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Kinetic Model of Pulsed Laser-Initiated Polymerization in the Presence of Chain Transfer to Monomer

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ABSTRACT: Taking account of chain transfer to monomer, the kinetics of pulsed laser-initiated polymerization was treated in this article. The molecular weight distribution function and the expressions of number- and weight-average degrees of polymerization for the resulting polymer were derived under pseudostationary state conditions. Theoretical analysis and numerical calculation demonstrate that the presence of monomer transfer results in a narrower molecular weight distribution. With the increasing chain transfer rate constant, the polydispersity index of the resulting polymer decreases and finally approaches 2. Values of average degrees of polymerization and the polydispersity index vibrate between maxima and minima periodically, and the amplitude of the vibration declines with the increasing monomer conversion. The molecular weight distribution curves from numerical calculation show characteristic sharp peaks, and chain transfer to monomer weakens the intensity of peaks except the low molecular weight side one. Termination by combination leads to a little narrower molecular weight distribution, and so does the low concentration of the primary radical generated by per laser pulse.

Introduction

About two decades ago Aleksandrov and co-workers[1] theoretically studied the molecular weight distribution (MWD) of the polymer generated from pulsed laser-initiated polymerization (PLP) under stationary state assumption. The number- and weight-average degrees of polymerization were derived based on the MWD function obtained and due to the prolix nature of the MWD function, the authors[1] adopted several poor approximations during the derivation. Genkin et al.[2] first proposed to measure the propagation rate constant k_p by using peaks in MWDs of the PLP originating polymer. It was Olaj and co-workers[3−5] who developed the pulsed laser polymerization method as a tool for evaluating individual kinetic constants of free radical polymerization on the convincing theoretical and experimental basis. Taking account of the fact that the rate of termination of growing radicals is a function of chain length, the authors[3−5] gave the expression of MWD and the formulas of average degrees of polymerization. Latter, Lu and co-workers[6] and O'Driscoll et al.[7] extended Olaj's work with Monte Carlo simulation. In all of the works aforementioned chain transfer was not taken into account. Recently, Deady et al.,[8] Hutchinson et al.,[9] and Yang and co-workers[10] investigated PLP systems with chain transfer by way of experiment and/or simulation; however, all of their work only focused on MWD and paid no attention to average molecular weights.

In this paper, a new kinetic model of PLP is developed in the presence of chain transfer to monomer. When termination occurs by both disproportionation and combination, expressions of the number- and weight-average degrees of polymerization and polydispersity index of the resultant polymer are given with accurate derivation. Furthermore, the molecular weight distribution function is rigorously derived. Numerical results indicate that there are characteristic sharp peaks in MWD curves, which is in agreement with the outcomes of simulation previously reported.

Kinetic Differential Equations

At first we define the following nomenclature: R_j is the growing j-mer concentration; P_j is the terminated j-mer concentration; M is the residual monomer concentration; k_p, k_t, and k_{tr} are the rate constants of propagation, termination, and chain transfer to monomer, respectively; k_{tc} and k_{td} are the respective rate constants of termination by combination and disproportionation; $k_t = k_{tc} + k_{td}$; $R(0)$ is the concentration of primary radical generated per laser pulse; $M(0)$ is the initial monomer concentration; T is the period between two successive pulses; τ is the continuous time variable ranging from 0 to T. Then the reaction scheme of a pulsed laser-initiated polymerization with chain transfer to monomer reads

instantaneous and periodical initiation

$$\mathrm{R}_j + \mathrm{M} \xrightarrow{k_p} \mathrm{R}_{j+1}$$

$$\mathrm{R}_j + \mathrm{M} \xrightarrow{k_{tr}} \mathrm{P}_j + \mathrm{R}_0$$

$$\mathrm{R}_m + \mathrm{R}_n \xrightarrow{k_{tc}} \mathrm{P}_{m+n}$$

$$\mathrm{R}_m + \mathrm{R}_n \xrightarrow{k_{td}} \mathrm{P}_m + \mathrm{P}_n$$

where we suppose that monomer transfer results in a terminated j-mer and a radical. The set of differential equations appropriate to the above reaction scheme is

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$$\frac{\mathrm{d}R_0}{\mathrm{d}t} = -(k_pM + k_tR)R_0 + k_{tr}MR - k_{tr}MR_0 \qquad (t \neq nT;\ n = 1, 2, ...) \quad (1a)$$

$$R_0|_{t=nT} = R_0|_{t=nT-0} + R(0) \quad (1b)$$

$$\frac{\mathrm{d}R_j}{\mathrm{d}t} = -(k_pM + k_tR)R_j + k_pMR_{j-1} - k_{tr}MR_j \qquad (j \geq 1) \quad (2)$$

$$\frac{\mathrm{d}M}{\mathrm{d}t} = -k_pMR - k_{tr}MR \quad (3)$$

$$\frac{\mathrm{d}P_j}{\mathrm{d}t} = \frac{1}{2}k_{tc}\sum_{i=0}^{j}R_iR_{j-i} + k_{td}RR_j + k_{tr}MR_j \quad (4)$$

where $R = \sum_{j=0}^{\infty}R_j$; $nT - 0$ is the moment less than nT but closely approaching it, t denotes reaction time, and R_0 is defined as the active zero-mer including the primary radical and the radical formed from monomer chain transfer. Apparently, the initial conditions of eqs 1−4 are

$$R_0|_{t=0} = R(0); \qquad R_j|_{t=0} = 0 \qquad (j \geq 1); \qquad M|_{t=0} = M(0); \qquad P_j|_{t=0} = 0$$

From eqs 1−3, we have

$$R^{(n)}(\tau) = \bar{R}^{(n)}(1 + k_t\bar{R}^{(n)}\tau)^{-1} \quad (5)$$

$$M^{(n)}(\tau) = \bar{M}^{(n)}(1 + k_t\bar{R}^{(n)}\tau)^{-r} \quad (6)$$

where $r = (k_p + k_{tr})/k_t$, $R^{(n)}(\tau)$ and $M^{(n)}(\tau)$ are the concentrations of radical and monomer at the moment τ in the nth pulse, respectively, $\bar{R}^{(n)} = R^{(n)}(0)$ and $\bar{M}^{(n)} = M^{(n)}(0)$. Thus $\bar{R}^{(1)} = R(0)$ and $\bar{M}^{(1)} = M(0)$.

