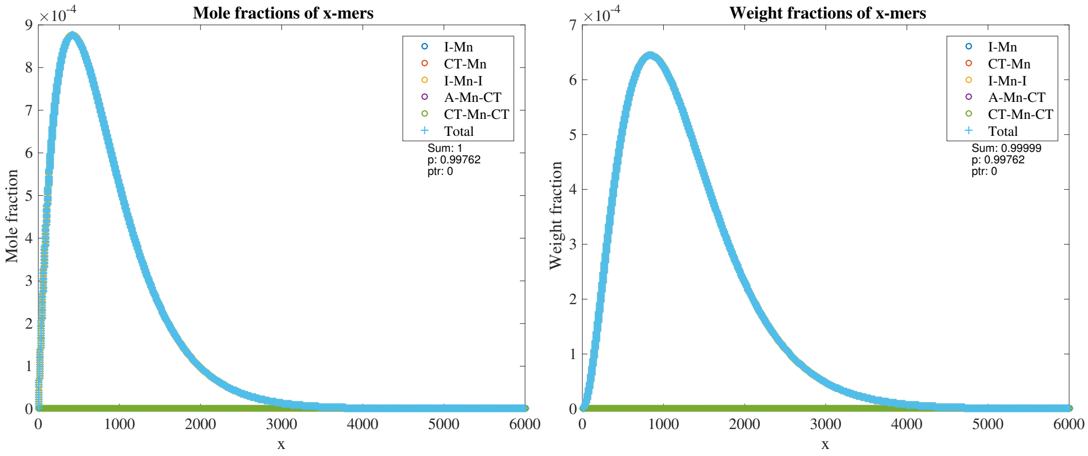
$$w_{x,3} = \frac{(1-p_{tr})^3}{2}(1-p)^3x(x-1)p^{x-2} \tag{45}$$

$$w_{x,4} = p_{tr}(1-p_{tr})^2(1-p)^3x(x-1)p^{x-2} \tag{46}$$

$$w_{x,5} = \frac{p_{tr}^2(1-p_{tr})}{2}(1-p)^3x(x-1)p^{x-2} \tag{47}$$

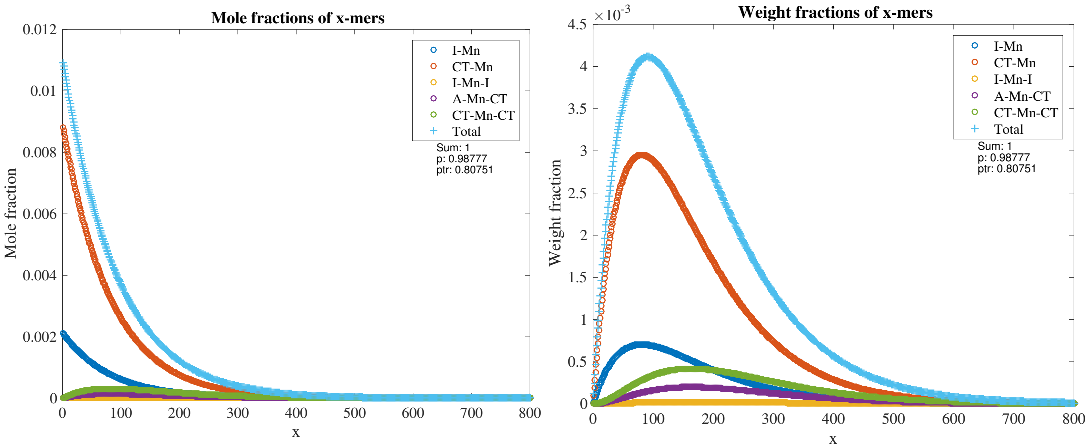
### 1.2 Calculated examples for mole and weight fractions

The reaction parameters for methacrylate photopolymerization from Odian[3] were used to calculate the effect of chain transfer agent on the mole and weight fractions of the product in $\Delta t$. These are given in Supporting Table 2. These values were used to calculate the values for $p$ and $p_{tr}$ used in Equations 34 to 38 and 43 to 47.



*(a)* Mole fractions of species 1-5, no transfer. *(b)* Weight fractions of species 1-5, no transfer.

*Supporting Figure 3:* Mole and weight fractions of species 1-5 when no transfer agent is used. $p = 0.9976$, $p_{tr} = 0$. Only combined species 3 is present.



*(a)* Mole fractions of species 1-5, transfer. *(b)* Weight fractions of species 1-5, transfer.

*Supporting Figure 4:* Mole and weight fractions of species 1-5 when agent is used. $p = 0.9878$, $p_{tr} = 0.8075$ with $C_{tr} = 20$ and $[\mathrm{CT}] = 1 \times 10^{-4}\,\mathrm{mol{\cdot}dm^{-3}}$. Chain length is greatly shortened. Transfer terminated short species dominate the mole fractions. Also the weight fractions are dominated by the transfer terminated product, but the shortest product contributes less to the weight fraction.

*Supporting Table 2:* Reaction parameters for methacrylate photopolymerization given in Odian.

| Quantity | Values | Units |
|---|---|---|
| $k_p$ | $7.96 \times 10^2$ | $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ |
| $k_c$ | $8.25 \times 10^6$ | $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ |
| $C_{tr}$ | Adjusted | $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ |
| [CT] | Adjusted | $\mathrm{mol\,dm^{-3}}$ |
| [M] | 0.20 | $\mathrm{mol\,dm^{-3}}$ |
| [R·] | $2.30 \times 10^{-8}$ | $\mathrm{mol\,dm^{-3}}$ |

