Kinetics and MWD in living polymerizations proceeding in ideally dispersed systems without mass transfer. Numerical simulations.

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Introduction

Living irreversible polymerization proceeding in ideally dispersed systems (equal volumes of droplets) differs qualitatively from the analogous processes carried on in a large volume.[1] Particularly, in the dispersed systems the chain length distribution (CLD) at complete conversion is narrower than the Poisson distribution and the CLD dispersity ($Đ$) depends on number of chains in each droplet n_C:

$$Đ = 1 + (DP_n - 1)(1 - 1/n_c)/(DP_n)^2$$

Equilibrium constants of reversible reactions proceeding in dispersed systems also depend on reactants distribution, being (for uniform distribution of reactants) much higher than in a large volume systems.[2]

Here we present for the first time results of numerical modeling of kinetics of the reversible living polymerization process proceeding in dispersed systems. Simulations were done by Monte Carlo method (Gillespie algorithm) and by numerical integration of kinetic differential equations.
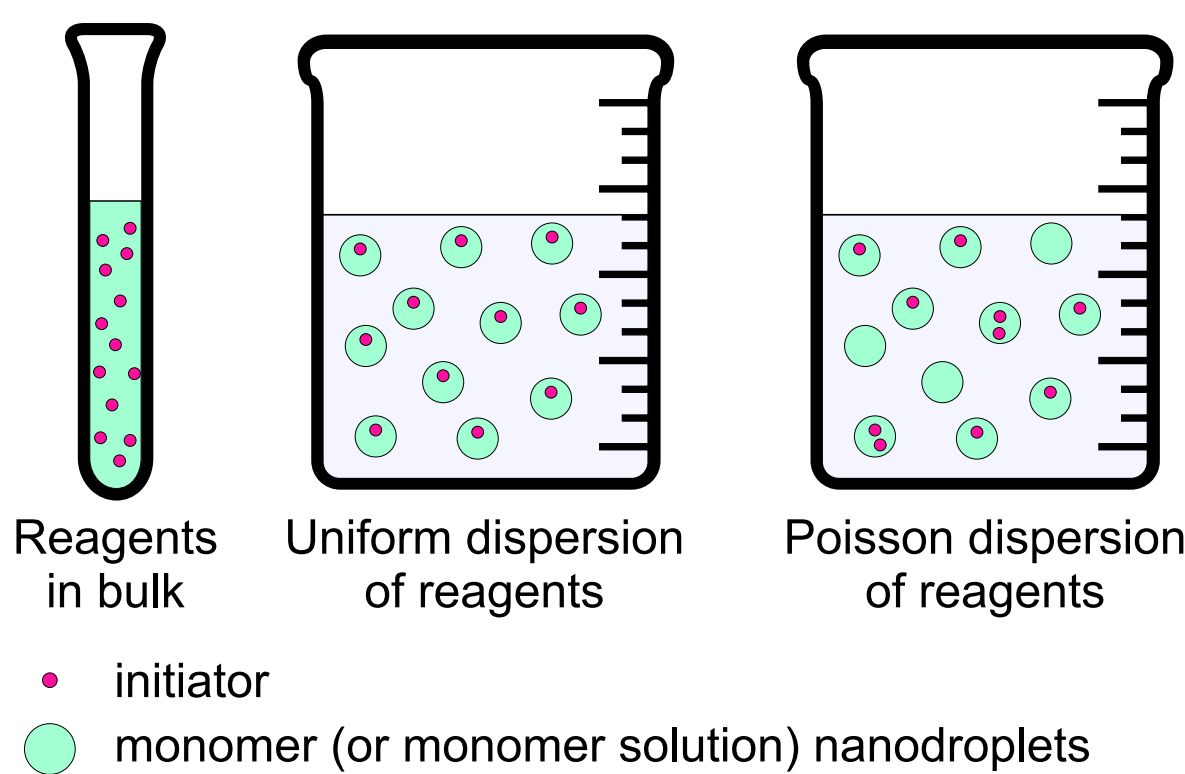
Studied systems are schematically shown in the Figure 1. They include polymerization in bulk (a large volume) and in two kinds of fine dispersions (nanodroplets of equal volume): the **ideal dispersion**, in which all droplets initially contain equal numbers of chains and monomer molecules, and the **Poisson dispersion**, in which reagents are randomly distributed among droplets.