If we assume that the polymerization system reaches the pseudosteady state after n^* pulses, then $\bar{R}^{(n)} = \bar{R}^{(n+1)} = \bar{R}$, where $n \geq n^*$, and hence

$$\bar{R} = R(0)/2 + \sqrt{R(0)^2/4 + R(0)/(k_tT)} \quad (7)$$

In fact, pseudosteady state can be reached within a very short period of time in PLP, as indicated by Monte Carlo simulation.[6,7] So n^* is a small integer comparing with the number of laser pulses in a practical polymerization process. Therefore, by using a close approximation we can obtain

$$R^{(n)}(\tau) = \bar{R}(1 + k_t\bar{R}\tau)^{-1} \quad (8)$$

$$M^{(n)}(\tau) = \bar{M}^{(n)}(1 + k_t\bar{R}\tau)^{-r} \quad (9)$$

In other words we have assumed that the total radical concentration reaches its pseudostationary value at the beginning of PLP, i.e., $n^* = 1$. In accordance with eq 9, monomer conversion at the moment τ in the nth pulse reads

$$X^{(n)}(\tau) = 1 - (1 + k_t\bar{R}T)^{-(n-1)r}(1 + k_t\bar{R}\tau)^{-r} \quad (10)$$

Evidently, $\bar{R}$ is the radical concentration immediately following a laser pulse.

Average Degrees of Polymerization

Assuming the decrease of monomer concentration is negligible during polymerization, Hutchinson et al.[9] have given the differential equations of the zeroth and first moments of the PLP resulting polymer in order to evaluate the molecular weight distribution; no analytical solutions have been provided. In this paper the expressions of number- and weight-average degrees of polymerization of PLP were calculated exactly. Before giving average molecular weights, it is necessary to derive the various moments of resulting polymer which contain chain radicals and terminated species. The first-order moment of total polymer in the nth pulse is given directly by

$$\sum_{j=0}^{\infty}j[R_j^{(n)}(\tau) + P_j^{(n)}(\tau)] = M(0) - M^{(n)}(\tau) = M(0)[1 - (1 + k_t\bar{R}T)^{-(n-1)r}(1 + k_t\bar{R}\tau)^{-r}] \quad (11)$$

From eqs 1, 2, and 4, we get the differential equations adapted to the zeroth and second moments:

$$\mathrm{d}\sum_{j=0}^{\infty}(R_j + P_j)/\mathrm{d}t = -\frac{1}{2}k_{tc}R^2 + k_{tr}MR \quad (12)$$

$$\mathrm{d}\sum_{j=0}^{\infty}j^2(R_j + P_j)/\mathrm{d}t = k_{tc}(\sum_{j=0}^{\infty}jR_j)^2 + 2k_pM\sum_{j=0}^{\infty}jR_j + k_pMR \quad (13)$$

Solving eqs 12 and 13, one obtains

$$\sum_{j=0}^{\infty}[R_j^{(n)}(\tau) + P_j^{(n)}(\tau)] = nR(0) - (n-1)\frac{k_{tc}\bar{R}^2T}{2(1 + k_t\bar{R}T)} - \frac{k_{tc}\bar{R}^2\tau}{2(1 + k_t\bar{R}\tau)} + \frac{k_{tr}}{k_p + k_{tr}}M(0) - \frac{k_{tr}}{k_p + k_{tr}}M(0)(1 + k_t\bar{R}T)^{-(n-1)r}(1 + k_t\bar{R}\tau)^{-r} \quad (14)$$

$$\sum_{j=0}^{\infty}j^2[R_j^{(n)}(\tau) + P_j^{(n)}(\tau)] = \int_0^T\sum_{i=1}^{n-1}\{k_{tc}[\sum_{j=0}^{\infty}jR_j^{(i)}(\tau')]^2 + 2k_pM^{(i)}(\tau')\sum_{j=0}^{\infty}jR_j^{(i)}(\tau') + k_pM^{(i)}(\tau')R^{(i)}(\tau')\}\,\mathrm{d}\tau' + \int_0^{\tau}\{k_{tc}[\sum_{j=0}^{\infty}jR_j^{(n)}(\tau')]^2 + 2k_pM^{(n)}(\tau')\sum_{j=0}^{\infty}jR_j^{(n)}(\tau') + k_pM^{(n)}(\tau')R^{(n)}(\tau')\}\,\mathrm{d}\tau' \quad (15)$$

In eq 15, $\sum_{j=0}^{\infty}jR_j$ is unknown temporarily. Combining eq 1 with eq 2 it can be determined by

$$\mathrm{d}\sum_{j=0}^{\infty}jR_j/\mathrm{d}t = -(k_tR + k_{tr}M)\sum_{j=0}^{\infty}jR_j + k_pMR \quad (16)$$