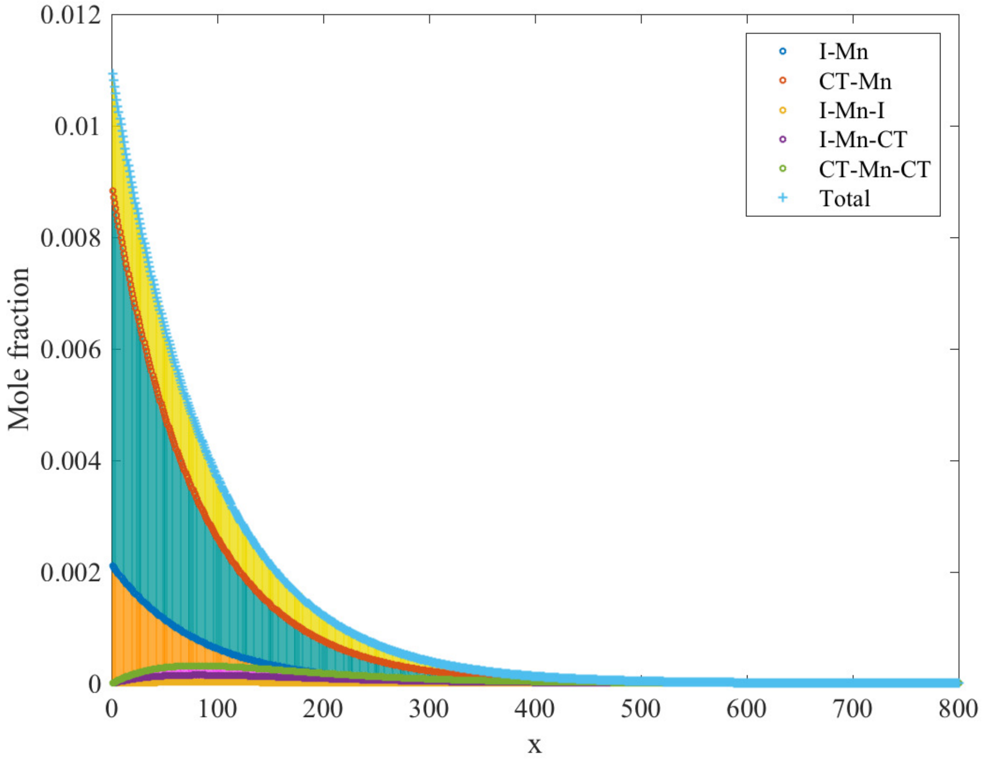
The mole and weight fractions for reaction without chain transfer agent is shown in Supporting Figure 3. No other product is formed except combined chains. As is seen in Supporting Figure 3b, the longer product contributes more to the weight fraction, shifting the distribution function to the direction of longer chains.

The picture changes drastically if chain transfer agent is present in the reaction mixture. The mole and weight fractions for this sort of reaction are shown in Supporting Figure 4. Here $C_{tr} = 20$, and $[\mathrm{CT}] = 1 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$. Even though $p$ goes down form 0.9976 only to 0.9878, the $p_{tr}$ rises to 0.8075 meaning that most of the kinetic chains are terminated by transfer instead of combination. This leads to drastic shortening of the chains so that short transfer terminated chains dominate the mole fraction as seen in Supporting Figure 4a. Some of the chains are very short chains that are unlikely to go through coil-to-globule transition. These species however dominate the mole fraction of the product, which would lead to the assumption of polymer charge density decreasing as these chains are excluded from the collapsed polymer particles.

### 1.3 Comparison with simulation

The validity of the closed form expressions were tested by comparing the calculated mole fractions with those obtained by simulating the probability tree in Supporting Figure 2. This essentially means that computer comes up with a random number, which is compared with the probability of propagation. If the number is smaller than the probability, the kinetic chain adds an unit, and if not, the chain is terminated. The mode of termination is decided by comparing the random number with the probability of termination by transfer or combination in a similar manner as with propagation. This process is repeated until the chain terminates and then a new kinetic chain is started.

Supporting Figure 5 shows the result for simulation of two million kinetic chains with $p = 0.9976$ and $p_{tr} = 0.8075$. The bar charts represent the result from simulation and the scatter plots the calculated mole fractions. As can be seen the bar charts align well with the calculated values, which indicates that the closed form expressions represent the probability tree in Supporting Figure 2 accurately. This naturally says nothing



*Supporting Figure 5:* Comparison of calculated mole fractions and simulated result. The scatter plots represent the values calculated from the closed form expressions and the bar charts the simulated result of 2 million kinetic chains.

about the fact whether the said probability tree is a reasonable description of the polymerization system.

## 1.4 Charge density of polymer and monomer loss due to transfer

In the case of precipitation polymerization of NIPAM we are interested in the average surface charge density of single chain globules given that there is some critical chain length $x_c$, which is required for the chains to contribute to the charge density. This is given by equation

$$\overline{\rho}_A = \frac{\sum_{x=x_c}^{\infty} z n_x}{\left(v_0 \sum_{x=x_c}^{\infty} (x-k) n_x\right)^{2/3}} \tag{48}$$

where $v_0$ is the volume occupied by one repeating unit, $z$ is the charge number of the $x$-mer and $k$ is 1 for species 1 and 2 and 2 for species 3-5 because we want to exclude the contribution of chain ends to the number of repeating units. Accounting for the different types of molecules we get

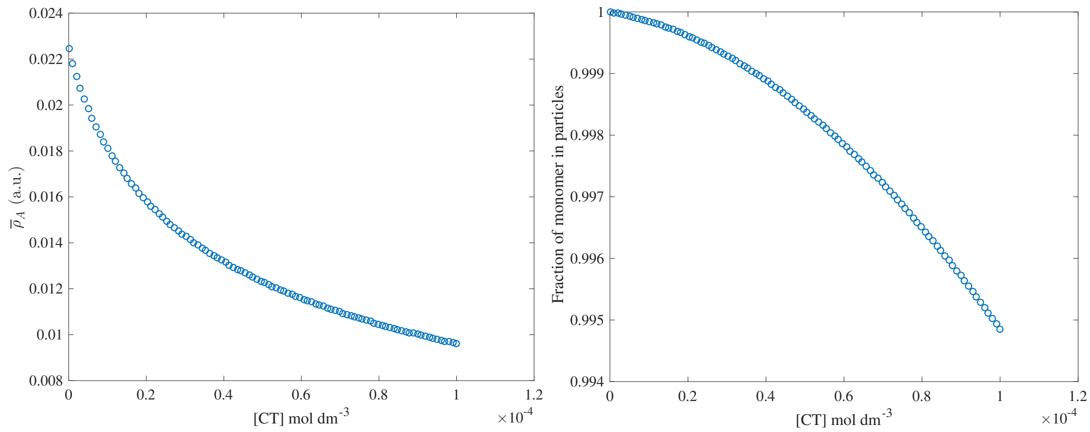
$$\overline{\rho}_A \propto \frac{\sum_{x=x_c+1}^{\infty} 1 \cdot n_{x,1} + \sum_{x=x_c+2}^{\infty} 2 \cdot n_{x,3} + \sum_{x=x_c+2}^{\infty} 1 \cdot n_{x,4}}{\left(\sum_{x=x_c+1}^{\infty} (x-1) n_{x,1} + \sum_{x=x_c+1}^{\infty} (x-1) n_{x,2} + \sum_{x=x_c+2}^{\infty} (x-2) n_{x,3} + \sum_{x=x_c+2}^{\infty} (x-2) n_{x,4} + \sum_{x=x_c+2}^{\infty} (x-2) n_{x,5}\right)^{2/3}} \tag{49}$$

Chains that have lower number of repeating units that some critical value $x_c$, are assumed not to undergo a coil-to-globule transition and are therefore excluded from the particles. We can estimate the significance of this process by calculating the fraction of monomer units that actually end up in the particles

$$\Lambda = \frac{\sum_{x=x_c}^{\infty} (x-k) n_x N}{\sum_{x=1}^{\infty} (x-k) n_x N} \tag{50}$$

The limits of summation and $k$ are appropriately modified for every type of species as in the case of Eq. 49.