The equilibrium constant K (expressed as the ratio of propagation and depropagation rate constants k_p/k_d) was assumed to be equal to: infinity (irreversible process), 5, or 50 l/mol. The mean number of chains in droplets n_C was equal to 0.5, 1, 2, 3, 4, 5, 10, 20, or infinity (polymerization in bulk). The following characteristics of the process (in relation to changes of K, n_C, and the type of dispersion): number-averaged and mass-averaged degree of polymerization (DP_n and DP_w), dispersity ($Đ$), chain length distribution, (apparent) equilibrium monomer concentration ($[M]_e$), and time of approaching the equilibrium, were analysed.

- initiator
- monomer (or monomer solution) nanodroplets

Figure 1. Modelled polymerization systems

Results

Figure 2. Evolution of monomer concentration [M], initiating species concentration $[M_1^*]$, number-average degree of polymerization DP_n, and dispersity $Đ$ in reversible polymerization carried on in ideal dispersion. $n_C = 1$, $K = 5$ L/mol.
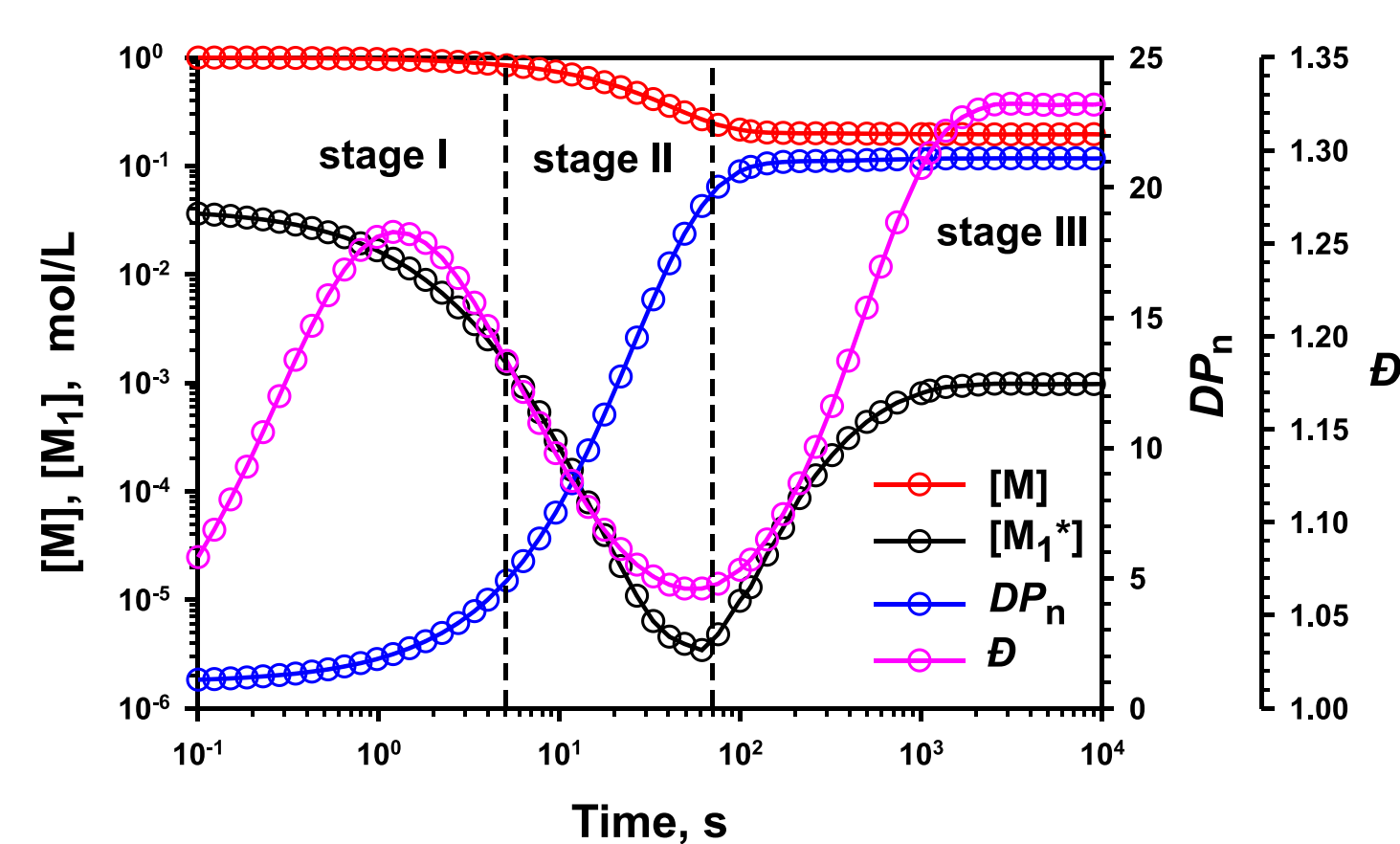
Similarly as in bulk systems, the entire process carried out in droplets can be divided into three stages, defined by values of propagation and depropagation rate constants.[3,4] Typically the first stage resembles the irreversible polymerization, in the second stage the polymer builds up and dispersity attains its minimum. Finally, in the third stage, depropagation reaction changes the narrow CLD into broaded equilibrium one (resembling the most probable one for large n_C).

