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Quantitative Studies of Some Aspects of Living Cationic Polymerization

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ABSTRACT: Kinetics of living cationic polymerization with two-step initiation was examined through computer calculations. The effect of equilibrium ionization on the progress of reaction was quantified. Various perturbations of this equilibrium were modeled, special attention being paid to those caused by chain transfer to initiator. The length of the relaxation time of ionization was found to be decisive in determining the character of polymerization. The initiation involving bifunctional initiators for which ionization of one group inhibits the reactivity of the other was contrasted with that involving a monofunctional initiator. The incremental mode of monomer addition was scrutinized. As was shown earlier,[5] such a mode of addition does not modify the course of living polymerization, provided that initiation and propagation are first order in monomer, albeit not necessarily first order in initiator or living polymers, and that all the species participating in the process remain in equilibrium with each other.

The purpose of this work is to clarify and quantify some aspects of living cationic polymerization. Living cationic polymerization of vinyl ethers and of some other monomers has been reported by Higashimura and his coworkers,[1] while Kennedy and his coleagues have reported an living cationic polymerization of isobutene and other vinyl monomers.[2]

Polymers and some model compounds terminated by tertiary Cl atoms become ionized and capable of initiating cationic living polymerization on addition of excess of BCl_3, provided that the reaction is performed in sufficiently polar solvents at very low temperature.[3] Under these conditions the equilibrium

$$-C(R)_2Cl + BCl_3 \Leftrightarrow -C^+(R)_2,BCl_4^-$$

provides the active ion pairs and termination is prevented due to its reversibility. The ensuing polymerization has been studied by Kennedy's group,[4] who postulated the following mechanism for this reaction; e.g.

$$PhC(CH_3)_2Cl + BCl_3 \Leftrightarrow PhC^+(CH_3)_2,BCl_4^-;\quad K$$

$$PhC^+(CH_3)_2,BCl_4^- + CH_2{=}C(CH_3)_2 \rightarrow PhC(CH_3)_2CH_2C^+(CH_3)_2,BCl_4^-;\quad k_c$$

$$-CH_2C^+(CH_3)_2,BCl_4^- + CH_2{=}C(CH_3)_2 \rightarrow -CH_2C(CH_3)_2CH_2C^+(CH_3)_2,BCl_4^-;\quad k_p$$

The first two steps represent a composite initiation involving a slow, rate-determining addition of the first monomer molecule to a stable benzylic or allylic carbenium ion. The last step describes a rapid propagation. Ramifications of this mechanism, and of similar ones, are considered in this paper. To make tractable the treatments outlined below, only the equilibria between the covalent species and their ion pairs are considered. For the sake of briefness the term carbenium ions is used in the text instead of carbenium ion pairs.

Slow Initiation of Living Polymers. Slow initiation followed by rapid propagation of living polymers was discussed by Szwarc et al.[5] Provided that the initiation and propagation are the only reactions consuming the monomer and assuming that both are first order in monomer, one deduces the following relation between the concentrations of monomer, M, and the initiator, I, established at any stage of the reaction:

$$dM/dI = 1 + G(I,I_0-I)/F(I,I_0-I) \qquad (1)$$

The concentration of growing polymers, P, is given by the stoichiometric condition requiring $P = I_0 - I$ where I_0 denotes the initial concentration of the initiator. F and G are the functions that describe the kinetic dependence of these two reactions on the concentrations of initiator and of the growing polymers (note: kinetics of these reactions need not be first order with respect to to the latter species).

The monomer concentration does not appear on the right side of eq 1 and therefore the shape of the graph relating M to I depends only on I_0 being independent of M_0, the initial concentration of the monomer. Change of M_0 leads to a parallel shift along the M axis of the curve relating M to I, without changing its shape. This is illustrated by Figure 1; its significance is discussed later. Equation 1 is valid even when more than one species participate in the initiation or propagation processes, provided that the equilibrium between them is maintained during the whole course of the reaction (see ref 5).