An example of Eq. 49 is plotted in Supporting Figure 6a and of Eq. 50 in Supporting Figure 6b. Here the critical number of monomer units in the chain was chose to be 10 and the chain transfer agent concentration was varied from 0 to $2 \times 10^{-4}$ mol·dm$^{-3}$ with reaction parameters of methacrylamide photopolymerization. As can be seen in Supporting Figure 6a the number of charges per polymerized monomer units in chains having more monomer units than 10 decreases with the chain transfer agent concentration. This should lead to less stabilization of precursor particles.



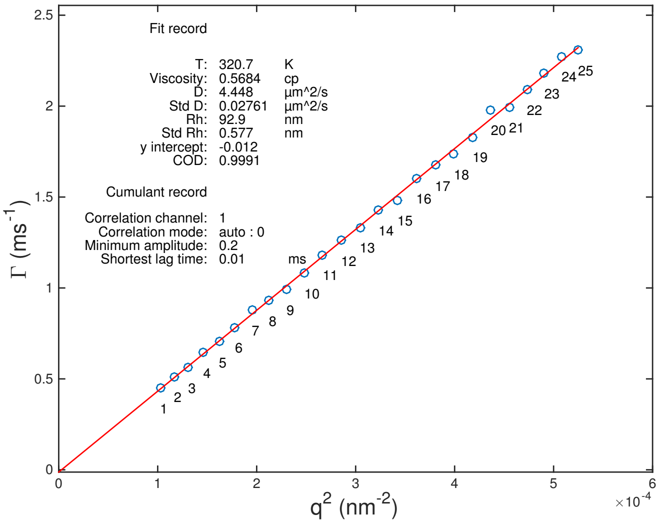
*(a)* Charge density of the polymer with concentration of chain transfer agent concentration.

*(b)* Fraction of monomer, which ends up in particles with chain transfer agent concentration.

*Supporting Figure 6:* Charge density of polymer and monomer loss with chain transfer agent concentration. Reaction parameters are the same as before but $[CT]$ is varied between 0 and $2 \times 10^{-4}$ mol·dm$^{-3}$. $x_c$ was chosen to be 10.

Because not all the chains are expected to go through coil-to-globule transformation the particle volume might also decrease. This is demonstrated in Supporting Figure 6b. In the case no chain transfer agent is present virtually all monomer ends up in the product. When transfer agent is added, the fraction of monomer belonging to chains capable of coil-to-globule transition decreases gradually.

The reaction composition however changes during the polymerization, and detailed simulation is required to calculate the real loss of monomer due to chains not exceeding the critical chain length for collapse. One also has to consider the possibility of the locus of polymerization moving from the continuous phase to the particle surfaces in a later stage: The active centers on the particle surface during the growth phase can add monomer directly from the continuous phase and therefore circumvent the exclusion problem. Furthermore, peroxide initiators are known to create active sites to the polymer backbone[4] to the extent that otherwise uncrosslinked particles gelate[5]. It is a possibility that active sites in solubilized polymer and particle surface react so that the particles actually scanvege solubilized polymer from the continuous phase.



Fit record

T: 320.7 K
Viscosity: 0.5684 cp
D: 4.448 µm^2/s
Std D: 0.02761 µm^2/s
Rh: 92.9 nm
Std Rh: 0.577 nm
y intercept: -0.012
COD: 0.9991

Cumulant record

Correlation channel: 1
Correlation mode: auto : 0
Minimum amplitude: 0.2
Shortest lag time: 0.01 ms

*Supporting Figure 7:* Decay rate from the second order cumulant fit ($\Gamma_2$) against $q^2$ for an arbitrary sample.

# 2 Experimental details

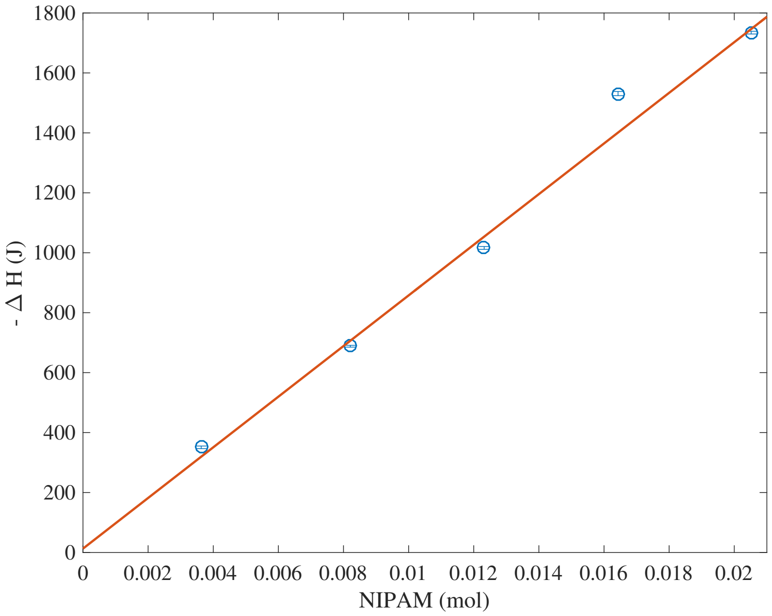
## 2.1 Dynamic light scattering characterization

The electric field correlation function $f^M$ at any given scattering vector magnitude $q$ (or angle) is a linear combination of exponentials, where each particle size fraction contributes one exponential weighted by the scattering weight and the form factor of that particle size fraction[6]

$$f^M = \int_0^\infty dD\,P(D)\exp(-Dq^2\tau)$$

Here $P(D)$ is the intensity weighted distribution function of diffusion coefficients $D$ and $\tau$ the lag time of the correlation function. Because the intensity weighting ($P(D)$) changes with $q$ (or angle) due to the nature of the scattering process, one can obtain severily biased results if the dynamic light scattering experiment is performed only at one angle. Real world problems arise, e.g., if one measures in a form factor minimum of particles that have dimensions comparable to the laser wavelength.

