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Tailoring of the Molecular Weight Distribution by Nonstationary (Free Radical) Polymerization Conditions

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Summary: The choice of quenched instationary polymerization (QUIP) conditions will influence the shape and the moments of the polymers formed. As the quench reaction deactivates all radicals present at a given time, the total molecular weight distribution will always be a superposition of the (quenched) radical chain length distribution (RCLD) and the polymer chain length distribution (PCLD). Model calculations were carried out taking into account the different types of initiation conditions. In principle, distributions with extremely low polydispersities (Poisson-type) can be obtained as well as broad structured or non-structured distributions. Polymerization conditions will also determine whether the radical spectrum dominates a certain region of the distribution.

Introduction

In free radical polymerization a number of different reactions like chain initiation, propagation, termination and sometimes transfer or additional side reactions occur always simultaneously, giving rise to a non uniform product. No matter how the polymerization is carried out, the polymers will always have different chain lengths and the molecular weight distribution is influenced by the genesis of the product. The synchronization of the initiation process and the suppression of the termination process will lead to polymers with very low polydispersities and the shape can be described by a Poisson distribution. Stationary polymerization conditions (without chain transfer) lead to products with a polydispersity ranging between 1.5 and 2 and a monomodale distribution. On the other hand, pseudostationary polymerization (e.g. pulsed laser polymerization[1]) will lead to multimodale, broad distributions where the location of the so called additional peaks is influenced by the choice of the experimental parameters.

Although tailoring of the molecular weight distribution can be done with respect to the moments and polydisperisty, the shape of the distribution, the copolymer composition and sequence distribution, the number of long or short chain branches etc. this

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contribution concentrates only on the first two characteristics of polymers prepared under quenched instationary polymerization (QUIP) conditions. The essential element common to all QUIP experiments[2-6] is the deactivation of all radicals at a certain time. This can be done by reaction with an efficient radical scavenger. As a consequence the maximum radical and polymer chain lengths are controlled by the maximum active life-time of the radicals and the type of termination reaction. The experimentally observable molecular weight distribution is always composed of the (almost instantaneously converted) radical chain length distribution (RCLD) and that of the polymers (PCLD) deactivated by bimolecular termination reaction. Depending on the choice of experimental conditions the contribution of the RCLD can be very prominent.

Starting with a simple kinetic scheme

$$\begin{aligned}
&\text{chain initiation :} && I_\mathrm{k} \longrightarrow R_0\\
&\text{chain propagation :} && R_\mathrm{i} + M \xrightarrow{k_\mathrm{p}} R_\mathrm{i+1}\\
&\text{chain termination :} && R_\mathrm{i} + R_\mathrm{j} \xrightarrow{k_\mathrm{t}} P_\mathrm{i}, P_\mathrm{j}, P_\mathrm{i+j}\\
&\text{quench reaction :} && R_\mathrm{i} + Q \xrightarrow{k_\mathrm{Q}} \text{inactive products}
\end{aligned}$$

the set of differential equations can be derived. I_k indicates a certain level of initiation, R_i is a polymer radical with chain length i, P_i an inactive polymer with chain length i, Q the inhibitor or quencher molecule, k_t the rate constant of termination, k_q the rate constant for the quench reaction. Analytical solutions for the RCLD were already derived for δ-pulse and non δ-pulse initiation conditions followed by a dark period, and a combination of finite initiation periods differing in their extent of initiation:

a) a dark period with duration t_D after an initiation period:

$$[R_\mathrm{i}]_{t_\mathrm{D}} = \frac{e^{-k_\mathrm{p}[M]t_\mathrm{D}}}{1 + k_\mathrm{t}[R_\mathrm{t}]_{t_\mathrm{D}=0}t_\mathrm{D}} \sum_{k=0}^{i} \frac{(k_\mathrm{p}[M]t_\mathrm{D})^k}{k!} [R_\mathrm{i-k}]_{t_\mathrm{D}=0} \tag{1}$$

$$[R_t]_{t_D} = \frac{[R_t]_{t_D=0}}{1 + k_t[R_t]_{t_D=0}\, t_D} \tag{2}$$

b) finite initiation period with duration t_j:

$$[R_\mathrm{i}]_{t_\mathrm{j}} = \frac{I(k_\mathrm{p}[M])^i}{U_\mathrm{j}e^{2t_\mathrm{j}/\tau_\mathrm{s,J}} + 1} \cdot \left\{ \begin{aligned} &U_\mathrm{j}e^{2t_\mathrm{j}/\tau_\mathrm{s,j}} B_\mathrm{j}^{-(i+1)} + A_\mathrm{j}^{-(i+1)} \\ &+ e^{-t_\mathrm{j}A_\mathrm{j}} \sum_{k=0}^{i} \frac{t_\mathrm{j}^k}{k!} \left\{ \frac{[R_\mathrm{i-k}]_{t_\mathrm{j}=0}}{I} \frac{U_\mathrm{j}+1}{(k_\mathrm{p}[M])^{\imath-k}} - \frac{U_\mathrm{j}}{B_\mathrm{j}^{\imath+1-k}} - \frac{1}{A_\mathrm{j}^{i+1-k}} \right\} \end{aligned} \right\} \tag{3}$$

$$[R_t]_{t_j} = R_{s,j} \tanh\left(t_j / \tau_{s,j}\right) \tag{4}$$

with the following abbreviation:

$$[R_t] = \sum_i [R_i] \qquad \frac{1}{\tau_{\mathrm{s,j}}} = \sqrt{I_{\mathrm{j}} k_{\mathrm{t}}} \qquad R_{\mathrm{s,j}} = \sqrt{\frac{I_{\mathrm{j}}}{k_{\mathrm{t}}}}$$

$$A_{\mathrm{j}} = k_{\mathrm{p}}[M] - 1/\tau_{\mathrm{s,j}} \qquad B_{\mathrm{j}} = k_{\mathrm{p}}[M] + 1/\tau_{\mathrm{s,j}} \qquad U_{\mathrm{j}} = \frac{R_{\mathrm{s,j}} + [R]_{t_{\mathrm{j}}=0}}{R_{\mathrm{s,j}} - [R]_{t_{\mathrm{j}}=0}}$$

These equations can be simplified if no radicals other than the initiating radicals (i.e. $[R_{\mathrm{i}}]_0 = 0$ for i=1,2...) were present at the begin of the period. The first corresponds to single δ-pulse conditions:

$$[R_{\mathrm{i}}]_{t_{\mathrm{D}}} = \frac{e^{-k_{\mathrm{p}}[M]t_{\mathrm{D}}}}{1 + k_{\mathrm{t}}[R_{\mathrm{t}}]_{t_{\mathrm{D}}=0} t_{\mathrm{D}}} \frac{\left(k_{\mathrm{p}}[M]t_{\mathrm{D}}\right)^i}{i!} [R_0]_{t_{\mathrm{D}}=0} \tag{1a}$$

and the following represents the RCLD for incomplete pre-effect conditions:

$$[R_{\mathrm{i}}]_{t_1} = \frac{I}{2k_{\mathrm{p}}[M]\cosh\left(t_1/\tau_{\mathrm{s,1}}\right)} \left\{ \begin{aligned} & \left(\frac{k_{\mathrm{p}}[M]}{A_1 B_1}\right)^{i+1} \left(e^{t_1/\tau_{\mathrm{s,1}}} A_1^{i+1} + e^{-t_1/\tau_{\mathrm{s,1}}} B_1^{i+1}\right) \\ & - e^{-k_{\mathrm{p}}[M]t_1} \sum_{k=0}^{i} \frac{\left(k_{\mathrm{p}}[M]t_1\right)^{i-k}}{(i-k)!} \left(\frac{k_{\mathrm{p}}[M]}{A_1 B_1}\right)^{k+1} \left(A_1^{k+1} + B_1^{k+1}\right) \end{aligned} \right\} \tag{3a}$$

Shape of the distribution curves

For the calculation of the superposition (RCLD+PCLD) the PCLD was calculated by numerical integration making use of the RCLD according to:

$$\frac{d[P_t]}{dt} = \alpha k_t [R_t]^2 + (1-\alpha)\frac{1}{2} k_t [R_t]^2 \tag{5}$$

$$\frac{d[P_i]}{dt} = \alpha k_t [R_i][R_t] + (1-\alpha)\frac{1}{2} k_t \sum_{k=0}^{i/2} [R_{i-k}][R_k] \tag{6}$$

with α being the fraction of termination by disproportionation. For odd i the upper limit is determined by integer division. The numerical result for the PCLD was controlled by summation over all i and comparison of the value with that calculated from the analytical solution for the total polymer concentration:

$$\text{initiation period:} \qquad [P_t] = \frac{n}{2}\left\{I \cdot t_{Ini} - R_s \tanh\left(t_{Ini}/\tau_s\right)\right\} + [P_t]_{t_{Ini}=0} \tag{7}$$

$$\text{dark period:} \qquad [P_t] = \frac{n}{2} \cdot \frac{k_t [R_t]^2_{t_D=0}\, t_D}{1 + k_t [R_t]_{t_D=0}\, t_D} + [P_t]_{t_D=0} \tag{8}$$

where n is 1 (2) for termination by combination (disproportionation).