An interesting ramification of eq 1 should be stressed. Since M does not appear on its right side, one infers that at constant I_0 the amount of initiator and monomer remaining on quenching the reaction depends only on the total amount of added monomer, irrespective of the mode of its addition. This conclusion is illustrated by Figure 1. Incremental 5-fold addition of monomer (see the sequence OABCDEFGHI) produces the same result as the addition of its total amount at the onset of the reaction (see O′A′C′E′G′I). Note, the segment O′A′ is identical with OA, A′C′, with BC, etc.

These general considerations were illustrated by some examples;[5] in the simplest one it is assumed that initiation is first order in initiator and that propagation is first order in the growing polymers. In such a case the integration of eq 1 yields[7]

$$M = M_0 + (1 + k_p/k_i)(I - I_0) + (k_p/k_i)I_0 \ln (I/I_0) \qquad (2)$$

The concentration of the residual initiator remaining after quantitative polymerization of the monomer is given then by eq 3. The curves drawn in Figure 1 were calculated on

$$M_0/I_0 = (1 - k_p/k_i)(1 - I/I_0) - (k_p/k_i) \ln (I/I_0) \qquad (3)$$

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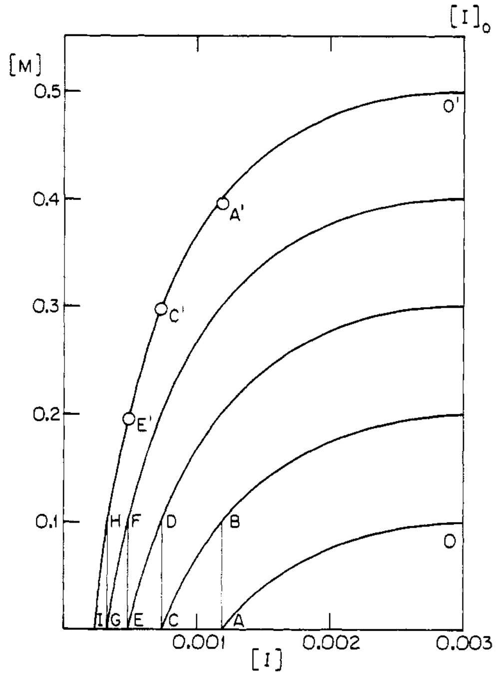

Figure 1. Dependence of residual monomer concentration on concentration of residual initiator for different initial concentrations of the monomer at constant $[I]_0 = 0.003$ M of the initiator.

the basis of this relation. Its inspection, as well as examination of Figure 1, reveals that I approaches 0 as M_0 approaches infinity [in some systems all the initiator is consumed before polymerization ceases (see ref 5)], and moreover for a constant ΔM_0 the respective $-\Delta I$'s tend to 0 as M_0 increases.

Equation 3 was modified by Kennedy et al.[6] Substituting I_{eff} for $1 - I/I_0$, one gets for $k_p/k_i \gg 1$ the approximate eq 4. Hence, a plot of $-\{I_{eff} + \ln(1 - I_{eff})\}$ vs M_0/I_0 should produce a straight line through the origin with a slope of k_i/k_p. Such a plot with slope of 9×10^{-3} is shown in ref 6.

$$M_0/I_0 = -(k_p/k_i)\{I_{eff} + \ln(1 - I_{eff})\} \qquad (4)$$

The variation of the monomer and initiator concentrations with time are of interest. The data were obtained by solving two simultaneous equations

$$\mathrm{d}I/\mathrm{d}t = -k_i I M \qquad (5)$$

$$\mathrm{d}M/\mathrm{d}t = -k_i I M - k_p(I_0 - I)M \qquad (6)$$

for selected values of rate constants and initial conditions. The lines shown in Figures 2–4 give the percentages of monomer and initiator as functions of time. The curves seen in Figure 2 were drawn for initial conditions closely resembling those maintained in the experiments described in ref 6. Inspection of Figure 2, as well as of Figure 1, reveals the trivial effect of initial monomer concentration upon the asymptotic value of the residual initiator, providing other parameters are kept constant. Similarly, the effects caused by an increase of k_p for two values of M_0 are shown in Figures 3 and 4. Additional data revealing the influence of various parameters on the asymptotic value of the residual initiator's concentration, i.e., upon I_{eff} are collected in Table I.