Figure 3. Evolution of dispersity $Đ$ in the reversible polymerization process carried on in dispersed system. Equilibrium constant $K = 5$ L/mol.
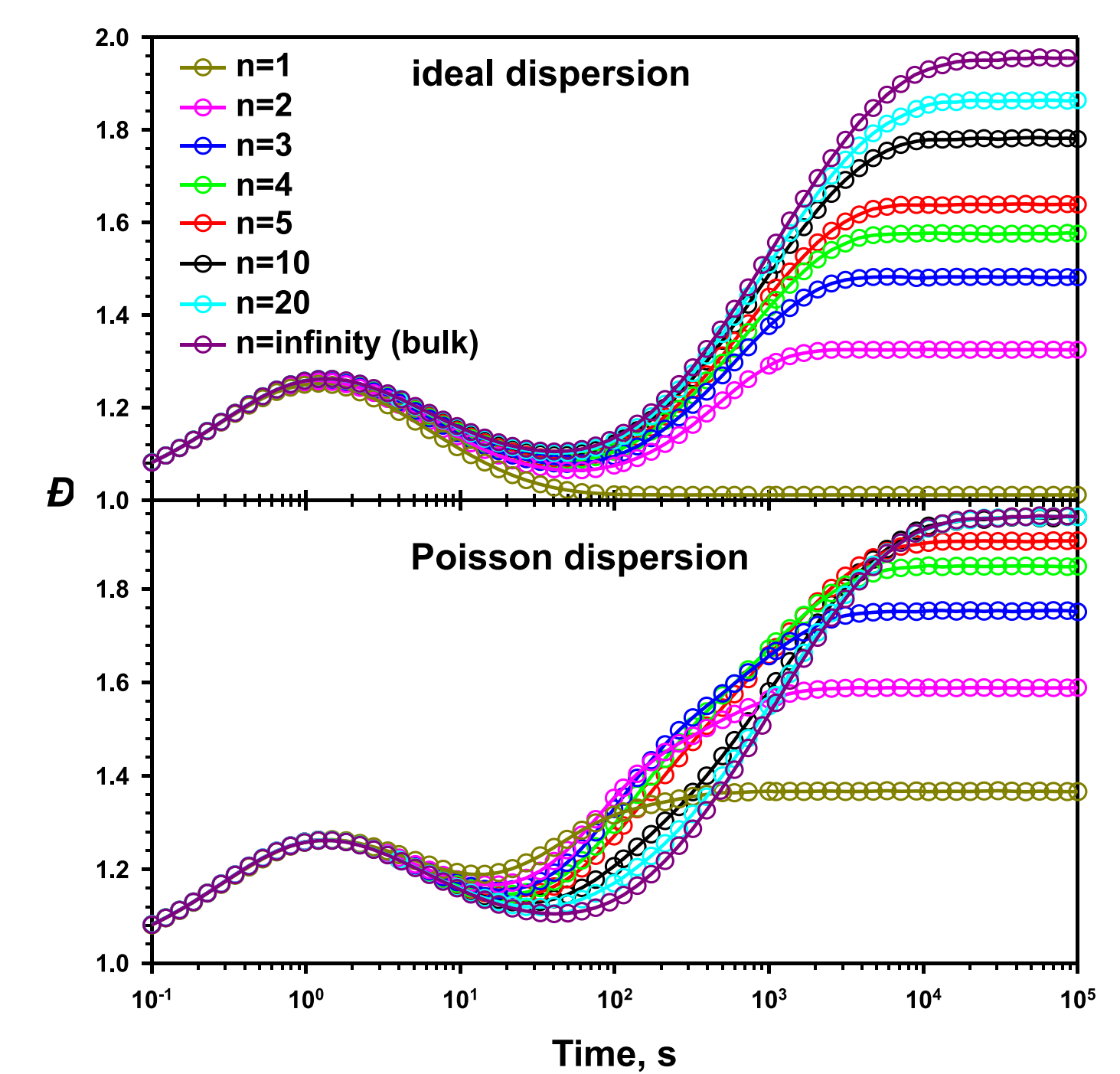
The dispersity at equilibrium increases with the mean number of chains in droplets n_C. The dependence is stronger for the ideal dispersion than for the Poisson dispersion. The dispersity is also significantly lower in case of dispersed systems than in bulk, especially for the ideal dispersion and low n_C.