The set of kinetic parameters for all calculations were: k_p=100 lmol^{-1}s^{-1}, $[M]$=10 moll^{-1}, k_t=10^8 lmol^{-1}s^{-1}. The concentration of initiating radicals, $[R_0]$ / moll^{-1}, and the rates of initiation I / moll^{-1}s^{-1} will be indicated separately.

a) For single δ-pulse conditions[2] the RCLD is clearly a Poisson distribution where the peak maximum and the points of inflection are located at:

$$k_p[M]t_D = L_{max}\exp\left(\frac{1}{2L_{max}}\right)\approx L_{max} \tag{9}$$

$$k_p[M]t_D = L_{low}\exp\left(\frac{1}{2L_{low}}+\sqrt{\frac{1}{L_{low}}}\right) \tag{10}$$

$$k_p[M]t_D = L_{high}\exp\left(\frac{1}{2L_{high}}-\sqrt{\frac{1}{L_{high}}}\right) \tag{11}$$

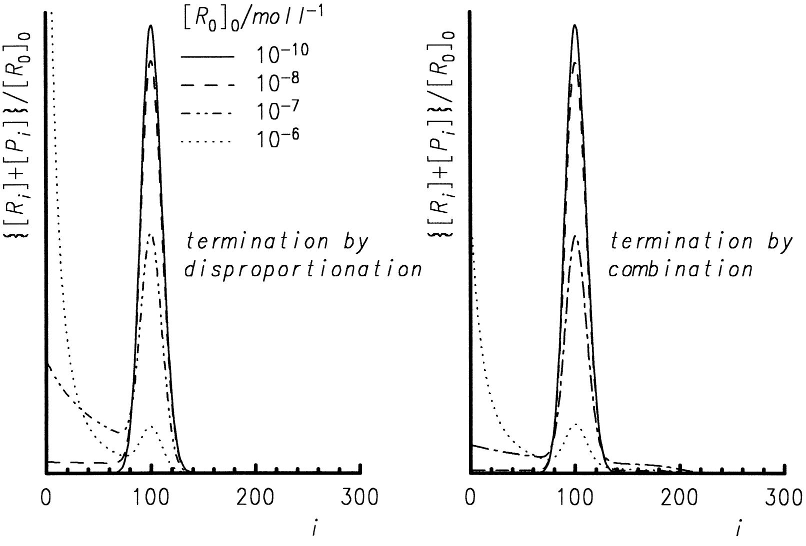

Figure 1. Calculated superpositions $\{[R_i]+[P_i]\}/[R_0]_0$ for different concentrations of initiating radicals under δ-pulse initiation conditions; duration of the dark period, t_D, was in all cases 100 ms.

The contribution of the radical peak to the convolute is more pronounced for a smaller concentration of the initiating radicals (c.f. Figure 1). The chain length of the peak maximum is identical with the maximum chain length of the radicals and corresponds to the number of propagation steps. The RCLD clearly dominates the convolute in the region of the peak maximum. The superimposed curves end slightly above the maximum active chain length for termination by disproportionation, whereas for termination by combination the curves will stretch to twice this value. It can also be seen that for a higher concentration of the initiating radicals the contribution of the PCLD will become more prominent.

b) For a finite initiation period[3] alone (incomplete pre-effect conditions) a broad distribution is obtained which can be characterized by a change in slope (c.f. Figure 2). For a high rate of initiation more inactive polymer contributes to the convolute and the initial slope is already steep. A more pronounced change in slope can be observed for lower rates of initiation. The maximum chain length is again influenced by the type of termination and the total polymerization time.