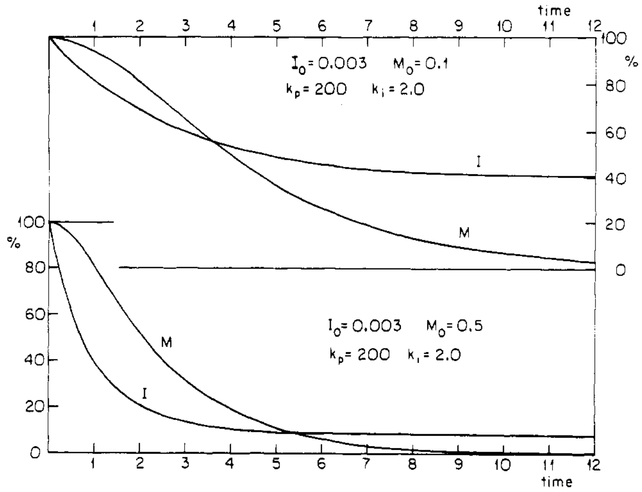

Figure 2. Time dependence of the percentage of residual monomer and initiator concentrations for $k_i = 2$ M^{-1} s^{-1} and $k_p = 200$ M^{-1} s^{-1}. Upper curves: $[I]_0 = 0.003$ M, $[M]_0 = 0.1$ M. Lower curves: $[I]_0 = 0.003$ M, $[M]_0 = 0.5$ M.

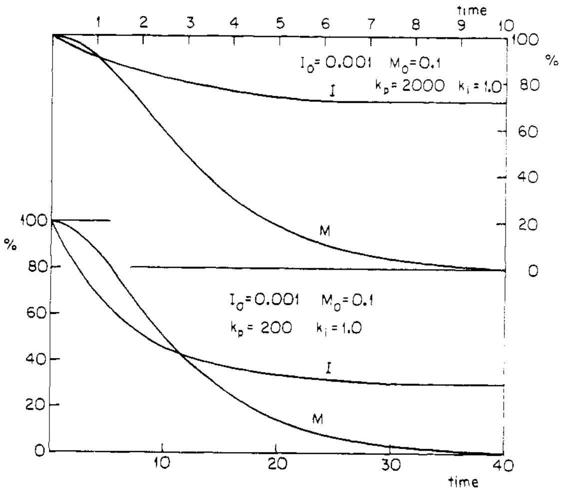

Figure 3. Time dependence of the percentage of residual monomer and initiator concentrations for $[I]_0 = 0.001$ M and $[M]_0 = 0.1$ M. Upper curves: $k_i = 1.0$ M^{-1} s^{-1}, $k_p = 2000$ M^{-1} s^{-1}. Lower curves: $k_i = 1.0$ M^{-1} s^{-1}, $k_p = 200$ M^{-1} s^{-1}.

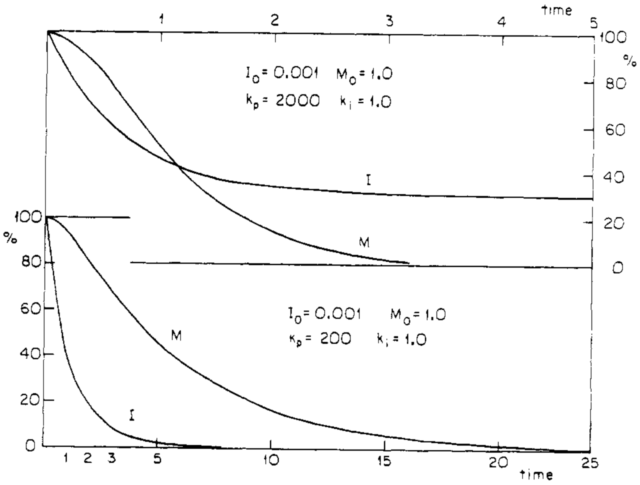

Figure 4. Time dependence of the percentage of residual monomer and initiator concentrations for $[I]_0 = 0.001$ M and $[M]_0 = 1.0$ M. Upper curves: $k_i = 1.0$ M^{-1} s^{-1}, $k_p = 2000$ M^{-1} s^{-1}. Lower curves: $k_i = 1.0$ M^{-1} s^{-1}, $k_p = 200$ M^{-1} s^{-1}.