Equation 16 results in

$$\sum_{j=0}^{\infty}jR_j^{(n)}(\tau) = \frac{\exp[-Z_n(\tau)]}{1 + k_t\bar{R}\tau}\left\{\frac{\bar{R}}{C_M}\exp[Z_n(\tau)] - \frac{\bar{R}}{C_M} + C_n\right\} \quad (17)$$

where

$$C_{\mathrm{M}} = k_{\mathrm{tr}}/k_{\mathrm{p}}$$

$$Z_{\mathrm{n}}(\tau) = \frac{k_{\mathrm{tr}}M(0)(1 + k_{\mathrm{t}}\bar{R}T)^{-(n-1)r}}{k_{\mathrm{t}}\bar{R}(1 - r)}[(1 + k_{\mathrm{t}}\bar{R}\tau)^{1-r} - 1]$$

$$C_{\mathrm{n}} = \sum_{i=1}^{n-1}\frac{\exp[-\sum_{j=i}^{n-1}Z_j(T)]}{(1 + k_{\mathrm{t}}\bar{R}T)^{n-i}}\left\{\frac{\bar{R}}{C_{\mathrm{M}}}\exp[Z_i(T)] - \frac{\bar{R}}{C_{\mathrm{M}}}\right\}$$

Replacing $\sum_{j=0}^{\infty}jR_j$ in eq 15 with eq 17, we gain the second-order moment of total polymer. Therefore at arbitrary reaction time t, if m symbolizes $[t/T]$, i.e., the integer part of t/T, then from eqs 11, 14, and 15, the expressions of the number- and weight-average degrees of polymerization for PLP can be finally derived:

$$\bar{P}_{\mathrm{n}} = \frac{\sum_{j=0}^{\infty}j[R_j^{(m+1)}(t - mT) + P_j^{(m+1)}(t - mT)]}{\sum_{j=0}^{\infty}[R_j^{(m+1)}(t - mT) + P_j^{(m+1)}(t - mT)]} \qquad (18)$$

$$\bar{P}_{\mathrm{w}} = \frac{\sum_{j=0}^{\infty}j^2[R_j^{(m+1)}(t - mT) + P_j^{(m+1)}(t - mT)]}{\sum_{j=0}^{\infty}j[R_j^{(m+1)}(t - mT) + P_j^{(m+1)}(t - mT)]} \qquad (19)$$

According to the definition, the polydispersity index is

$$D = \bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}} \qquad (20)$$

All of the above equations are derived rigorously under pseudostationary conditions. When there is no chain transfer to monomer, i.e., $k_{\mathrm{tr}} = 0$, the formulas of the above molecular parameters can be largely simplified, and we only need to substitute 0 for k_{tr}. As far as the second-order moment of resulting polymer is concerned in the case of $k_{\mathrm{tr}} = 0$, we can look for a more straightforward manner to find the related expression, i.e., to derive the following equation directly from the set of kinetic differential equations:

$$\sum_{j=0}^{\infty}jR_j^{(n)}(\tau) = \frac{k_{\mathrm{p}}M(0)}{(k_{\mathrm{t}} - k_{\mathrm{p}})(1 + k_{\mathrm{t}}\bar{R}\tau)}[(1 + k_{\mathrm{t}}\bar{R}T)^{-(n-1)r}(1 + k_{\mathrm{t}}\bar{R}\tau)^{1-r} - (1 + k_{\mathrm{t}}\bar{R}T)^{-(n-1)}] \qquad (21)$$

With the equations given above we can easily estimate various molecular parameters and gain an insight into the influence of monomer transfer on PLP.

Molecular Weight Distribution

By means of the moment method and supposing monomer concentration keeping constant, Hutchinson and co-workers[9] have reckoned the MWD for the PLP originating polymer. In the present mathematical model, the derivation of MWDs is based upon the chain radical concentration. From eqs 1, 2, 8, and 9, the concentration of chain radicals with j monomeric units at the moment τ in the nth pulse can be obtained by induction:

$$R_j^{(n)}(\tau) = \frac{R(1)}{1 + k_{\mathrm{t}}\bar{R}\tau}\sum_{m=0}^{n-2}\frac{\exp[-q_{n,m}(\tau)][q_{n,m}(\tau)]^j}{(1 + k_{\mathrm{t}}\bar{R}T)^m j!} + \frac{R(2)}{1 + k_{\mathrm{t}}\bar{R}\tau} \times \frac{\exp[-q_{n,n-1}(\tau)][q_{n,n-1}(\tau)]^j}{(1 + k_{\mathrm{t}}\bar{R}T)^{n-1}j!} + \frac{\bar{R}\alpha\beta^j}{1 + k_{\mathrm{t}}\bar{R}\tau} \times \left\{1 - \sum_{m=0}^{n-1}\sum_{i=0}^{j-1}\frac{\exp[-q_{n,m}(\tau)][q_{n,m}(\tau)]^i}{(1 + k_{\mathrm{t}}\bar{R}T)^m i!} + \sum_{m=0}^{n-2}\sum_{i=0}^{j-1}\frac{\exp[-q_{n,m}(\tau)][q_{n,m}(\tau)]^i}{(1 + k_{\mathrm{t}}\bar{R}T)^{(m+1)}i!}\right\} \qquad (22)$$

where

$$\alpha = \frac{k_{\mathrm{tr}}}{k_{\mathrm{p}} + k_{\mathrm{tr}}} \qquad \beta = \frac{k_{\mathrm{p}}}{k_{\mathrm{p}} + k_{\mathrm{tr}}}$$

$$R(1) = \beta^j\left[R(0) - \alpha\bar{R} + \frac{\alpha\bar{R}}{1 + k_{\mathrm{t}}\bar{R}T}\right] \qquad R(2) = \beta^j[R(0) - \alpha\bar{R}]$$

$$q_{n,m}(\tau) = \frac{(k_{\mathrm{p}} + k_{\mathrm{tr}})[1 + (mT + \tau)k_{\mathrm{t}}\bar{R}]M^{(n)}(\tau) - (k_{\mathrm{p}} + k_{\mathrm{tr}})\bar{M}^{(n)}}{k_{\mathrm{t}}\bar{R}(1 - r)}$$

