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Quasiliving Carbocationic Polymerization. X. Molecular Weight Averages and Polydispersity

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A B S T R A C T

In quasiliving polymerizations with reversible chain transfer (QL_{0R} systems), polymers with narrow molecular weight distribution can be obtained. It has been shown that while in true living systems (L_{00}) $R = 1$, and in quasiliving systems with irreversible chain transfer (QL_{01}) $R = 2$ is the limiting value of polydispersity, in QL_{0R} systems $r = 4/3$ is the polydispersity to which the distribution of the polymer tends with increasing polymerization time. This limit is independent of the rate of reinitiation; the course of the R vs t curves is, however, determined by the various rate constants.

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INTRODUCTION

Living polymerizations produce polymers with very narrow molecular weight distributions, i.e., the polydispersity approaches unity ($R = \overline{DP}_w / \overline{DP}_n \approx 1$), because termination and chain transfer are absent.

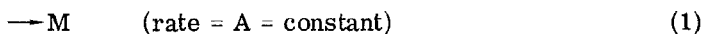
In quasiling polymerizations where reversible termination and/or reversible chain transfer may occur, the molecular weight distributions are still quite narrow. As predicted in the classification [1], polydispersities of $1 < R < 2$ are expected and, in fact, have been found experimentally.

Slow initiation may broaden the distribution even in true living systems. The initiation can, however, be neglected in dynamic systems in which polymerization is sustained by continuous, steady monomer addition. In the following, the molecular weight distributions in such dynamic systems are analyzed and characterized by the average degrees of polymerization. As in Ref. 1, it is assumed that 1) initiation is complete prior to monomer addition, and 2) polymerization is irreversible.

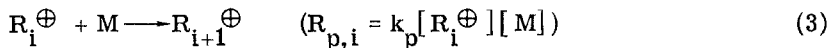
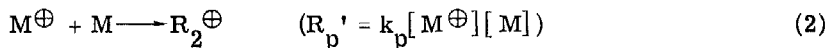
MODEL AND DIFFERENTIAL EQUATIONS

Since a differentiation between the absence or reversibility of termination would unnecessarily complicate derivations, the treatment is restricted to a model which includes, besides monomer input, only the propagation, chain transfer, and reinitiation steps:

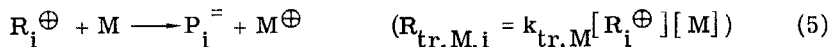
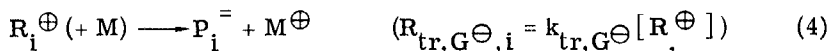
Monomer input:



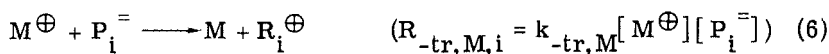
Propagation:



Chain transfer:



Reinitiation:



where M = monomer, M^{\oplus} = monomer carbocation, R_i^{\oplus} = growing active cation, and P_i^{\ominus} = olefin-terminated (dormant) polymer, both of i -length (consisting of i units, $i \geq 2$). As in Ref. 1, the sums of the concentrations

$$\sum_{i=2}^{\infty} [R_i^{\oplus}] = [R^{\oplus}] \quad \text{and} \quad \sum_{i=2}^{\infty} [P_i^{\ominus}] = [P^{\ominus}] \quad (7)$$

give the total amount of these species. The effective active center concentration, $[I]_0$, is given by

$$[I]_0 = [M^{\oplus}] + [R^{\oplus}] \quad (8)$$

The above set of reactions can be described by a set of differential equations. For the monomer:

$$d[M]/dt = A - (R_p' + R_p) - (R_{tr,G^{\ominus}} + R_{tr,M}) + R_{-tr,M} \quad (9)$$

(see Eq. 12 in Ref. 1), where the R rates are the sums of the individual rates, e.g.,

$$R_p = \sum_{i=2}^{\infty} R_{p,i} = k_p[M] \sum_{i=2}^{\infty} [R_i^{\oplus}] = k_p[M][R^{\oplus}] \quad (10)$$

For the monomer cation:

$$d[M^{\oplus}]/dt = -R_p' + (R_{tr,G^{\ominus}} + R_{tr,M}) - R_{-tr,M} \quad (11)$$

(see Eq. 10 in Ref. 1). For the individual $[R_i^{\oplus}]$ concentrations we obtain:

$$i = 2: \quad d[R_2^{\oplus}]/dt = R_p' - R_{p,2} - (R_{tr,G^{\ominus},2} + R_{tr,M,2}) + R_{-tr,M,2} \quad (12)$$

$$i > 2: \quad d[R_i^\oplus]/dt = R_{p,i-1} - R_{p,i} - (R_{tr,G^\ominus,i} + R_{tr,M,i}) + R_{-tr,M,i} \quad (13)$$