Living and Dormant Initiator. The full activity of all the initiators is implied in the derivation of eqs 3 and 4. However, in cationic polymerization initiated by initiators activated by BCl_3 an equilibrium is established between the inactive initiator and the respective active carbenium ions (or ion pairs). The latter are the actual initiators, and hence only a fraction of all the nominal initiators is available for direct initiation at any time. It is necessary, therefore, to investigate the effect of this

Table I

For $I_0 = 0.001$, $M_0 = 0.1$, $k_i = 1.0$ (in mol/L)

k_p	100	125	150	175	200	300	500	1000	2000
lim I/I_0	0.160	0.204	0.242	0.274	0.303	0.390	0.494	0.617	0.716

For $I_0 = 0.001$, $M_0 = 0.1$, $k_p = 200$ (in mol/L)

k_i	0.5	1.0	2.0	5.0
lim I/I_0	0.450	0.303	0.160	0.032

For $M_0 = 0.1$, $k_i = 1.0$, $k_p = 200$ (in mol/L)

$10^3 I_0$	0.2	0.5	1.0	1.5	2.0	3.0	5.0
lim I/I_0	0.031	0.160	0.303	0.391	0.451	0.531	0.620

equilibrium upon the polymerization.

Denote by I_n the concentration of the inactive initiator, by I^+ that of the respective carbenium ion pairs, and by I the total concentration of the initiator; i.e., $I = I_n + I^+$, while $I^+/I_n = K[\mathrm{BCl_3}] = K'$. Hence, $I^+ = \alpha I$ where $\alpha = K'/(1 + K')$. A similar equilibrium is expected to relate growing ionized polymers P^+ and the dormant un-ionized polymers P_n. It demands that $P^+/P_n = K_1[\mathrm{BCl_3}]$ and hence $P^+ = \beta P$, where $\beta = K_1'/(1 + K_1')$ and $K_1' = K_1[\mathrm{BCl_3}]$. Here P denotes the total concentration of the polymers, living and dormant. K_1 is expected to be smaller than K, and then $\beta < \alpha$.

A stoichiometric relation again gives $P = I_0 - I$, with I_0 denoting the initial concentration of all the initiator in whatever form. Progress of polymerization is described the kinetic scheme

$$I_n + \mathrm{BCl_3} \Leftrightarrow I^+ + \mathrm{BCl_4^-};\quad K$$

$$I^+ + M \rightarrow P^+;\quad k_i$$

$$P^+ + M \rightarrow P^+;\quad k_p$$

leading to the differential equations

$$-\mathrm{d}I/\mathrm{d}t = k_i I^+ M \tag{7}$$

$$-\mathrm{d}M/\mathrm{d}t = k_i I^+ M + k_p \beta (I_0 - I) M \tag{8}$$

provided that the equilibrium between the inactive dormant species and the active carbenium ions is maintained during its whole course. Hence

$$\mathrm{d}M/\mathrm{d}I = 1 + (k_p/k_i)\beta(I_0 - I)/I^+ \tag{9}$$

or

$$\mathrm{d}M/\mathrm{d}I = 1 + (k_p/k_i)(\beta/\alpha)(I_0/I - 1) \tag{10}$$

Integration yields

$$M_0 - M = [1 - (k_p/k_i)(\beta/\alpha)](I_0 - I) - (k_p/k_i)(\beta/\alpha) I_0 \ln (I_0/I) \tag{11}$$