The derivation of eq 22 is given in the Appendix in detail. From eq 4, we define

$$\Delta P_j^{(n)}(\tau) = \int_0^{\tau}\left[\frac{k_{\mathrm{tc}}}{2}\sum_{i=0}^{j}R_i^{(n)}(\tau')R_{j-i}^{(n)}(\tau') + k_{\mathrm{td}}R^{(n)}(\tau')R_j^{(n)}(\tau') + k_{\mathrm{tr}}M^{(n)}(\tau')R_j^{(n)}(\tau')\right]\mathrm{d}\tau' \qquad (23)$$

It is evident that $\Delta P_j^{(n)}(\tau)$ represents the concentration of terminated polymer with chain length j generated during the time interval from the beginning to the moment τ in the nth pulse. Naturally, $\Delta P_j^{(n)}(T)$ is the concentration of terminated j-mers formed in the complete nth pulse. Therefore

$$P_j^{(n)}(\tau) = \sum_{i=1}^{n-1}\Delta P_j^{(i)}(T) + \Delta P_j^{(n)}(\tau) \qquad (24)$$

At an arbitrary reaction time t, under the definition $m = [t/T]$, we get the functions of the normalized MWDs from eqs 22 and 24, which are the distributions of chain radicals (W_j*), terminated species (W_j'), and total polymer (W_j), respectively:

$$W_j^* = \frac{jR_j^{(m+1)}(t - mT)}{\sum_{j=0}^{\infty} j[R_j^{(m+1)}(t - mT) + P_j^{(m+1)}(t - mT)]} \qquad (25)$$

$$W_j' = \frac{jP_j^{(m+1)}(t - mT)}{\sum_{j=0}^{\infty} j[R_j^{(m+1)}(t - mT) + P_j^{(m+1)}(t - mT)]} \qquad (26)$$

$$W_j = W_j^* + W_j' \qquad (27)$$

With the theoretical formulas developed here we can predict the molecular weight distribution of the polymer formed in PLP with chain transfer to monomer. If there is no chain transfer, expressions of MWDs can be simplified greatly by substituting 0 for k_{tr} in pertinent equations.

Numerical Results and Discussion

By the aid of a 486 PC computer, several numerical examples are given below. Some authors[6,7] have pointed out that the PLP systems can rapidly reach pseudosteady state, for instance, at the end of the second or third pulse. Generally speaking, this is correct. However, under some special conditions, such as low primary radical concentration generated by per laser pulse, the PLP system approaches the stationary state rather slowly. In Figure 1 we provide an example of PLP system, in which the radical concentration reaches its pseudostationary value roughly after six pulses. Figure 2 shows the variation of monomer conversion with reaction time. The change of the radical concentration in every period as shown in Figure 1 leads to the wave profile in Figure 2.

It is conceivable that the periodic nature of the chain initiation in PLP system yields corresponding periodic character of molecular parameters of the resultant polymer. Figures of both average degrees of polymerization and polydispersity index vs monomer conversion show such a periodicity as illustrated in Figures 3−7. On the low conversion side of the curves, values of average degrees of polymerization and polydispersity index vibrate on a large scale, and with the increasing monomer conversion, the vibration amplitude decreases. This interesting conclusion well agrees with that of Monte Carlo simulation.[6] Figures 3−5 indicate the influence of monomer transfer on average degrees of polymerization and polydispersity index of PLP resulting polymer. With the increasing k_{tr}, both chain length and polydispersity index decrease, and finally the latter parameter approaches 2. This conclusion is similar to that reported previously for ionic polymerization with monomer transfer.[11] Figure 6 illuminates the influence of the termination mechanism. Termination by combination results in a little narrower molecular weight distribution, which seems not to coincide with that reported by Yang et al.[10] A lower concentration of primary radicals generated per laser pulse also yields a rather narrow MWD, as demonstrated in Figure 7.

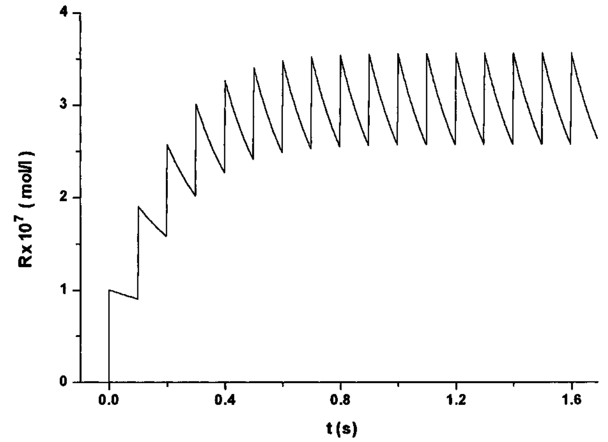

Figure 1. Plot of radical concentration versus reaction time, $k_t = 1.1 \times 10^7$ L·mol^{-1}·s^{-1}, $R(0) = 1.0 \times 10^{-7}$ mol·L^{-1}, $T = 0.1$ s, $n^* \approx 6$.