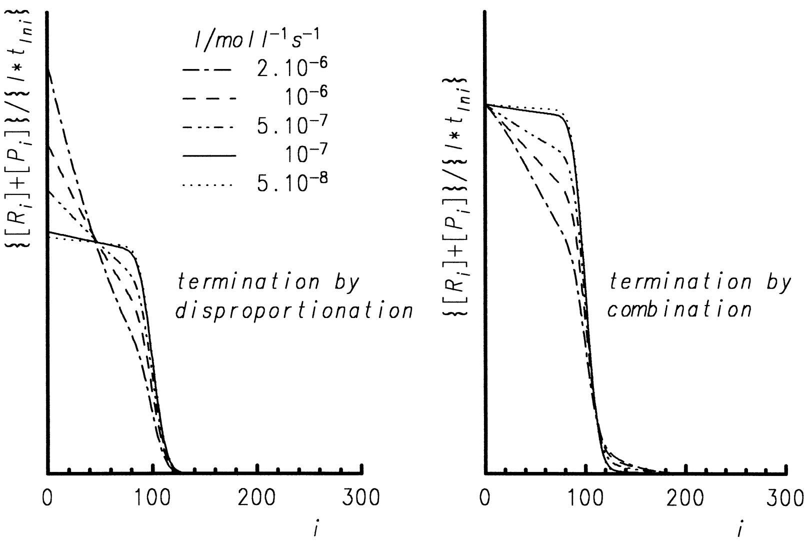

Figure 2. Calculated superpositions $\{[R_i]+[P_i]\}/\{I*t_{Ini}\}$ for different constant rates of initiation; duration of the initiation period, t_{Ini}, was in all cases 100 ms.

The point of inflection on the deep down slope can be described be Equation 9 when t_D and L_{max} are replaced by the duration of the initiation period, t_{Ini}, and the chain length of the peak minimum in the first derivative, L_{min}, respectively:

$$k_p[M]\,t_{Ini} \approx L_{\min} \qquad \text{(9a)}$$

The combination of two periods differing[3],[4] in the rate of initiation will also give rise to characteristic distribution curves depending on the sequence of high and low (or no) extent of initiation. An additional peak appears in the distribution which stems from the quenched RCLD when the rate of initiation of the second period is smaller than for the first one (c.f. Figure 3). The location of this peak is shifted to higher chain lengths when the duration of the second period is increased. The corresponding points of inflection are related to the duration of the different initiation periods by:

$$k_\mathrm{p}[M]t_2 = L_\mathrm{low}\exp\left(\frac{1}{2L_\mathrm{low}}\right) \tag{12}$$

$$k_\mathrm{p}[M](t_1 + t_2) = L_\mathrm{high}\exp\left(\frac{1}{2L_\mathrm{high}}\right) \tag{13}$$

$$k_\mathrm{p}[M]t_1 \approx L_\mathrm{high} - L_\mathrm{low} \tag{14}$$

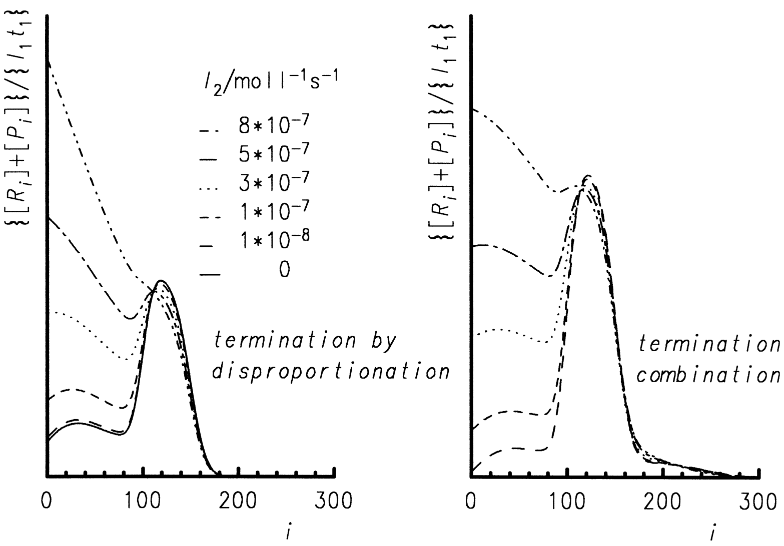

Figure 3. Calculated superpositions for a combination of two initiation periods: t_1=50 ms, $I_1=10^{-6}$ moll^{-1}s^{-1}. The rate of initiation of the second period was varied but always lower than that of the first period; t_2=100 ms.

c) The combination of more than two periods[4] differing in the rate of initiation can be used to generate multimodale chain length distributions. Depending on the experimental conditions either well structured or only weakly modulated distributions will be obtained. Besides equally spaced initiation periods a variety of combinations with respect to the duration of initiation period and level of initiation is possible.