To get reliable results, it is necessary to perform the dynamic light scattering experiment at multiple angles and resolve the average decay rate ($\Gamma_2$) of each field correlation function e.g. by cumulant analysis, which is applicable to samples with monomodal particle size distribution of moderate width. Subscript 2 stands for second order cumulant fit. One can then resolve the average diffusion coefficient from



*Supporting Figure 8:* Reaction enthalpy with NIPAM concentration. The heat of polymerization of NIPAM was determined to be 84.5 ±0.3 kJ $\text{mol}^{-1}$ with intercept of 13 ±4 J

.

$$\Gamma_2 = Dq^2$$

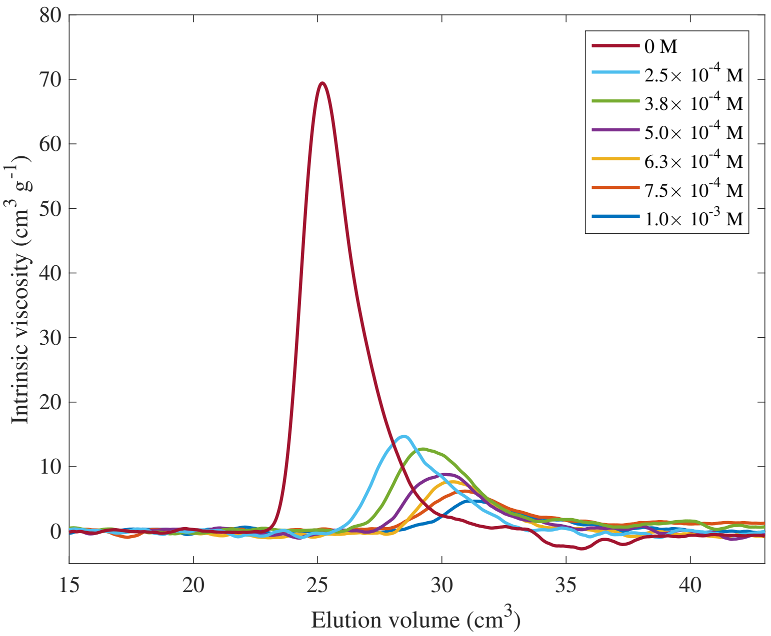
by linear fitting. An example of a good and reliable result is given in Supporting Figure 7. The standard deviation of the fit parameters can be estimated by standard procedures and propagated to the quantities of interest by Gaussian error propagation.

## 2.2 Heat of polymerization

Supporting Figure 8 shows reaction enthalpy with the amount of NIPAM. Reaction enthalpies were obtained by numerically integrating the traces shown in Figure 2A of the main paper. The heat of polymerization of NIPAM was determined to be 84.5 ± 0.3 kJ $\text{mol}^{-1}$.

## 2.3 SEC characterization of 2-mercaptoethanol modulated polymerization

Supporting Figure 9 shows SEC eluograms of PNIPAM synthesized at room temperature in water in the presence of 2-mercaptoethanol (ME). The polymerization was carried out below the VPTT to minimize any branching reactions taking place in the collapsed particles at high polymer volume fraction, which would make the SEC analysis unfeasible. Even a small addition of ME results in a large drop in the intrinsic



*Supporting Figure 9:* SEC eluograms for PNIPAM samples synthesized in the presence of 2-mercaptoethanol (ME). Significant drop in intrinsic viscosity and the shift of the signal to higher retention volume indicates that ME acts as a chain transfer agent. ME concentrations are given in the legend. NIPAM concentration was $8.1 \times 10^{-2}$ mol dm$^{-3}$, and APS and TEMED concentrations were $1.71 \times 10^{-3}$ mol dm$^{-3}$ and $1.81 \times 10^{-3}$ mol dm$^{-3}$, respectively, in every batch.

viscosity signal and a shift of the signal to higher retention volume. This corresponds to decrease in the molecular weight and confirms that ME acts as a chain transfer agent.

## 2.4 Parameters for Flory-Schulz calculations

According to the hypothesis presented in this paper the initiation rate during the nucleation phase sets the upper limit to the number of particles in the batch and the surface charge density of the primary globules determines to which extent they aggregate. That is, short chains, which form small globules, have high surface charge and aggregate less than longer chains. This is because each chain has 0 to 2 charged initiator fragments (depending on modes of initiation and termination), but variable number of repeating units. In other words, this simple model assumes that

$$n \propto R_i \cdot \overline{\rho}_A \propto R_i \cdot \frac{q}{A} \propto R_i \cdot \frac{q}{\bar{x}_c^{2/3}}$$

where $n$ is number density of particles, $R_i$ initiation rate during the nucleation phase, $\overline{\rho}_A$ average surface charge density of globules, $q$ average number of charges per chain, $A$

the average surface area of the primary globules and $\bar{x}_c$ the average number of repeating units in chains that exceed the critical length for coil-to-globule transition.

The first approximation for $\bar{x}_c$ during the nucleation period under given experimental conditions can be obtained from Flory-Schulz distributions for radical chain polymerization. Some of the reaction parameters are set, such as reaction temperatures and reactant concentrations, others are unknown. The task is therefore to find a set of reaction parameters leading to $n$, that qualitatively reproduces characteristics of experimental final particle volume data. A requirement for the reaction parameters is that the values have to be within typical ranges reported for radical solution polymerization systems.

Reaction parameters for methyl acrylate polymerization compiled by Odian[3] were used as the starting point; Odian also lists typical ranges for the parameters. These are shown in Supporting Table 3.

*Supporting Table 3:* Ranges of typical values of parameters in radical solution polymerization, values for methyl acrylate polymerization and the values used to generate the plots in the main article. Ranges and methyl acrylate values are taken from Odian[3], section 3-8. Non-catalyzed potassium persulfate (KPS) dissociation constants are from Kolthoff and Miller[7]. Here $k_p$ is rate constant of propagation, $E_p$ activation energy of propagation, $k_t$ rate constant of coupling, $E_t$ activation energy of coupling, $k_d$ rate constant of initiator dissociation, $k_{d,\mathrm{redox}}$ rate constant of initiator dissociation in redox system and $c_s$ chain transfer constant.