Figure 4. Evolution of monomer concentration [M] in reversible polymerization process carried on in the ideal and Poisson dispersions. $K = 5$ L/mol.
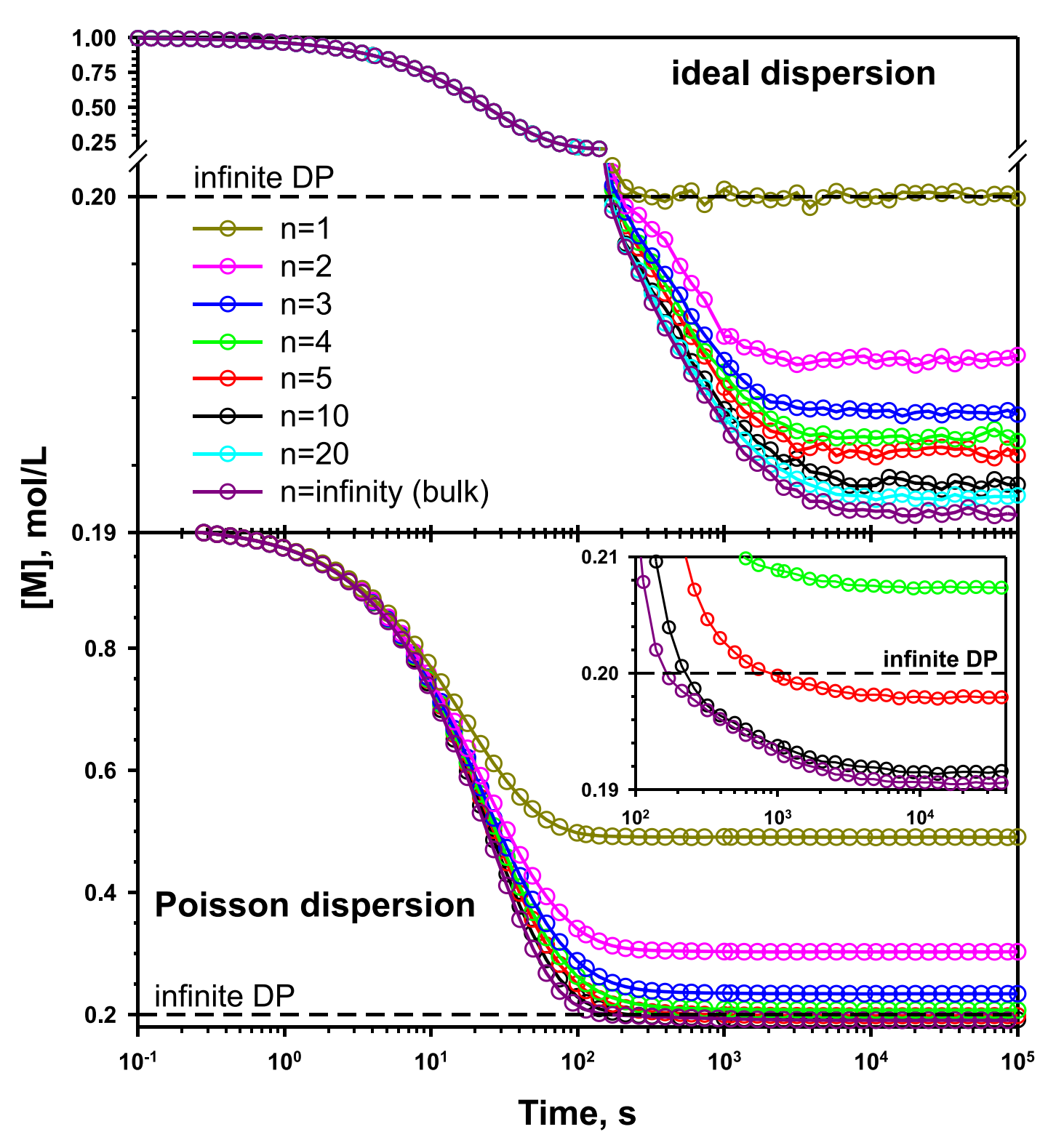
The (apparent) equilibrium monomer concentration $[M]_e$ depends on the number of chains in droplets, being the highest for the lowest number of chains in droplets. It is worth to note that in the case of ideal dispersion, for $n_C=1$, the monomer equilibrium concentration corresponds to $[M]_e$ value in the bulk system with infinite degree of polymerization.

Much higher values of $[M]_e$ in the case of the Poisson dispersion and a low mean number of chains in droplets stem from presence of the unreacted monomer in the fraction of droplets having no initiator molecules.