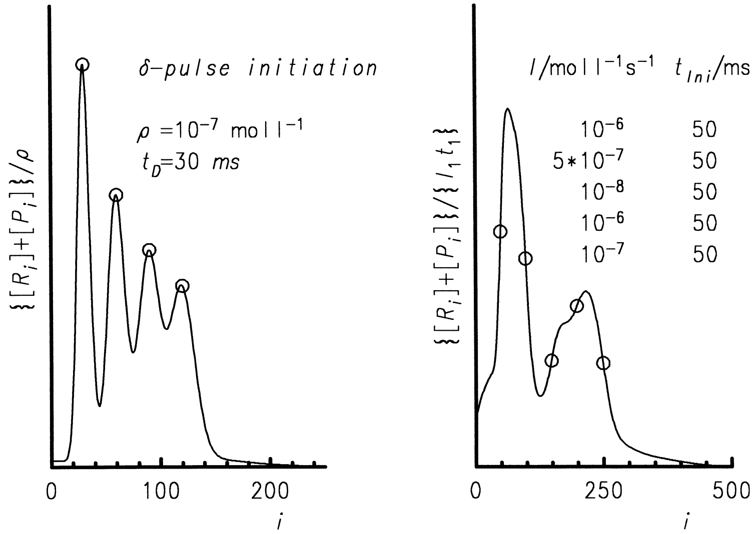

Figure 4. Calculated superpositions for QUIP systems for a combination of 4 δ-pulses separated by dark time (left) or a combination of 5 finite initiation periods (right).

Average degrees of polymerization and polydispersities

In order to gain information of how the moments and average degrees of polymerization depend on the experimental conditions the case of single δ-pulse initiation was inspected more thoroughly for termination by disproportionation. Summation over all chain lengths *i* (from 0 to infinity) for the RCLD and PCLD were carried out according to:

$$\lambda^k_{RCLD} = \sum_{i=0}^{\infty} i^k \cdot [R_i]_{t_D} = \frac{e^{-k_p[M]t_D}}{1 + k_t[R_t]_{t_D=0} t_D} [R_0]_{t_D=0} \sum_{i=0}^{\infty} i^k \cdot \frac{(k_p[M]t_D)^i}{i!} \tag{15}$$

$$\begin{aligned} \lambda^k_{PCLD} &= \sum_{i=0}^{\infty} i^k \cdot [P_i]_{t_D} = k_t \sum_{i=0}^{\infty} i^k \cdot \int [R_t]_{t_D} [R_i]_{t_D} dt_D \\ &= k_t \int [R_t]_{t_D} \sum_{i=0}^{\infty} i^k \cdot [R_i]_{t_D} dt_D \end{aligned} \tag{16}$$

$$\lambda^k_{\text{superposition}} = \sum_{i=0}^{\infty} i^k \cdot \{[R_i] + [P_i]\} \tag{17}$$

The moments were used to calculate the average degrees of polymerization for the RCLD, PCLD (R_n, R_w, P_n, P_w) as well as those for the superposition (S_n, S_w) separately. With the proper choice of the quencher molecule and quench reaction the RCLD and

PCLD will become either physically separable[7] or can be detected separately.[8] The following abbrevations were used:

$$k_{\mathrm{p}}[M] = \frac{1}{\pi} \qquad k_{\mathrm{t}}[R_t]_{t=0} = \frac{1}{\tau} \qquad \frac{[R_i]_{t=0}}{[R_t]_{t=0}} = \rho_{\mathrm{i},0}$$

$$R_n = \frac{\sum i[R_i]}{\sum [R_i]} = \sum i\rho_{\mathrm{i},0} + \frac{t}{\pi} \tag{18}$$

$$R_w = \frac{\sum i^2[R_i]}{\sum i[R_i]} = \frac{\sum i^2\rho_{i,0} + \frac{t}{\pi}\sum(2i+1)\rho_{\mathrm{i},0} + \left(\frac{t}{\pi}\right)^2}{\sum i\rho_{\mathrm{i},0} + \frac{t}{\pi}} \tag{19}$$