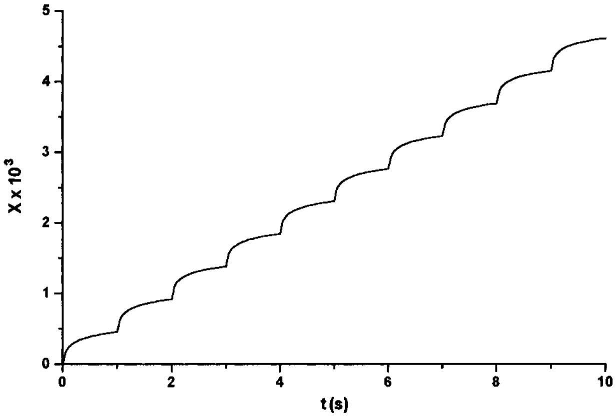

Figure 2. Plot of monomer conversion versus reaction time, $k_p = 1000$ L·mol^{-1}·s^{-1}, $k_t = 1.0 \times 10^7$ L·mol^{-1}·s^{-1}, $k_{tc} = k_{td} = 5.0 \times 10^6$ L·mol^{-1}·s^{-1}, $k_{tr} = 0$, $R(0) = 1.0 \times 10^{-5}$ mol·L^{-1}, $M(0) = 10$ mol·L^{-1}, $T = 1.0$ s, $n^* \approx 2$.

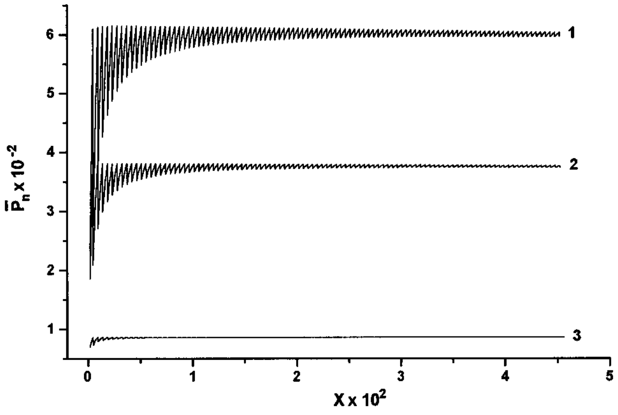

Figure 3. Plot of number-average degree of polymerization versus monomer conversion, $k_p = 1000$ L·mol^{-1}·s^{-1}, $k_t = 1.0 \times 10^7$ L·mol^{-1}·s^{-1}, $k_{tc} = k_{td} = 5.0 \times 10^6$ L·mol^{-1}·s^{-1}, $R(0) = 1.0 \times 10^{-5}$ mol·L^{-1}, $M(0) = 10$ mol·L^{-1}, $T = 1.0$ s: (1) $k_{tr} = 0$ L·mol^{-1}·s^{-1}, (2) $k_{tr} = 1.0$ L·mol^{-1}·s^{-1}, (3) $k_{tr} = 10.0$ L·mol^{-1}·s^{-1}.

Figures 8−12 are the calculated MWD curves of the PLP resulting polymer. It is clear that the molecular weight distribution for PLP is different from that for common free radical polymerization, and the difference is manifested by the presence of a series of peaks. It is this feature of PLP that facilitates the measurement of individual propagation rate constant k_p. According to the inflection point on the sharp peak of the MWD curve near the chain length L_0 given by[4]

$$L_0 = k_p M(0) T$$

one can easily evaluate k_p value because the other two parameters in the above equation are measurable or controllable. This technique is believed to be a direct

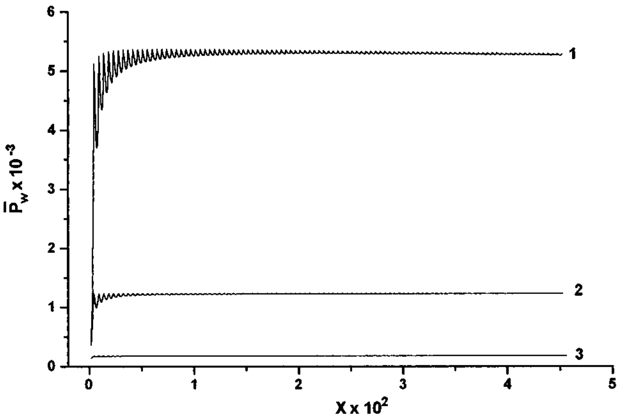

Figure 4. Plot of weight-average degree of polymerization versus monomer conversion: (1) $k_{\mathrm{tr}} = 0$ L·mol^{-1}·s^{-1}, (2) $k_{\mathrm{tr}} = 1.0$ L·mol^{-1}·s^{-1}, (3) $k_{\mathrm{tr}} = 10.0$ L·mol^{-1}·s^{-1}. Other reaction conditions are identical with those in Figure 3.

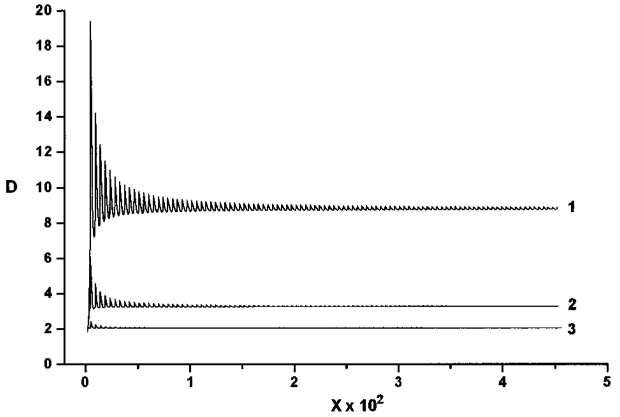

Figure 5. Influence of chain transfer to monomer on polydispersity index: (1) $k_{\mathrm{tr}} = 0$ L·mol^{-1}·s^{-1}, (2) $k_{\mathrm{tr}} = 1.0$ L·mol^{-1}·s^{-1}, (3) $k_{\mathrm{tr}} = 10.0$ L·mol^{-1}·s^{-1}. Other reaction conditions are identical with those in Figure 3.