Figure 5. Dependence of the time of approaching equilibrium on the mean number of chains in droplets n_C. Equilibrium constant $K = 5$ L/mol.
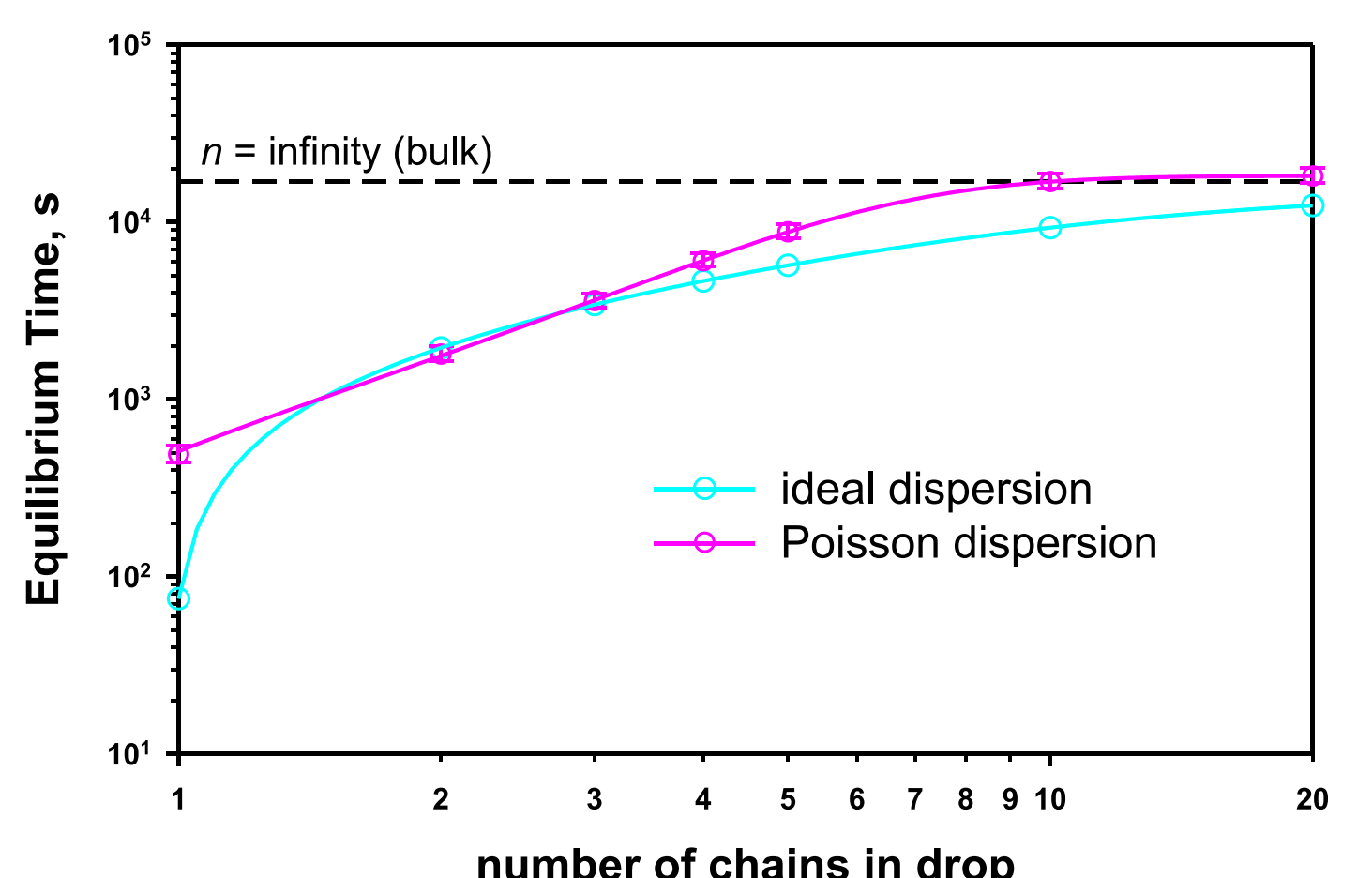
The equilibration time was defined as a time at which value of dispersity $Đ$ differs no more than 0.3% from the final value of $Đ$ (cf. Figure 3). For dispersed systems characterizing by the low mean number of chains in droplets the equilibration time is much shorter than for polymerization conducted in bulk.