In accordance with Eq. (8), summation of Eqs. (12) and (13) for all i 's gives Eq. (11) with the opposite sign. The individual $[P_i^-]$ concentrations change according to the following differential equations:

$$i \geq 2: \quad d[P_i^-]/dt = (R_{tr,G^\ominus,i} + R_{tr,M,i}) - R_{-tr,M,i} \quad (14)$$

The sum of these equations is:

$$d[P^-]/dt = (R_{tr,G^\ominus} + R_{tr,M}) - R_{-tr,M} \quad (15)$$

(see Eq. 11 in Ref. 1).

Additional quantities and differential equations are needed if we want to describe the molecular weight distribution by the number- and weight-average degrees of polymerization. If

$$U = [M] + [M^\oplus] + \sum_{i=2}^{\infty} [R_i^\oplus] + \sum_{i=2}^{\infty} [P_i^-] \quad (16)$$

stands for the total number of molecules in the system,

$$V = [M] + [M^\oplus] + \sum_{i=2}^{\infty} i[R_i^\oplus] + \sum_{i=2}^{\infty} i[P_i^-] \quad (17)$$

stands for the total number of monomer units (first moment of concentrations), and

$$W = [M] + [M^\oplus] + \sum_{i=2}^{\infty} i^2 [R_i^\oplus] + \sum_{i=2}^{\infty} i^2 [P_i^-] \quad (18)$$

stands for the second moment of concentrations, then the averages and the polydispersity are, by definition, as follows:

$$\overline{DP}_n = V/U, \quad \overline{DP}_w = W/V, \quad \text{and} \quad R = UW/V^2 \quad (19)$$

The differential equations of the above moments can be obtained by multiplying Eqs. (12), (13), and (14) by the corresponding i 's and i^2 's, respectively, and by summing for all i 's. The same equations can be derived by appropriate definition and use of generating functions [2].

$$d\left(\sum_{i=2}^{\infty} i[R_i^{\oplus}]\right)/dt = 2R_p' + R_p - (k_{tr,G\ominus} + k_{tr,M}[M]) \sum_{i=2}^{\infty} i[R_i^{\oplus}] + k_{-tr,M}[M^{\oplus}] \sum_{i=2}^{\infty} i[P_i^{\ominus}] \tag{20}$$

$$d\left(\sum_{i=2}^{\infty} i^2[R_i^{\oplus}]\right)/dt = 4R_p' + R_p + 2k_p[M] \sum_{i=2}^{\infty} i[R_i^{\oplus}] - (k_{tr,G\ominus} + k_{tr,M}[M]) \sum_{i=2}^{\infty} i^2[R_i^{\oplus}] + k_{-tr,M}[M^{\oplus}] \sum_{i=2}^{\infty} i^2[P_i^{\ominus}] \tag{21}$$

$$d\left(\sum_{i=2}^{\infty} i[P_i^{\ominus}]\right)/dt = (k_{tr,G\ominus} + k_{tr,M}[M]) \sum_{i=2}^{\infty} i[R_i^{\oplus}] - k_{-tr,M}[M^{\oplus}] \sum_{i=2}^{\infty} i[P_i^{\ominus}] \tag{22}$$

$$d\left(\sum_{i=2}^{\infty} i^2[P_i^{\ominus}]\right)/dt = (k_{tr,G\ominus} + k_{tr,M}[M]) \sum_{i=2}^{\infty} i^2[R_i^{\oplus}] - k_{-tr,M}[M^{\oplus}] \sum_{i=2}^{\infty} i^2[P_i^{\ominus}] \tag{23}$$

Using the above differential equations, we obtain for the derivatives of U, V, and W:

$$\frac{dU}{dt} = \frac{d[M]}{dt} + \frac{d[P^{\ominus}]}{dt} \tag{24}$$

$$\frac{dV}{dt} = A \quad (25)$$

$$\frac{dW}{dt} = A + 2R_p' + 2k_p[M] \sum_{i=2}^{\infty} i[R_i^{\oplus}] \quad (26)$$

MOLECULAR WEIGHT AVERAGES AND POLYDISPERSITY

Solution of the above differential equation system in terms of simple expressions is possible only when $k_{tr,G^{\ominus}}$, $k_{tr,M'}$ and $k_{-tr,M}$ are zero, i.e., for the L_{00} system. Obviously, the result is the well-known Poisson distribution [3].