| Parameter | Units | Typical range | Methyl acrylate | Value used |
|---|---|---|---|---|
| $k_p\,(60\,°\mathrm{C})$ | $\mathrm{dm^3\,mol^{-1}s^{-1}}$ | $10^2$ to $10^4$ | $2.09 \times 10^3$ | $5.3 \times 10^3$ |
| $E_p$ | $\mathrm{kJ\,mol^{-1}}$ | 16 to 25 | $29.7 \times 10^3$ | $29.7 \times 10^3$ |
| $k_t\,(60\,°\mathrm{C})$ | $\mathrm{dm^3\,mol^{-1}s^{-1}}$ | $10^6$ to $10^8$ | $9.5 \times 10^6$ | $9.5 \times 10^6$ |
| $E_t$ | $\mathrm{kJ\,mol^{-1}}$ | 1 to 23 | $22.2 \times 10^3$ | $22.2 \times 10^3$ |
|  |  |  | KPS (non-catalyzed) |  |
| $k_d\,(50\,°\mathrm{C})$ | $\mathrm{s^{-1}}$ | $10^{-6}$ to $10^{-4}$ | $1.6 \times 10^{-6}$ | $3.4 \times 10^{-5}$ |
| $k_d\,(60\,°\mathrm{C})$ | $\mathrm{s^{-1}}$ | $10^{-6}$ to $10^{-4}$ | $5.0 \times 10^{-6}$ | $8.2 \times 10^{-5}$ |
| $k_d\,(70\,°\mathrm{C})$ | $\mathrm{s^{-1}}$ | $10^{-6}$ to $10^{-4}$ | $1.4 \times 10^{-5}$ | $1.9 \times 10^{-4}$ |
| $k_d\,(80\,°\mathrm{C})$ | $\mathrm{s^{-1}}$ | $10^{-6}$ to $10^{-4}$ | $3.9 \times 10^{-5}$ | $3.9 \times 10^{-4}$ |
| $k_{d,\mathrm{redox}}\,(60\,°\mathrm{C})$ | $\mathrm{dm^3mol^{-1}s^{-1}}$ | $10^{-6}$ to $10^{-4}$ | $10$ to $1000 \times k_d$ | $750 \times k_d\,(60\,°\mathrm{C})$ |
| $c_s\,(60\,°\mathrm{C})$ | – | $10^{-6}$ to 50 | – | 10 |

Methyl acrylate polymerization rate parameters were refined by a least squares procedure in order to find a possible set of parameters that would describe the experimental data acceptably. All the $k_d$ parameters were free parameters; for $k_p$ and $k_t$ only the value at 60 °C was a free parameter. The values for other reaction temperatures were calculated by scaling with the corresponding activation energies ($E_x$) according to

$$k_x(T) = k(60°\mathrm{C}) \cdot \exp\left(\frac{E_x}{R}\left[\frac{1}{333.15\,\mathrm{K}} - \frac{1}{T}\right]\right)$$

where $R$ is the gas constant. A small program was written to solve the optimization problem

$$\min_{\mathbf{x}} ||\overline{V}_{p,M,T} - \overline{V}_{p,M}(\mathbf{x})||_2^2$$

where $||\cdot||_2$ stands for vector 2-norm, $\overline{V}_{p,M,T}$ refers to average particle volume at monomer concentration [M] and temperature $T$ in Figure 4A of the main paper. Vector $\mathbf{x}$ contains the model parameters and $\overline{V}_{p,M}(\mathbf{x})$ is the model expression for the average particle volume

$$\overline{V}_{p,M}(\mathbf{x}) = A \times \frac{[\mathrm{M}]}{\overline{\rho}_{A,m,t} \cdot k_d(T)/k_d(50°\mathrm{C})}$$

The surface charge density is calculated from

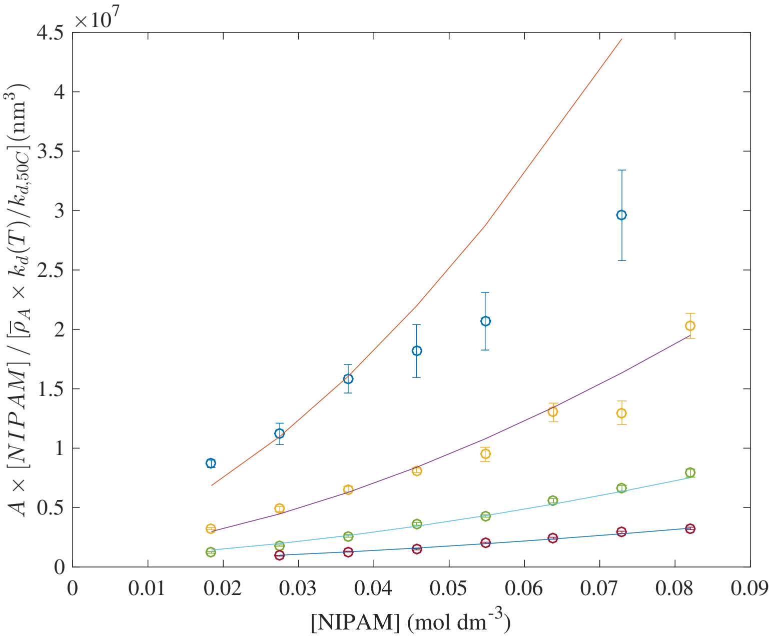
$$\overline{\rho}_A = \frac{\overline{n}_{xc,1} + 2\overline{n}_{xc,3} + \overline{n}_{xc,4}}{\overline{x}_{xc}^{2/3}}$$

with mole fractions as given in the main paper (Equations 3 to 7). Assuming that the charged fragments are located at the globule surface and that the globule density is constant, this expression is correct up to a constant factor ($v_0^{-2/3}$), see Eq. 2 in main paper). Constant $A$ absorbs $V_M$, absolute particle number density $n$ and other proportionality constants that were left out in the derivation of the scaling law. The parameter vector $\mathbf{x}$ therefore contains

$$\mathbf{x} = [A\ k_p\,(60\,°\mathrm{C})\ k_t\,(60\,°\mathrm{C})\ k_d\,(50\,°\mathrm{C})\ k_d\,(60\,°\mathrm{C})\ k_d\,(70\,°\mathrm{C})\ k_d\,(80\,°\mathrm{C})]$$

necessary to calculate the mole fractions from Flory-Schulz equations given in the manuscript. Rate constants for propagation ($k_p$) and termination ($k_t$) were scaled to other temperatures using the activation energies, as explained above. Depending on the initial guesses, one can find a local minimum so that the data fits approximately, as shown by Supporting Figure 10. The calculated result does agree with the largest particles well. This can be explained by the fact that the largest particles polymerized at 50 °C start to sediment during the polymerization and the sample for the dynamic light scattering experiment can be taken only from the stable but smaller particles that remain dispersed in water.

The kinetic parameters obtained by least squares minimization are given in Supporting Table 3. One should not consider these values to be specific to NIPAM polymerization per se; if the extent of aggregation of primary globules is proportional to the charge



*Supporting Figure 10:* $\overline{V}_{p,M}(\mathbf{x})$, with $\mathbf{x}$ determined by least squares procedure. The deviation of the largest particles is due to sedimentation during the polymerization, as explained in the text.

density of polymer, this set is one set of parameters that produces polymer charge density capable of describing the experimental data qualitatively in the case of precipitation polymerization of NIPAM.