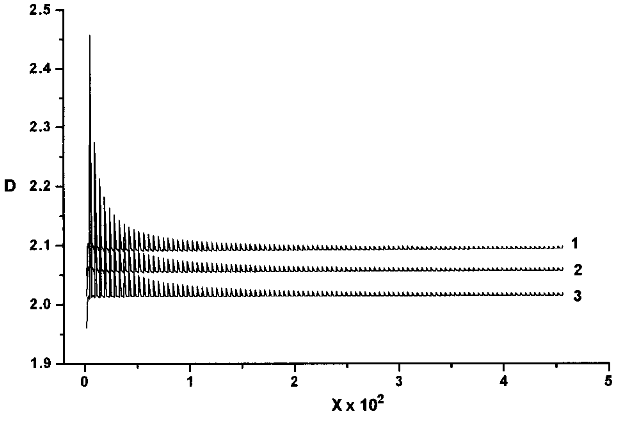

Figure 6. Effect of termination mechanism on polydispersity index, $k_{\mathrm{p}} = 1000$ L·mol^{-1}·s^{-1}, $k_{\mathrm{t}} = 1.0 \times 10^{7}$ L·mol^{-1}·s^{-1}, $k_{\mathrm{tr}} = 10.0$ L·mol^{-1}·s^{-1}, $R(0) = 1.0 \times 10^{-5}$ mol·L^{-1}, $M(0) = 10$ mol·L^{-1}, $T = 1.0$ s: (1) $k_{\mathrm{tc}} = 0$, $k_{\mathrm{td}} = 1.0 \times 10^{7}$ L·mol^{-1}·s^{-1}; (2) $k_{\mathrm{tc}} = k_{\mathrm{td}} = 5.0 \times 10^{6}$ L·mol^{-1}·s^{-1}; (3) $k_{\mathrm{tc}} = 1.0 \times 10^{7}$ L·mol^{-1}·s^{-1}, $k_{\mathrm{td}} = 0$.

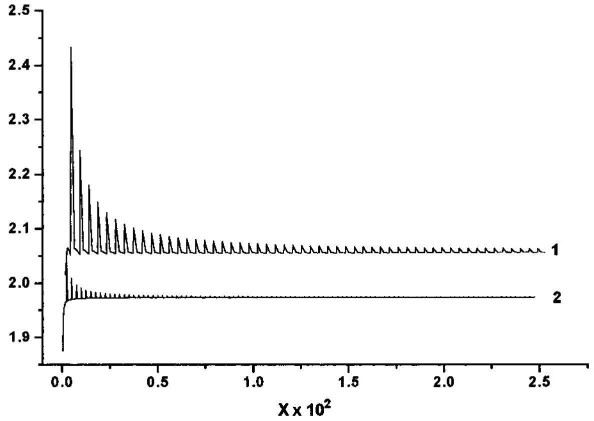

Figure 7. Effect of initial free radical concentration, $R(0)$, on polydispersity index, $k_{\mathrm{p}} = 1000$ L·mol^{-1}·s^{-1}, $k_{\mathrm{t}} = 1.0 \times 10^{7}$ L·mol^{-1}·s^{-1}, $k_{\mathrm{tc}} = k_{\mathrm{td}} = 5.0 \times 10^{6}$ L·mol^{-1}·s^{-1}, $k_{\mathrm{tr}} = 10.0$ L·mol^{-1}·s^{-1}, $M(0) = 10$ mol·L^{-1}, $T = 1.0$ s: (1) $R(0) = 1.0 \times 10^{-5}$ mol·L^{-1}, (2) $R(0) = 1.0 \times 10^{-6}$ mol·L^{-1}.

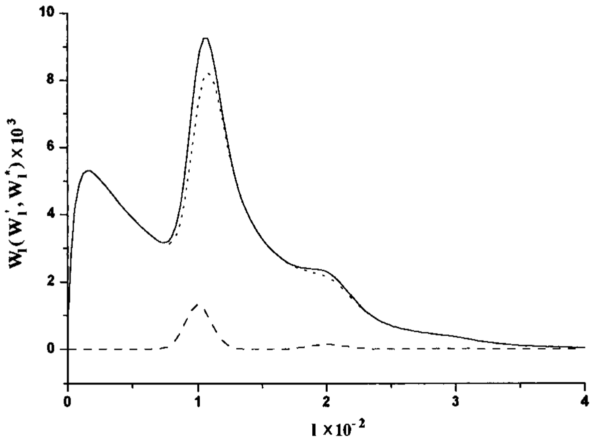

Figure 8. Normalized molecular weight distribution of resulting polymer, $k_{\mathrm{p}} = 100$ L·mol^{-1}·s^{-1}, $k_{\mathrm{t}} = 1.1 \times 10^{7}$ L·mol^{-1}·s^{-1}, $k_{\mathrm{tc}} = 1.0 \times 10^{7}$ L·mol^{-1}·s^{-1}, $k_{\mathrm{td}} = 1.0 \times 10^{6}$ L·mol^{-1}·s^{-1}, $k_{\mathrm{tr}} = 0$, $R(0) = 1.0 \times 10^{-5}$ mol·L^{-1}, $M(0) = 10$ mol·L^{-1}, $T = 0.1$ s, $t = 1.0$ s (t is the reaction time): (dashed line) chain radicals, (dotted line) terminated polymer, (solid line) total polymer. This key also applies to Figures 9–12.