In case of the QL_{01} systems, i.e., when irreversible transfer occurs, the differential equation system can easily be solved for the steady state. The assumption of stationarity of the processes is well established in such a dynamic system; as will be shown, the abrupt changes of quantities like $[M]$, $[M^{\oplus}]$, and $[R^{\oplus}]$ are completed within a very short time.

The situation is similar also when reinitiation of the olefin-terminated molecules occurs, i.e., when chain transfer is reversible. The solution of the differential equations for such QL_{0R} systems can be expressed in closed analytical form but only for relatively long polymerization times. It will be shown that the general solution increasingly approximates the "large t" solutions with increasing time.

1. L_{00} Systems

According to our model, initiation is complete at the beginning of the polymerization, i.e., only monomer carbocations are present in the system at $t = 0$. Thus $[M^{\oplus}]_0 = U_0 = V_0 = W_0 = [I]_0$; any other concentrations are zero. With these initial conditions, introducing the short notation

$$E = \exp(-k_p[I]_0 t) \quad (27)$$

we obtain the following results:

$$[M] = A(1 - E)/k_p [I]_0 \quad (28)$$

$$[M^\oplus] = [I]_0 - [R^\oplus] = [I]_0 \exp \left\{ A(1 - E)/k_p [I]_0 \right\} - At/[I]_0 \quad (29)$$

$$\sum_{i=2}^{\infty} i[R_i^\oplus] = [I]_0 + At - [M] - [M^\oplus] \quad (30)$$

$$U = [I]_0 + [M] \quad (31)$$

$$V = [I]_0 + At \quad (32)$$

$$W = [I]_0 + \left\{ 3 - 2A(1 - E)/k_p [I]_0^2 \right\} At + A^2 t^2 / [I]_0 - 2A(1 - A/k_p [I]_0)(1 - E)/k_p [I]_0 - A^2(1 - E^2)/k_p^2 [I]_0^3 \quad (33)$$

Stationarity in these systems will be reached very soon, i.e., when E becomes negligible compared to unity ($E \ll 1$). For example if $k_p = 10^6 \text{ M}^{-1}\text{s}^{-1}$ and $[I]_0 = 10^{-3} \text{ M}$, $E < 0.01$ within 0.005 s .

\overline{DP}_n , \overline{DP}_w , and R can be expressed by U , V , and W using Eqs. (19).

With increasing time they can be better and better approximated by the following expressions:

$$\overline{DP}_n \approx \frac{At}{[I]_0 + A/k_p [I]_0} \quad (34)$$

$$\overline{DP}_w \approx At/[I]_0 \quad (35)$$

$$R \approx 1 + A/k_p [I]_0^2 \quad (36)$$

The deviation from the well-known $R = 1$ value for living systems is due to the fact that in dynamic systems $[M]$ decreases only to a steady-state value and not to zero. This value is, however, very small; for example, using the above k_p and $[I]_0$, and applying an $A = 10^{-2} \text{ Ms}^{-1}$ monomer feeding rate, the limiting value of R is 1.01. The time dependence of R is shown in Fig. 1.

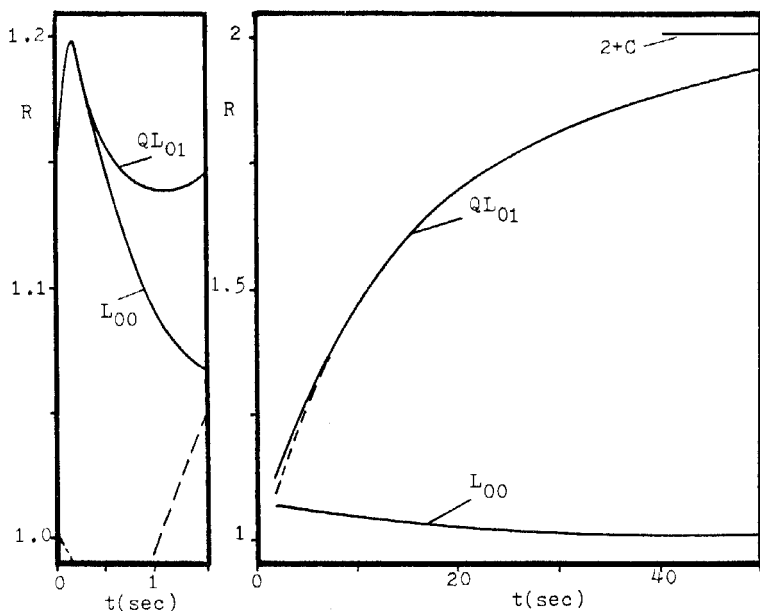


FIG. 1. Time dependence of polydispersity in a living system (L_{00}) and in a quasilinging system with irreversible transfer (QL_{01}). Curves were calculated by using $[I]_0 = 10^{-3} \text{ M}$, $A = 10^{-2} \text{ Ms}^{-1}$, $k_p = 10^6 \text{ M}^{-1}\text{s}^{-1}$, and, in the QL_{01} case, $k_{tr,G\ominus} = 10^{-1} \text{ s}^{-1}$ and $k_{tr,M} = 0$. Dotted line: calculated by using steady-state assumption (QL_{01}).