Results

Figure 6. Chain length distribution in the reversible polymerization processes carried on in dispersed systems. $K = 5$ L/mol.
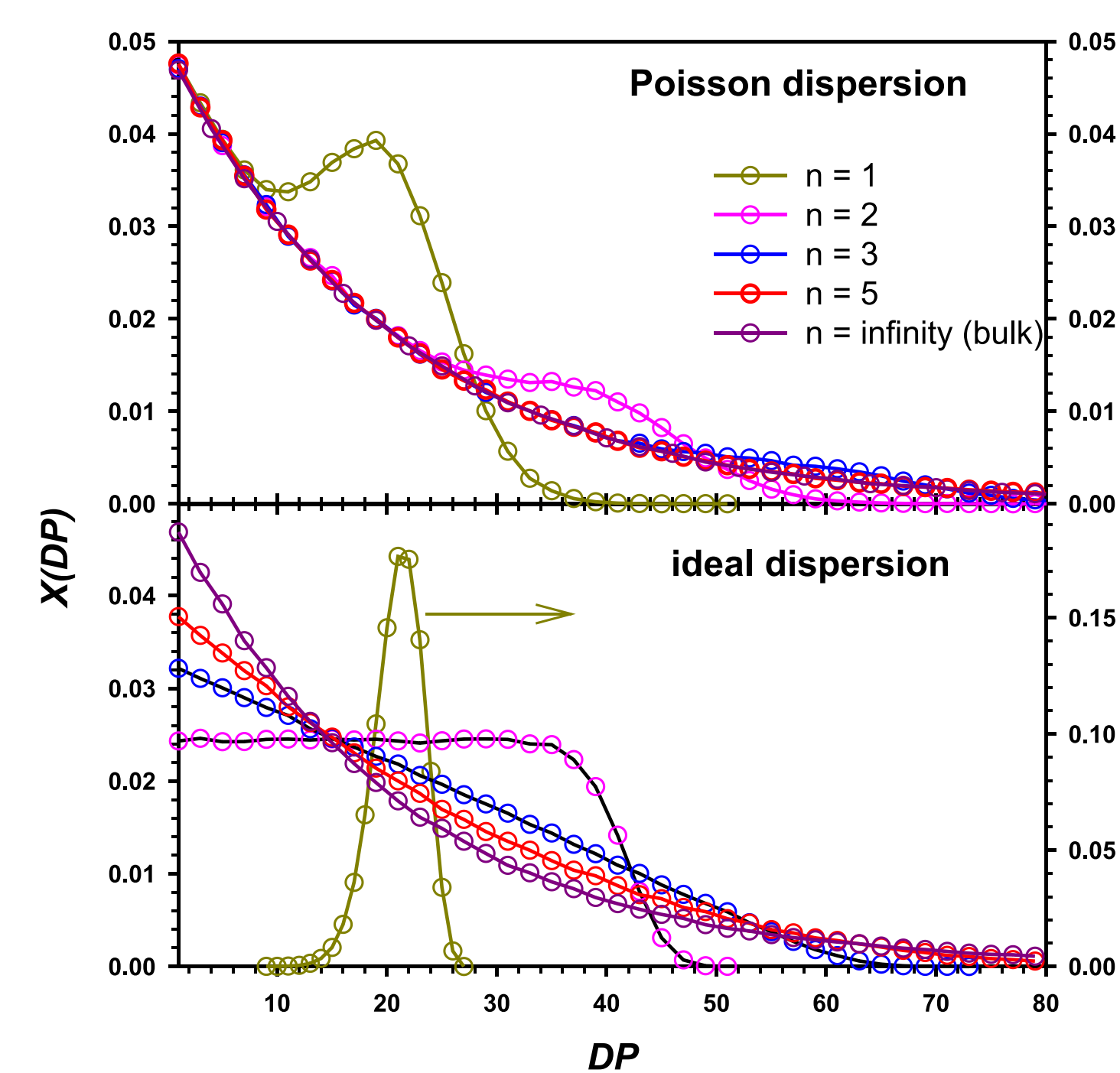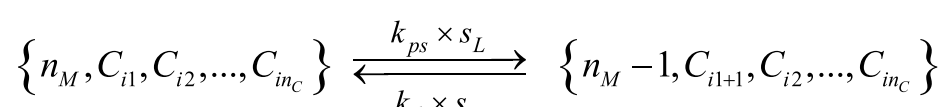
CLD depends on type of dispersion and mean number of chains in droplets; in the case of ideal dispersion the CLD is similar to that observed for the polyaddition in dispersed system.[1] For the Poisson dispersions CLDs are very close to the most probable distribution, at least for $n_C > 3$.