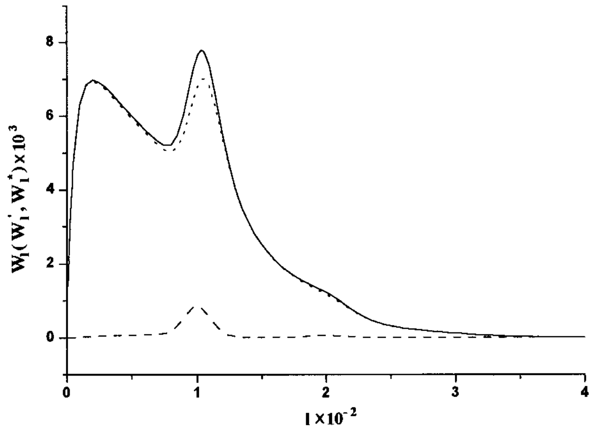

Figure 9. Effect of chain transfer to monomer on molecular weight distribution, $k_{\mathrm{tr}} = 0.5$ L·mol^{-1}·s^{-1}. Other reaction conditions are identical with those in Figure 8.

and reliable method for estimating the value of k_{p}.[3–10,12] The polymerization systems of some monomers, such as styrene and methacrylates,[8,13–15] have been successfully investigated with this technique. In this paper, calculated MWD curves show the characteristic sharp peak around chain length L_0. From Figures 8–12 it is obvious that the peaks of chain radical distribution appear exactly at chain length L_0 and its integer multiples, while the peaks of dead polymer and total polymer locate at slightly above L_0, $2L_0$, etc. This is why the inflection point on the sharp peak is the best estimation of L_0. Besides the peaks described above, there is a relatively broad peak lies at the low molecular weight side, which is a consequence of the termination reactions occurring during the dark period.

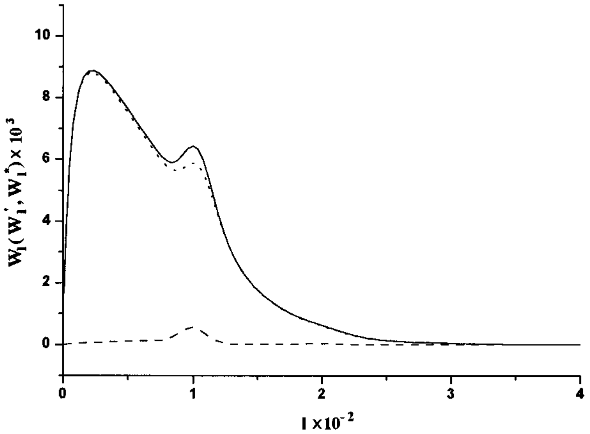

Figure 10. Influence of chain transfer to monomer on molecular weight distribution, k_{tr} = 1.0 L·mol^{-1}·s^{-1}. Other reaction conditions are identical with those in Figure 8.

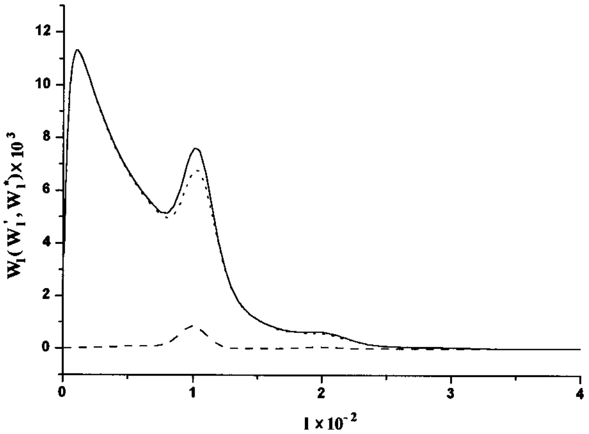

Figure 11. Effect of termination mechanism on molecular weight distribution, k_{tc} = 1.0 × 10^6 L·mol^{-1}·s^{-1}, k_{td} = 1.0 × 10^7 L·mol^{-1}·s^{-1}. Other reaction conditions are identical with those in Figure 9.

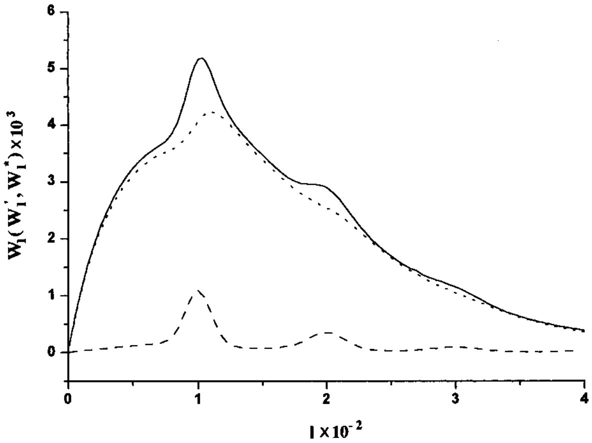

Figure 12. Influence of initial free radical concentration on molecular weight distribution, $R(0)$ = 1.0 × 10^{-6} mol·L^{-1}. Other reaction conditions are identical with those in Figure 9.

Figures 8–10 illustrate the effect of monomer transfer on the MWD. With the intensification of monomer transfer, the relatively broad peak located at the low molecular weight side enlarges gradually, while the sharp peak near L_0 becomes weaker and weaker, which is almost erased from the distribution curve at a large value of k_{tr}. Meanwhile, weak peaks near the integer multiples of L_0 disappear by degrees. These results agree with the outcomes of Monte Carlo simulation.[10]

It is worth mentioning that in Hutchinson and coworkers' paper,[9] when k_{tr}/k_p increases from 8 × 10^{-6} to 2 × 10^{-4}, the height of the primary peak in the vicinity of L_0 remains essentially unchanged. It is possible that the value of k_{tr}/k_p is so small that the influence of chain transfer on the primary peak is almost invisible. Although chain transfer to monomer weakens the peaks near L_0 and its integer multiples, the location of peaks remains invariable. So the approach of PLP for estimating k_p is suitable for systems with moderate chain transfer to monomer.