Some of the batches were initiated with potassium persulfate (KPS) and some by ammonium persulfate - N,N,N',N'- tetramethylethylenediamine (APS-TEMED) redox system. The dissociation constant for redox system is typically several orders of magnitude higher than that of the corresponding persulfate by thermal decomposition.[3] Under certain circumstances, the use of redox initiation offers additional benefits beyond the fun factor. It is a property of APS-TEMED initiation that initiator induced cross-linking is greatly diminished,[5] which is essential when the effect of initiation rate on particle number density is investigated. Presence of initiator induced cross-linking leads to decrease in the number of particles with increasing initiator concentration, whereas the opposite is observed when the additional cross-linking is suppressed.[8] Furthermore, in situations where it is difficult to get rid of all the oxygen in the reaction medium (e.g. in calorimeter), the high initiation rate provided by redox initiator system helps to diminish any disturbances caused by trace amounts of oxygen.

*Supporting Table 4:* Reaction parameters for KPS initiated batches at different temperatures. Horizontal lines denote batches that were polymerized simultaneously.

| Figure | T (°C) | [NIPAM] (mmol dm$^{-3}$) | [KPS] (mmol dm$^{-3}$) | $R_h$ (nm) | STD (nm) |
|---|---|---|---|---|---|
| 4A | 50 | 73.0 | 1.6 | 192 | 4 |
| 4A | 50 | 54.8 | 1.6 | 170 | 3 |
| 4A | 50 | 45.7 | 1.6 | 163 | 3 |
| 4A | 50 | 36.6 | 1.6 | 156 | 2 |
| 4A | 50 | 27.5 | 1.6 | 139 | 2 |
| 4A | 50 | 18.4 | 1.6 | 127.5 | 0.8 |
| 4A | 60 | 82 | 1.6 | 170 | 2 |
| 4A | 60 | 73.0 | 1.6 | 146 | 2 |
| 4A | 60 | 63.9 | 1.6 | 146 | 2 |
| 4A | 60 | 54.8 | 1.6 | 131 | 1.4 |
| 4A | 60 | 45.7 | 1.6 | 124.8 | 0.5 |
| 4A | 60 | 36.6 | 1.6 | 116.1 | 0.7 |
| 4A | 60 | 27.5 | 1.6 | 105.2 | 0.8 |
| 4A | 60 | 18.4 | 1.6 | 91.7 | 0.4 |
| 4A | 70 | 82 | 1.6 | 123.5 | 0.9 |
| 4A | 70 | 73.0 | 1.6 | 116.5 | 0.7 |
| 4A | 70 | 63.9 | 1.6 | 110.0 | 0.6 |
| 4A | 70 | 54.8 | 1.6 | 100.8 | 0.4 |
| 4A | 70 | 45.7 | 1.6 | 95.4 | 0.5 |
| 4A | 70 | 36.6 | 1.6 | 85.5 | 0.6 |
| 4A | 70 | 27.5 | 1.6 | 75.5 | 0.6 |
| 4A | 70 | 18.4 | 1.6 | 66.4 | 0.6 |
| 4A | 80 | 82 | 1.6 | 91.9 | 0.5 |
| 4A | 80 | 73.0 | 1.6 | 88.6 | 0.5 |
| 4A | 80 | 63.9 | 1.6 | 83.3 | 0.5 |
| 4A | 80 | 54.8 | 1.6 | 78.5 | 0.4 |
| 4A | 80 | 45.7 | 1.6 | 70.9 | 0.4 |
| 4A | 80 | 36.6 | 1.6 | 67.6 | 0.3 |
| 4A | 80 | 27.5 | 1.6 | 61.0 | 0.3 |

# 3 Experimental data

The reactant compostions and hydrodynamic radii for all the batches featured in this work are listed in Supporting Tables 4 to 9 . Data is organized based on the figures they appear in the main paper.

*Supporting Table 5:* Reaction parameters for APS-TEMED initiated batches with variable APS concentration. Horizontal lines denote batches that were polymerized simultaneously.

| Figure | T (°C) | [APS] (mmol dm$^{-3}$) | [TEMED] (mmol dm$^{-3}$) | [NIPAM] (mmol dm$^{-3}$) | $R_h$ (nm) | STD (nm) |
|---|---|---|---|---|---|---|
| 4B | 60 | 2.5 | 17 | 54.9 | 90.6 | 0.7 |
| 4B | 60 | 2.2 | 17 | 54.9 | 92.1 | 0.7 |
| 4B | 60 | 1.8 | 17 | 54.9 | 93.3 | 0.5 |
| 4B | 60 | 1.5 | 17 | 54.9 | 96.4 | 0.8 |
| 4B | 60 | 5.8 | 17 | 54.9 | 87.4 | 0.5 |
| 4B | 60 | 5.0 | 17 | 54.9 | 88.0 | 0.6 |
| 4B | 60 | 4.2 | 17 | 54.9 | 85.5 | 0.6 |
| 4B | 60 | 3.3 | 17 | 54.9 | 89.1 | 0.5 |
| 4B | 60 | 2.5 | 17 | 54.9 | 87.7 | 0.7 |
| 4B | 60 | 1.7 | 17 | 54.9 | 90.9 | 0.8 |
| 4B | 60 | 0.9 | 17 | 54.9 | 101.9 | 0.6 |
| 4B | 60 | 0.6 | 17 | 54.9 | 108.2 | 0.5 |
| 4B | 60 | 3.3 | 17 | 54.9 | 89.3 | 0.6 |
| 4B | 60 | 2.9 | 17 | 54.9 | 92.0 | 0.6 |
| 4B | 60 | 2.5 | 17 | 54.9 | 88.7 | 0.4 |
| 4B | 60 | 2.2 | 17 | 54.9 | 91 | 0.6 |
| 4B | 60 | 1.8 | 17 | 54.9 | 92.9 | 0.6 |
| 4B | 60 | 1.4 | 17 | 54.9 | 96.6 | 0.5 |
| 4B | 60 | 1.0 | 17 | 54.9 | 102 | 0.7 |
| 4B | 60 | 0.6 | 17 | 54.9 | 120 | 0.7 |

*Supporting Table 6:* Reaction parameters for various N,N'-methylenebisacrylamide (BIS) batches. Horizontal lines denote batches that were polymerized simultaneously.