Figure 6. Comparison of equilibrium chain length distributions in polymerization processes carried on in various systems. $k_d = 0$ or 0.2 l/mol s. $n_C = 1$ or infinity.
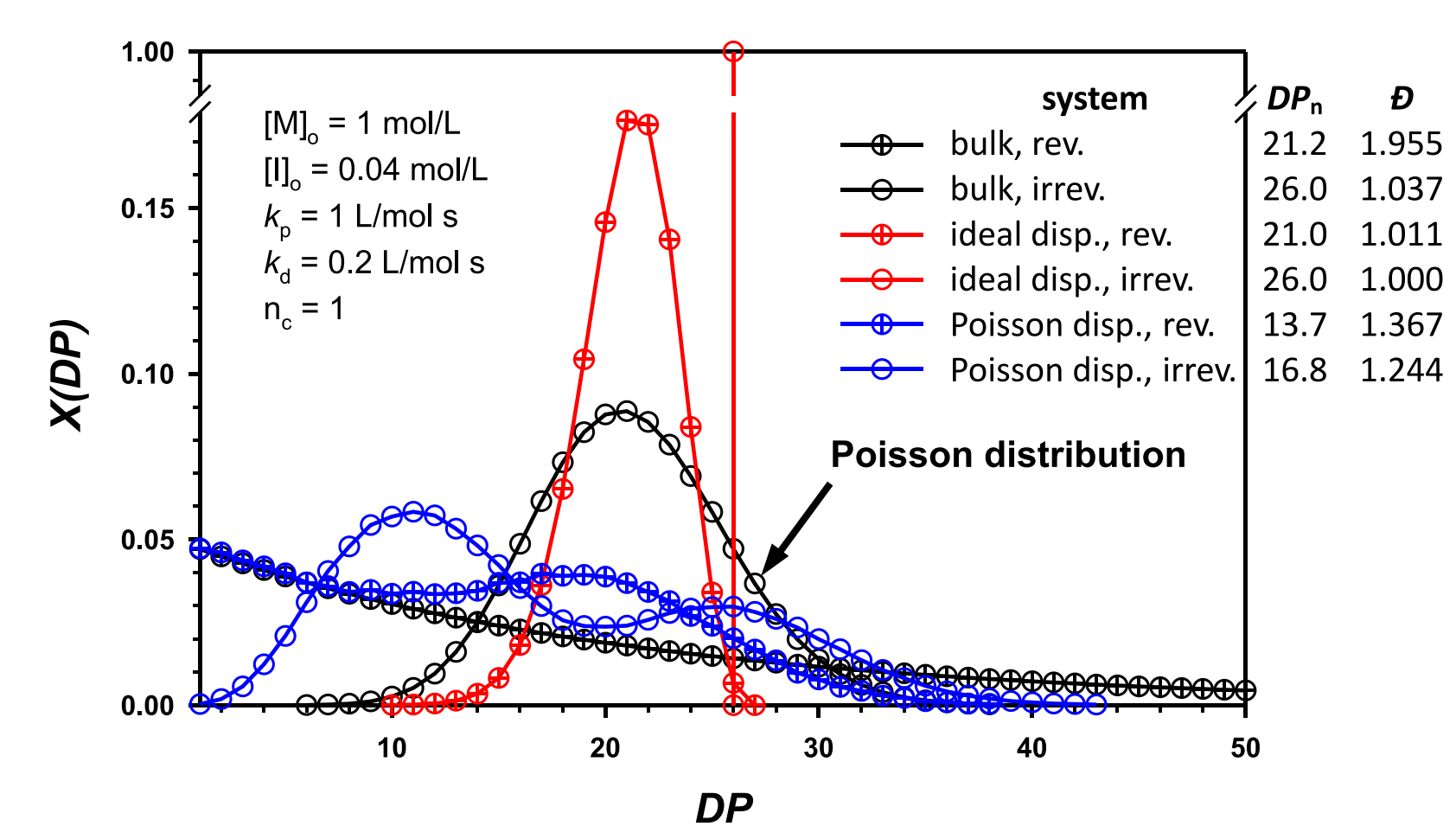
The chain length distribution in the ideal dispersion is always narrower than in bulk for both reversible or irreversible processes. Reversible process conducted in the Poisson dispersion also yields product with narrower CLD then in bulk system.

system	DP_n	$Đ$
bulk, rev.	21.2	1.955
bulk, irrev.	26.0	1.037
ideal disp., rev.	21.0	1.011
ideal disp., irrev.	26.0	1.000
Poisson disp., rev.	13.7	1.367
Poisson disp., irrev.	16.8	1.244

$[M]_0 = 1$ mol/L
$[I]_0 = 0.04$ mol/L
$k_p = 1$ l/mol s
$k_d = 0.2$ l/mol s
$n_C = 1$