2. QL_{01} Systems

To solve the differential equations for this case, we assume that stationarity exists from the beginning of the polymerization, i.e., we use the same approximation as in Ref. 1. Thus, already at $t = 0$:

$$[M] = A/k_p [I]_0 \quad (37)$$

$$[M^\oplus] = [I]_0 - [R^\oplus] = C[I]_0 \quad (38)$$

where C is the overall chain transfer constant (see Eq. 30 in Ref. 1):

$$C = \frac{k_{tr,G^\ominus} + k_{tr,M}^{[M]}}{k_p^{[M]} + k_{tr,G^\ominus} + k_{tr,M}^{[M]}} \quad (39)$$

With these initial conditions, introducing the short notation

$$E' = \exp [-(k_{tr,G^\ominus} + k_{tr,M}^{[M]})t] \quad (40)$$

we obtain the following results:

$$[P^-] = CA t \quad (41)$$

$$\sum_{i=2}^{\infty} i[R_i] = \frac{1 - C^2}{C} [I]_0 (1 - E') \quad (42)$$

$$U = [I]_0 + [M] + CA t \quad (43)$$

$$V = [I]_0 + [M] + At \quad (44)$$

$$W = [I]_0 + [M] + \left(1 + \frac{2}{C}\right)At - \frac{2[I]_0(1 - C)^2(1 + C)}{C^2} (1 - E') \quad (45)$$

The polymerization degree averages can be expressed by U, V, and W using Eqs. (19). The time dependence of the polydispersity, calculated this way and compared with the results of the numerical integration of the differential equation system without using the steady-state assumption, is shown in Fig. 1. For long times the averages and the polydispersity have limiting values:

$$DP_n \approx 1/C \quad (46)$$

$$DP_w \approx 1 + 2/C \quad (47)$$

$$R \approx 2 + C \quad (48)$$

The polydispersity tends, as expected, to the value 2 (the deviation is small, $C \approx 1/DP_n$).

3. QL₀R Systems

We use the same approximations as in Ref. 1, i.e., we apply the following steady-state values:

$$[M] = A/k_p [I]_0 \quad (49)$$

$$[M^\oplus] = [I]_0 - [R^\oplus] = C'[I]_0 \quad (50)$$

where C' is a time-dependent overall chain transfer "constant" (see Eq. 20 in Ref. 1):

$$C' = \frac{k_{tr,G^\ominus} + k_{tr,M}[M]}{k_p[M] + k_{tr,G^\ominus} + k_{tr,M}[M] + k_{-tr,M}[P^-]} \quad (51)$$

As shown in Ref. 1, using these values we obtain for $[P^-]$ the following expression (see Eq. 27 in Ref. 1):

$$[P^-] = \frac{CA\tau}{0.5 + \sqrt{0.25 + C^2A\tau/2\gamma}} \quad (52)$$

where

$$\gamma = \frac{k_{tr,G^\ominus} + k_{tr,M}[M]}{k_{-tr,M}} \quad (53)$$

As can be seen, if $k_{-tr,M} = 0$, $\gamma = \infty$, and $C' \rightarrow C$, Eq. (50) \rightarrow (38), Eq. (52) \rightarrow (41). For long polymerization times we obtain the following approximations:

$$[P^-] \approx \sqrt{2\gamma A\tau} \quad (54)$$

$$[M^\oplus] \approx [I]_0 \sqrt{\frac{\gamma}{2A\tau}} \quad (55)$$

To solve differential Eq. (20) for $\sum_{i=2}^{\infty} i[R_1^\oplus]$, we may notice that the

first two terms on its right-hand side, $2R_p'$ and R_p , can be neglected compared to the other terms at large times. Thus we have:

$$d\left(\sum_{i=2}^{\infty} i[R_i^{\oplus}]\right)/dt = k_{-tr,M}([M^{\oplus}] \sum_{i=2}^{\infty} i[P_i^{\ominus}] - \gamma \sum_{i=2}^{\infty} i[R_i^{\oplus}]) \quad (56)$$