| Figure | T (°C) | [NIPAM] (mmol dm$^{-3}$) | BIS (mol-%) | [KPS] (mmol dm$^{-3}$) | $R_h$ (nm) | STD (nm) |
|---|---|---|---|---|---|---|
| 6 | 70 | 104.4 | 0 | 1.6 | 180 | 1.3 |
| 6 | 70 | 86.8 | 0 | 1.6 | 161 | 1.2 |
| 6 | 70 | 77.0 | 0 | 1.6 | 147 | 1.1 |
| 6 | 70 | 63.9 | 0 | 1.6 | 132 | 1.1 |
| 6 | 70 | 49.6 | 0 | 1.6 | 117.7 | 0.9 |
| 6 | 70 | 9.1 | 0 | 1.6 | 56.0 | 0.4 |
| 6 | 70 | 95.3 | 0 | 1.6 | 174 | 2 |
| 6 | 70 | 82.2 | 0 | 1.6 | 151.7 | 0.6 |
| 6 | 70 | 70.5 | 0 | 1.6 | 145.3 | 0.6 |
| 6 | 70 | 56.1 | 0 | 1.6 | 121.8 | 0.5 |
| 6 | 70 | 43.1 | 0 | 1.6 | 104.8 | 0.5 |
| 6 | 70 | 29.4 | 0 | 1.6 | 93.7 | 0.2 |
| 6 | 70 | 25.7 | 0 | 1.6 | 71.4 | 0.3 |
| 6 | 70 | 5.2 | 0 | 1.6 | 64.3 | 0.4 |
| 6 | 70 | 83.5 | 0 | 1.6 | 156.6 | 0.5 |
| 6 | 70 | 69.4 | 0 | 1.6 | 136.9 | 0.9 |
| 6 | 70 | 61.6 | 0 | 1.6 | 129.7 | 0.5 |
| 6 | 70 | 51.1 | 0 | 1.6 | 115.5 | 0.3 |
| 6 | 70 | 39.7 | 0 | 1.6 | 103.0 | 0.4 |
| 6 | 70 | 29.2 | 0 | 1.6 | 89.3 | 0.7 |
| 6 | 70 | 17.8 | 0 | 1.6 | 75.9 | 0.2 |
| 6 | 70 | 7.3 | 0 | 1.6 | 53.9 | 0.9 |
| 6 | 70 | 104.4 | 1.0 | 1.6 | 180 | 2 |
| 6 | 70 | 86.8 | 1.0 | 1.6 | 166 | 2 |
| 6 | 70 | 77.0 | 1.0 | 1.6 | 149 | 2 |
| 6 | 70 | 63.9 | 1.0 | 1.6 | 136.2 | 0.9 |
| 6 | 70 | 49.6 | 1.0 | 1.6 | 124.0 | 0.8 |
| 6 | 70 | 36.5 | 1.0 | 1.6 | 108 | 0.4 |
| 6 | 70 | 22.2 | 1.0 | 1.6 | 87.4 | 0.2 |
| 6 | 70 | 9.1 | 1.0 | 1.6 | 56.3 | 0.4 |
| 6 | 70 | 104.4 | 2.5 | 1.6 | 197 | 5 |
| 6 | 70 | 86.8 | 2.5 | 1.6 | 177 | 1.4 |
| 6 | 70 | 77.0 | 2.5 | 1.6 | 163 | 2 |
| 6 | 70 | 63.9 | 2.5 | 1.6 | 153.8 | 1.2 |
| 6 | 70 | 49.6 | 2.5 | 1.6 | 135 | 0.6 |
| 6 | 70 | 36.5 | 2.5 | 1.6 | 117.6 | 0.6 |
| 6 | 70 | 22.2 | 2.5 | 1.6 | 94.6 | 0.4 |
| 6 | 70 | 9.1 | 2.5 | 1.6 | 66.1 | 0.6 |
| 6 | 70 | 104.4 | 5.0 | 1.6 | 203 | 2 |
| 6 | 70 | 86.8 | 5.0 | 1.6 | 187 | 4 |
| 6 | 70 | 77.0 | 5.0 | 1.6 | 179 | 1.5 |
| 6 | 70 | 63.9 | 5.0 | 1.6 | 160 | 1.3 |
| 6 | 70 | 49.6 | 5.0 | 1.6 | 142.9 | 0.9 |
| 6 | 70 | 36.5 | 5.0 | 1.6 | 121 | 0.3 |
| 6 | 70 | 22.2 | 5.0 | 1.6 | 100.8 | 0.6 |

*Supporting Table 7:* Reaction parameters for batches with constant NIPAM-to-2-mercaptoethanol (ME) ratio. Horizontal lines denote batches that were polymerized simultaneously.

| Figure | T (°C) | [NIPAM] (mmol dm$^{-3}$) | [APS] (mmol dm$^{-3}$) | [TEMED] (mmol dm$^{-3}$) | [ME] (mmol dm$^{-3}$) | $R_h$ (nm) | STD (nm) |
|---|---|---|---|---|---|---|---|
| 7A | 60 | 82.1 | 1.6 | 3.4 | 0 | 118.0 | 0.7 |
| 7A | 60 | 72.9 | 1.6 | 3.4 | 0 | 113.7 | 1.4 |
| 7A | 60 | 63.8 | 1.6 | 3.4 | 0 | 103.9 | 0.6 |
| 7A | 60 | 54.8 | 1.6 | 3.4 | 0 | 98.4 | 0.6 |
| 7A | 60 | 45.7 | 1.6 | 3.4 | 0 | 87.0 | 0.5 |
| 7A | 60 | 36.5 | 1.6 | 3.4 | 0 | 82.6 | 0.6 |
| 7A | 60 | 27.5 | 1.6 | 3.4 | 0 | 73.7 | 0.7 |
| 7A | 60 | 18.4 | 1.6 | 3.4 | 0 | 65.7 | 0.4 |
| 7A | 60 | 82.1 | 1.6 | 3.4 | 0.66 | 147 | 1.1 |
| 7A | 60 | 72.9 | 1.6 | 3.4 | 0.58 | 136 | 1 |
| 7A | 60 | 63.8 | 1.6 | 3.4 | 0.51 | 120.4 | 0.8 |
| 7A | 60 | 54.8 | 1.6 | 3.4 | 0.44 | 113.7 | 0.6 |
| 7A | 60 | 45.7 | 1.6 | 3.4 | 0.37 | 102.6 | 0.6 |
| 7A | 60 | 36.5 | 1.6 | 3.4 | 0.29 | 88.8 | 0.5 |
| 7A | 60 | 27.5 | 1.6 | 3.4 | 0.22 | 80.4 | 0.6 |
| 7A | 60 | 18.4 | 1.6 | 3.4 | 0.15 | 71.5 | 0.5 |
| 7A | 60 | 82.1 | 1.6 | 3.4 | 0.99 | 157 | 1.5 |
| 7A | 60 | 72.9 | 1.6 | 3.4 | 0.88 | 151 | 1 |
| 7A | 60 | 63.8 | 1.6 | 3.4 | 0.77 | 135 | 1 |
| 7A | 60 | 54.8 | 1.6 | 3.4 | 0.66 | 124 | 1 |
| 7A | 60 | 45.7 | 1.6 | 3.4 | 0.55 | 111.9 | 0.7 |
| 7A | 60 | 36.5 | 1.6 | 3.4 | 0.44 | 93.1 | 0.4 |
| 7A | 60 | 27.5 | 1.6 | 3.4 | 0.33 | 83.2 | 0.4 |
| 7A | 60 | 18.4 | 1.6 | 3.4 | 0.22 | 72.8 | 0.5 |
| 7A | 60 | 72.9 | 1.6 | 3.4 | 1.17 | 174 | 1 |
| 7A | 60 | 63.8 | 1.6 | 3.4 | 1.0 | 165 | 2 |
| 7A | 60 | 54.8 | 1.6 | 3.4 | 0.88 | 145 | 3 |
| 7A | 60 | 36.5 | 1.6 | 3.4 | 0.59 | 118.9 | 0.8 |
| 7A | 60 | 27.5 | 1.6 | 3.4 | 0.44 | 107.0 | 0.8 |
| 7A | 60 | 18.4 | 1.6 | 3.4 | 0.29 | 89.6 | 0.6 |