Mathematical model

$$\{n_M, C_{i1}, C_{i2}, ..., C_{in_c}\} \underset{k_d \times s_R}{\overset{k_{ps} \times s_L}{\rightleftharpoons}} \{n_M - 1, C_{i1+1}, C_{i2}, ..., C_{in_c}\}$$

The equation describes a reversible transformation of a droplet containing n_c chains (C_X of various lengths) and n_M monomer molecules, due to one act of propagation (proceeding on a chain numerated arbitrarily as the first and having DP equal to $i1$). k_{ps} and k_d are stochastic rates of propagation and depropagation; s_L and s_R are statistical factors for forward and reverse reactions.

s_L = 1: when $i1$ (DP of chain 1: C_{i1}) differs from DP of other chains

s_L = j: when j chains (left droplet) have DP equal to $i1$

s_R = 1: when $i1+1$ (DP of the increased chain 1: C_{i1+1}) differs from DP of other chains in a droplet on the right-hand side

s_R = k: when k chains in the product droplet have DP equal to $i1+1$

For $n_c = 2$ the following set of differential kinetic equations describes the entire polymerization process, where $Fr\{n_M, C_i, C_j\}$ means number fraction of droplets of composition defined by parameters given in braces:

$$\left(\frac{dFr\{n_{M0}, C_1, C_1\}}{dt}\right) = -k_{ps} \times 2 \times n_{M0} \times Fr\{n_{M0}, C_1, C_1\} + k_d \times Fr\{n_{M0} - 1, C_1, C_2\}$$

$$\left(\frac{dFr\{n_{M0} - 1, C_1, C_2\}}{dt}\right) = k_{ps} \times 2 \times n_{M0} \times Fr\{n_{M0}, C_1, C_1\} - k_d \times Fr\{n_{M0} - 1, C_1, C_2\} - k_{ps}(n_{M0} - 1) \times Fr\{n_{M0} - 1, C_1, C_2\} + k_d \times Fr\{n_{M0} - 2, C_1, C_3\} + 2k_d \times Fr\{n_{M0} - 2, C_2, C_2\}$$

...

$$\left(\frac{dFr\{n_{M0} - i, C_1, C_{i+1}\}}{dt}\right) = k_{ps} \times (n_{M0} - i + 1) \times Fr\{n_{M0} - i + 1, C_1, C_i\} - k_d \times Fr\{n_{M0} - i, C_1, C_{i+1}\} - k_{ps}(n_{M0} - i) \times Fr\{n_{M0} - i, C_1, C_{i+1}\} + k_d \times Fr\{n_{M0} - i - 1, C_1, C_{i+2}\} \qquad i = 2, ..., n_{M0} - 1$$

$$\left(\frac{dFr\{0, C_1, C_{n_{M0}+1}\}}{dt}\right) = k_{ps} \times Fr\{1, C_1, C_{n_{M0}}\} - k_d \times Fr\{0, C_1, C_{n_{M0}+1}\}$$

...

$$\left(\frac{dFr\{n_{M0} + 2 - j, C_j, C_j\}}{dt}\right) = k_{ps} \times (n_{M0} + 3 - j - i) \times (Fr\{n_{M0} + 3 - j - i, C_j, C_{i-1}\} \times s_{j-i-1} + Fr\{n_{M0} + 3 - j - i, C_{j-1}, C_i\} \times s_{j-i-1}) - k_d \times 2 \times Fr\{n_{M0} + 2 - j, C_j, C_j\} - k_{ps}(n_{M0} + 2 - j - i) \times 2 \times Fr\{n_{M0} + 2 - j, C_j, C_j\} + k_d \times (Fr\{n_{M0} + 1 - j - i, C_j, C_{i+1}\} \times s_{j+i+1} + Fr\{n_{M0} + 1 - j - i, C_j, C_{i+1}\} \times s_{j+i+1}) \qquad i \geq j > 1, i + j < n_{M0} + 2$$

$s_{u,v} = \begin{cases} 1 \text{ when } u \neq v \\ 2 \text{ when } u = v \end{cases}$

$$\left(\frac{dFr\{0, C_i, C_{n_{M0}+2-i}\}}{dt}\right) = k_{ps} \times (Fr\{1, C_{i-1}, C_{n_{M0}+2-i}\} \times s_{n_{M0}+3-2i} + Fr\{1, C_i, C_{n_{M0}+1-i}\} \times s_{n_{M0}+1-2i}) - k_d \times 2 \times Fr\{0, C_i, C_{n_{M0}+2-i}\} \qquad i > 1$$

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