$$\frac{R_w}{R_n} = \frac{\sum i^2\rho_{\mathrm{i},0} + \frac{t}{\pi}\sum(2i+1)\rho_{\mathrm{i},0} + \left(\frac{t}{\pi}\right)^2}{\left\{\sum i\rho_{\mathrm{i},0} + \frac{t}{\pi}\right\}^2} \tag{20}$$

$$P_n = \frac{\sum i[P_i]}{\sum [P_i]} = \sum i\rho_{\mathrm{i},0} + \frac{\tau}{\pi}\left\{-1 + \frac{\tau+t}{t}\ln\left\{1+\frac{t}{\tau}\right\}\right\} \tag{21}$$

$$P_w = \frac{\sum i^2[P_i]}{\sum i[P_i]}$$

$$= \frac{\sum i^2\rho_{\mathrm{i},0} + 2\left(\frac{\tau}{\pi}\right)^2 + \frac{t}{\pi}\left\{\sum(2i+1)\rho_{\mathrm{i},0} + \frac{t}{\pi}\right\} - 2\left(\frac{\tau}{\pi}\right)\frac{\tau+t}{t}\ln\left\{1+\frac{t}{\tau}\right\}}{\sum i\rho_{\mathrm{i},0} + \frac{\tau}{\pi}\left[-1 + \frac{\tau+t}{t}\ln\left\{1+\frac{t}{\tau}\right\}\right]} \tag{22}$$

$$\frac{P_w}{P_n} = \frac{\sum i^2\rho_{\mathrm{i},0} + 2\left(\frac{\tau}{\pi}\right)^2 + \frac{t}{\pi}\left\{\sum(2i+1)\rho_{\mathrm{i},0} + \frac{t}{\pi}\right\} - 2\left(\frac{\tau}{\pi}\right)\frac{\tau+t}{t}\ln\left\{1+\frac{t}{\tau}\right\}}{\left\{\sum i\rho_{\mathrm{i},0} + \frac{\tau}{\pi}\left[-1 + \frac{\tau+t}{t}\ln\left\{1+\frac{t}{\tau}\right\}\right]\right\}^2} \tag{23}$$

When no radicals and polymers were present before the δ-pulse initiation the equation can be simplified to:

$$R_n = \frac{t}{\pi} \quad (18a) \qquad R_w = 1 + \frac{t}{\pi} \quad (19a) \qquad \frac{R_w}{R_n} = 1 + \frac{\pi}{t} \quad (20a)$$

The radical spectrum is clearly a Poisson distribution – as expected. The higher the contribution of the RCLD to the total distribution the better will be the similarity to a Poisson distribution. As can be seen in Figure 1 this will be the case if the concentration of initiating radicals is small.

$$P_n = \frac{\tau}{\pi}\left\{-1+\frac{\tau+t}{t}\ln\left\{1+\frac{t}{\tau}\right\}\right\} \tag{21a}$$

In principle, all moments are subject to three factors, namely the average times necessary for a propagation ($\pi = 1/k_p[M]$) and a termination event ($\tau = 1/k_t[R_t]_{t=0}$), respectively, as well as the duration of the dark time. Higher number average degrees of polymerization can be achieved by an increase in the dark time, whereas a higher concentration of initiating radicals will lead to smaller values.

$$P_w = \frac{2\frac{\tau}{\pi}+t\left\{\frac{1}{\tau}+\frac{1}{\pi}\right\}-2\frac{\tau}{\pi}\frac{\tau+t}{t}\ln\left\{1+\frac{t}{\tau}\right\}}{-1+\frac{\tau+t}{t}\ln\left\{1+\frac{t}{\tau}\right\}} \tag{22a}$$

$$\frac{P_w}{P_n} = \frac{2+t\frac{\pi}{\tau}\left\{1+\frac{\pi}{\tau}\right\}-2\frac{\tau+t}{t}\ln\left\{1+\frac{t}{\tau}\right\}}{\left\{-1+\frac{\tau+t}{t}\ln\left\{1+\frac{t}{\tau}\right\}\right\}^2} \tag{23a}$$