*Supporting Table 8:* Reaction parameters for batches with constant 2-mercaptoethanol (ME) concentration. Horizontal lines denote batches that were polymerized simultaneously.

| Figure | T (°C) | [NIPAM] (mmol dm$^{-3}$) | [APS] (mmol dm$^{-3}$) | [TEMED] (mmol dm$^{-3}$) | [ME] (mmol dm$^{-3}$) | $R_h$ (nm) | STD (nm) |
|---|---|---|---|---|---|---|---|
| 7B | 60 | 82.1 | 1.6 | 3.4 | 0 | 118.0 | 0.7 |
| 7B | 60 | 72.9 | 1.6 | 3.4 | 0 | 113.7 | 1.4 |
| 7B | 60 | 63.8 | 1.6 | 3.4 | 0 | 103.9 | 0.6 |
| 7B | 60 | 54.8 | 1.6 | 3.4 | 0 | 98.4 | 0.6 |
| 7B | 60 | 45.7 | 1.6 | 3.4 | 0 | 87.0 | 0.5 |
| 7B | 60 | 36.5 | 1.6 | 3.4 | 0 | 82.6 | 0.6 |
| 7B | 60 | 27.5 | 1.6 | 3.4 | 0 | 73.7 | 0.7 |
| 7B | 60 | 18.4 | 1.6 | 3.4 | 0 | 65.7 | 0.4 |
| 7B | 60 | 82.1 | 1.6 | 3.4 | 0.16 | 126.3 | 0.5 |
| 7B | 60 | 72.9 | 1.6 | 3.4 | 0.16 | 122.7 | 0.9 |
| 7B | 60 | 63.8 | 1.6 | 3.4 | 0.16 | 121.5 | 0.6 |
| 7B | 60 | 54.8 | 1.6 | 3.4 | 0.16 | 111.3 | 0.7 |
| 7B | 60 | 45.7 | 1.6 | 3.4 | 0.16 | 106.1 | 0.6 |
| 7B | 60 | 36.5 | 1.6 | 3.4 | 0.16 | 101.5 | 0.7 |
| 7B | 60 | 27.5 | 1.6 | 3.4 | 0.16 | 100.7 | 0.6 |
| 7B | 60 | 18.4 | 1.6 | 3.4 | 0.16 | 97.0 | 0.6 |
| 7B | 60 | 82.1 | 1.6 | 3.4 | 0.33 | 145.0 | 0.8 |
| 7B | 60 | 72.9 | 1.6 | 3.4 | 0.33 | 140 | 1 |
| 7B | 60 | 63.8 | 1.6 | 3.4 | 0.33 | 138.4 | 0.8 |
| 7B | 60 | 54.8 | 1.6 | 3.4 | 0.33 | 129.0 | 0.8 |
| 7B | 60 | 45.7 | 1.6 | 3.4 | 0.33 | 124.1 | 0.6 |
| 7B | 60 | 36.5 | 1.6 | 3.4 | 0.33 | 121.6 | 0.7 |
| 7B | 60 | 27.5 | 1.6 | 3.4 | 0.33 | 120.3 | 0.7 |
| 7B | 60 | 18.4 | 1.6 | 3.4 | 0.33 | 116.3 | 0.8 |
| 7B | 60 | 63.8 | 1.6 | 3.4 | 0.65 | 173 | 3 |
| 7B | 60 | 54.8 | 1.6 | 3.4 | 0.65 | 163 | 1.2 |
| 7B | 60 | 45.7 | 1.6 | 3.4 | 0.65 | 167 | 3 |
| 7B | 60 | 36.5 | 1.6 | 3.4 | 0.65 | 165 | 2 |
| 7B | 60 | 27.5 | 1.6 | 3.4 | 0.65 | 179 | 2 |

*Supporting Table 9:* Reaction parameters for batches with constant NIPAM, APS and TEMED concentrations.

| Figure | T (°C) | [NIPAM] (mmol dm$^{-3}$) | [APS] (mmol dm$^{-3}$) | [TEMED] (mmol dm$^{-3}$) | [ME] (mmol dm$^{-3}$) | $R_h$ (nm) | STD (nm) |
|---|---|---|---|---|---|---|---|
| 7C | 60 | 36.5 | 7.8 | 0.86 | 0.44 | 140 | 1.2 |
| 7C | 60 | 36.5 | 7.8 | 0.86 | 0.38 | 131.6 | 0.7 |
| 7C | 60 | 36.5 | 7.8 | 0.86 | 0.31 | 127.7 | 0.7 |
| 7C | 60 | 36.5 | 7.8 | 0.86 | 0.25 | 114.1 | 0.6 |
| 7C | 60 | 36.5 | 7.8 | 0.86 | 0.19 | 105.9 | 0.5 |
| 7C | 60 | 36.5 | 7.8 | 0.86 | 0.13 | 92.6 | 0.5 |
| 7C | 60 | 36.5 | 7.8 | 0.86 | 0.63 | 90.3 | 0.6 |
| 7C | 60 | 36.5 | 7.8 | 0.86 | 0 | 87.3 | 0.4 |

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