Comparing Figure 11 with Figure 9, we know that combination termination weakens the low molecular weight side peak, but the height and the location of the peak near L_0 remains roughly unchanged. This result is in agreement with that of Yang's,[10] but differs from that reported by Deady.[8] We hold that this difference is caused by the presence of chain transfer in our polymerization system. When the primary radical concentration generated per laser pulse decreases, the low molecular weight side peak declines in intensity, even disappears. Meanwhile the peaks lying at the positions near the integer multiples of L_0 become more apparent even though there is chain transfer (check Figures 9 and 12). As indicated in Figure 7, the polydispersity of the resulting polymer formed in the conditions of Figure 9 is a little larger than that of the polymer generated under the conditions of Figure 12; i.e., the molecular weight distribution shown in Figure 9 is a little wider than that given in Figure 12. It seems that the low molecular weight part of the resulting polymer in Figure 9 plays an important role in polydispersity.

Finally, it is expected that in accordance with the kinetic theory developed here one can predict the molecular parameters of the PLP resulting polymer, such as average degrees of polymerization, polydispersity index, and molecular weight distribution, which will facilitate further study on pulsed laser-initiated polymerization.

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Appendix

Equation 22 was obtained by induction. The derivation of the concentration of chain radicals with j monomeric units in the first pulse is

1. $j = 0$

From eq 1, one gains

$$\frac{\mathrm{d}R_0^{(1)}(\tau)}{\mathrm{d}\tau} = -[(k_p + k_{tr})\bar{M}^{(1)}(1 + k_t\bar{R}\tau)^{-r} + k_t\bar{R}(1 + k_t\bar{R}\tau)^{-1}]R_0^{(1)}(\tau) + k_{tr}\bar{M}^{(1)}\bar{R}(1 + k_t\bar{R}\tau)^{-1-r} \quad \text{(A1)}$$

then

$$R_0^{(1)}(\tau) = \exp[-\int_0^\tau P_{1,0}(u)\,\mathrm{d}u]\{\int_0^\tau Q_{1,0}(u)\exp[\int_0^u P_{1,0}(v)\,\mathrm{d}v]\,\mathrm{d}u + C_{1,0}\} \quad \text{(A2)}$$

where

$$P_{1,0}(u) = (k_p + k_{tr})\bar{M}^{(1)}(1 + k_t\bar{R}u)^{-r} + k_t\bar{R}(1 + k_t\bar{R}u)^{-1}$$

$$Q_{1,0}(u) = k_{tr}\bar{M}^{(1)}\bar{R}(1 + k_t\bar{R}u)^{-1-r} \qquad C_{1,0} = R_0^{(1)}(0) = R(0)$$

From eq A2, we find

$$R_0^{(1)}(\tau) = \frac{R(0) - \alpha\bar{R}}{1 + k_t\bar{R}\tau}\exp[-q_{1,0}(\tau)] + \frac{\alpha\bar{R}}{1 + k_t\bar{R}\tau} \quad \text{(A3)}$$

2. $j = 1$

From eq 2

$$\frac{dR_1^{(1)}(\tau)}{d\tau} = -[(k_p + k_{tr})\bar{M}^{(1)}(1 + k_t\bar{R}\tau)^{-r} + k_t\bar{R}(1 + k_t\bar{R}\tau)^{-1}]R_1^{(1)}(\tau) + k_p\bar{M}^{(1)}(1 + k_t\bar{R}\tau)^{-r}R_0^{(1)}(\tau) \quad \text{(A4)}$$

So we have

$$R_1^{(1)}(\tau) = \exp[-\int_0^\tau P_{1,1}(u)\,du]\{\int_0^\tau Q_{1,1}(u) \times \exp[\int_0^u P_{1,1}(v)\,dv]\,du + C_{1,1}\} \quad \text{(A5)}$$

where

$$P_{1,1}(u) = P_{1,0}(u) \qquad Q_{1,1}(u) = k_p\bar{M}^{(1)}(1 + k_t\bar{R}u)^{-r}R_0^{(1)}(u)$$

$$C_{1,1} = R_1^{(1)}(0) = 0$$

Then from eq A5 we get

$$R_1^{(1)}(\tau) = \frac{\beta[R(0) - \alpha\bar{R}]}{1 + k_t\bar{R}\tau}\exp[-q_{1,0}(\tau)]q_{1,0}(\tau) + \frac{\bar{R}\alpha\beta}{1 + k_t\bar{R}\tau}\{1 - \exp[-q_{1,0}(\tau)]\} \quad \text{(A6)}$$

3. Arbitrary j

By induction one obtains

$$R_j^{(1)}(\tau) = \frac{\beta^j[R(0) - \alpha\bar{R}]}{1 + k_t\bar{R}\tau}\exp[-q_{1,0}(\tau)][q_{1,0}(\tau)]^j/j! + \frac{\bar{R}\alpha\beta^j}{1 + k_t\bar{R}\tau}\{1 - \exp[-q_{1,0}(\tau)]\sum_{i=0}^{j-1}\{[q_{1,0}(\tau)]^i/i!\}\} \quad \text{(A7)}$$

Similarly, we can find the distribution function of chain radicals in the nth pulse.

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