Obviously, for long times

$$\sum_{i=2}^{\infty} i[P_i^{\ominus}] \approx At - \sum_{i=2}^{\infty} i[R_i^{\oplus}] \quad (57)$$

and we can substitute Eqs. (55) and (57) in (56):

$$d\left(\sum_{i=2}^{\infty} i[R_i^{\oplus}]\right)/dt = k_{-tr,M} \left\{ [I]_0 \sqrt{\gamma At/2} - (\gamma + [I]_0 \sqrt{\gamma/2At}) \sum_{i=2}^{\infty} i[R_i] \right\} \quad (58)$$

Since the ever-decreasing $[I]_0 \sqrt{\gamma/2At}$ can soon be neglected compared to γ , the solution of Eq. (58), using the initial condition $(\sum_{i=2}^{\infty} i[R_i^{\oplus}])_0 = 0$, is as follows:

$$\sum_{i=2}^{\infty} i[R_i^{\oplus}] = k_{-tr,M} [I]_0 \sqrt{\gamma A/2} \exp(-k_{-tr,M} \gamma t) \int \sqrt{t} \exp(k_{-tr,M} \gamma t) dt \quad (59)$$

For large t 's the above integral can well be approximated by

$$\int \sqrt{t} \exp(k_{-tr,M} \gamma t) dt \approx \frac{1}{k_{-tr,M}} \sqrt{t} \exp(k_{-tr,M} \gamma t) \quad (60)$$

and we obtain from Eq. (59):

$$\sum_{i=2}^{\infty} i[R_i^{\oplus}] \approx [I]_0 \sqrt{At/2\gamma} \quad (61)$$

For U , V , and W the following expressions hold for long polymerization times:

$$U \approx \sqrt{2\gamma At} \quad (62)$$

$$V \approx At \quad (63)$$

$$W \approx \frac{4}{3\sqrt{2\gamma}} \sqrt{(At)^3} \quad (64)$$

The polymerization degree averages and the polydispersity can be calculated by using Eqs. (9):

$$\overline{DP}_n \approx \sqrt{At/2\gamma} \quad (65)$$

$$\overline{DP}_w \approx \frac{4}{3} \sqrt{At/2\gamma} \quad (66)$$

$$R \approx 4/3 \quad (67)$$

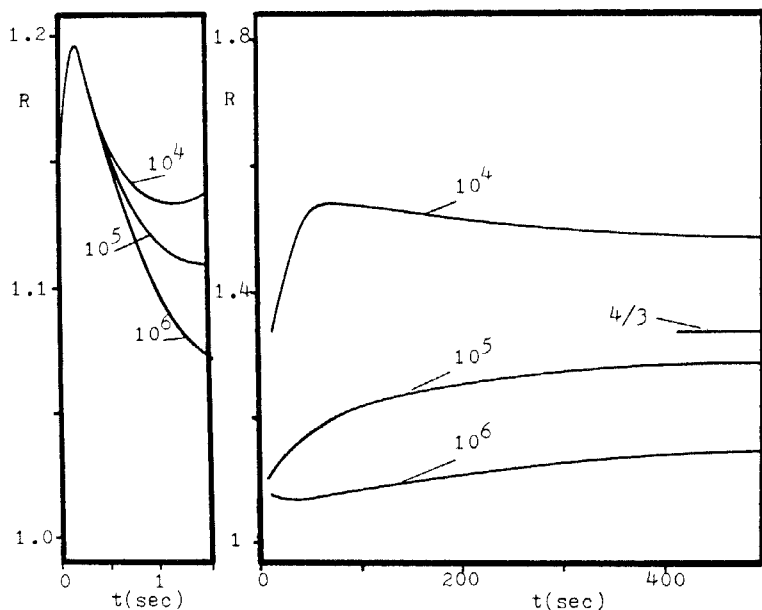


FIG. 2. Time dependence of polydispersity in quasiliving systems with reversible transfer (QL_{0R}). Curves were calculated with the same rate constants as QL_{01} (see Fig. 1) and by using $k_{-tr,M} = 10^4$, 10^5 , and 10^6 s^{-1} , respectively.

Thus the limiting polydispersity is $4/3$ in quasiliving systems of the type QL_{0R} . This value, like the $R=2$ limit in QL_{01} systems, is independent of the value of the rate constants.

Figure 2 shows the time dependence of R for various $k_{-tr,M}$ values, calculated by numerical integration of the differential equation system without using approximations. As can be seen, with increasing time the R 's approach the limiting value on different curves, depending on the value of the reinitiation rate constant.

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