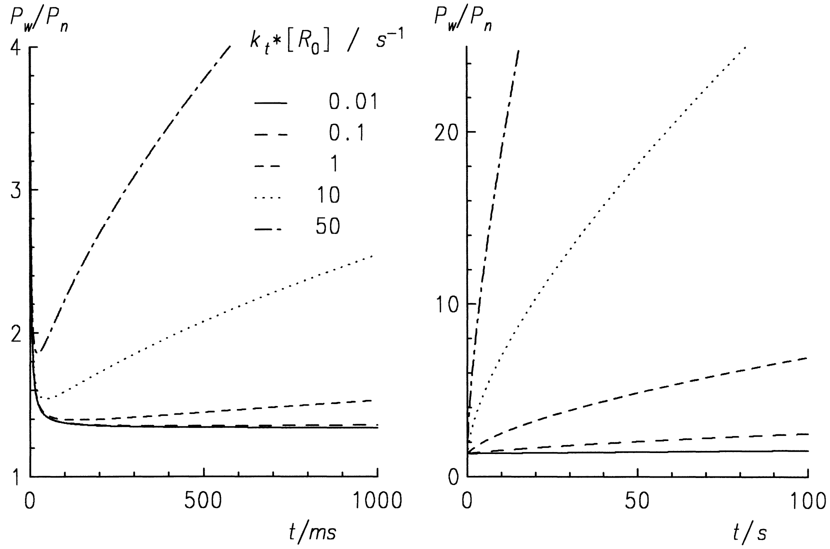

Figure 5. Calculated polydispersities of the PCLD under single δ-pulse initiation conditions.

In Figure 5 the short and long time behavior of the polydispersity of the PCLD is presented. If the average time necessary for bimolecular termination is long polydispersties well below 2 even up to a dark time duration of 100 ms can be achieved.

If on the other hand a high concentration of initiating radicals is generated during the δ-pulse high values of polydispersities will be encountered from the begin.

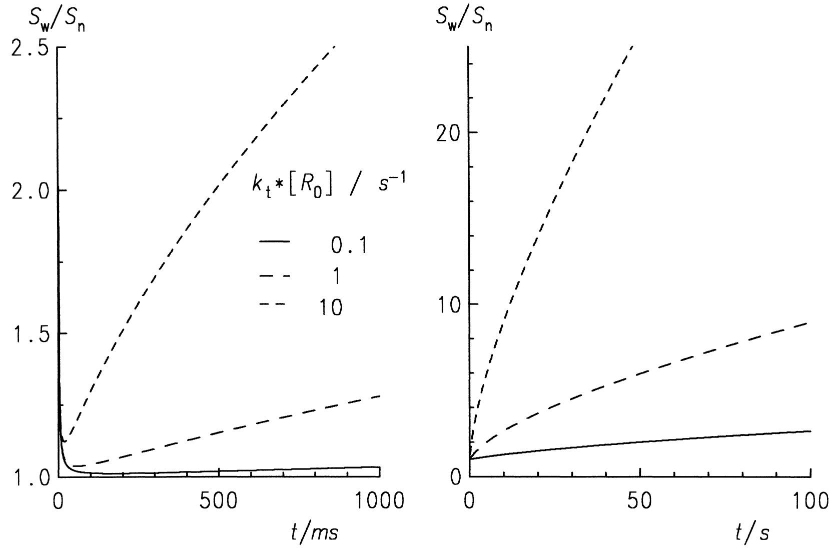

Figure 6. Calculated polydispersities for the superposition (RCLD+PCLD) under single δ-pulse initiation conditions.

Qualitatively the same arguments are valid for the polydispersity of the superimposed distribution as can be seen from Figure 6 and the following equations:

$$S_n = \frac{\tau}{\pi}\ln\left\{1+\frac{t}{\tau}\right\} \qquad (24)$$

$$S_w = \frac{\frac{t}{\tau}+2\frac{t}{\pi}}{\ln\left\{1+\frac{t}{\tau}\right\}} - 2\frac{\tau}{\pi} \qquad (25)$$

$$\frac{S_w}{S_n} = \frac{\frac{t}{\tau}\left(\frac{\pi}{\tau}+2\right)-2\ln\left\{1+\frac{t}{\tau}\right\}}{\left\{\ln\left\{1+\frac{t}{\tau}\right\}\right\}^2} \qquad (26)$$

Conclusion

The choice of experimental conditions, in particular the extent and duration of initiation will influence the shape of the resulting chain length distribution. Under instationary polymerization conditions the experimentally measureable distribution is always a superposition of the RCLD and PCLD. It was demonstrated that the polydispersity alone without the additional information of the shape can give rise to misleading interpretations. Special points of the different distribution curves can be used to extract directly the information about the rate constant of propagation.

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