At complete monomer conversion and for $(k_p/k_i)(\beta/\alpha) \gg 1$, the approximate relation is valid

$$M_0/I_0 = -(k_p/k_i)(\beta/\alpha)(1 - I/I_0 + \ln I/I_0) \tag{12}$$

or in the notation $1 - I/I_0 = I_{\mathrm{eff}}$

$$M_0/I_0 = -(k_p/k_i)(\beta/\alpha)\{I_{\mathrm{eff}} + \ln (1 - I_{\mathrm{eff}})\} \tag{13}$$

Equations 12 and 13 resemble eqs 3 and 4, but the factor k_p/k_i is replaced by $(k_p/k_i)(\beta/\alpha)$. Thus the lim I/I_0 again is independent of the mode of monomer addition and the plots of

$$-\{I_{\mathrm{eff}} + \ln (1 - I_{\mathrm{eff}})\} \text{ vs } M_0/I_0$$

again should be linear, passing through the origin, but with higher slopes of $(k_i/k_p)(\alpha/\beta)$ instead of k_i/k_p. Lack of knowledge of α/β values makes questionable the assignment of the experimentally determined slopes to k_i/k_p. However, since the ratio α/β decreases and approaches 1 as the concentration of $\mathrm{BCl_3}$ increases, the ratio k_i/k_p might be determined by extrapolating the values of the slopes as a function of $\mathrm{BCl_3}$ concentrations to its infinite value.

Table II
$\beta_0 k_p$ = 200 M^{-1} s^{-1}, αk_i = 1.0 M^{-1} s^{-1},[a] I_0 = 0.002 M, and M_0 = 0.1 M

no. of additions	β/β_0	I_∞/I_0	R[b]	$R/\sum M$[c]	$R/\sum M$ test[d]
1st	1.0	0.451	0.247	0.247	0.247
2nd	0.9	0.291	0.524	0.262	0.248
3rd	0.8	0.193	0.836	0.279	0.248
4th	0.7	0.127	1.193	0.298	0.248
5th	0.6	0.0797	1.609	0.322	0.249

[a] αk_i and βk_p are the "effective" initiation and propagation constants. [b] $R = I_\infty/I_0 - 1 - \ln (I_\infty/I_0)$. [c] $\sum M$ is the total amount of added monomer. [d] The $R/\sum M$ test is the result obtained for constant $\beta = \beta_0$.

These considerations might rationalize some peculiarities reported[4] by the Kennedy group, who found some plots of $-\{I_{\mathrm{eff}} + \ln (1 - I_{\mathrm{eff}})\}$ vs M_0/I_0 to be concave. The parameters α and β are affected by polarity of solvent. Presumably β decreases more steeply than α as solvent polarity is reduced. Each incremental monomer addition reduces the solvating power of the reaction medium; it therefore increases α/β and raises the respective point in the pertinent plot. A decrease of k_p caused by an increase in the hydrocarbon fraction of the medium provides an alternative explanation of these pecularities.

To assess the magnitude of such effects, eqs 7 and 8 were used to compute the limiting value of I/I_0 for M decreasing to 0 from its initial value of M_0 = 0.1 mol/L. Thereafter these calculations were repeated by using the thus obtained limiting values of I^+ and I in conjunction with M_0 = 0.1 mol/L as new starting parameters (the addition of the next monomer increment). This procedure was repeated over and over until five increments of monomer were "added" to the reactor. While α was kept constant, at 10^{-2}, β was gradually diminished from 1×10^{-3} at the first addition to 0.9×10^{-3} at the second, etc., reaching 0.6×10^{-3} at the last monomer addition. The results listed in Table II show an increase not only of $-\{I_{\mathrm{eff}} + \ln (1 - I_{\mathrm{eff}})\}$ with each added monomer increment but also of its ratio to $\sum M$ (the total monomer added), demonstrating the concave shape of the plot of $-\{I_{\mathrm{eff}} + \ln (1 - I_{\mathrm{eff}})\}$ vs $\sum M$.

Living and Dormant Bifunctional Initiators. Use of bifunctional initiators, e.g., $\mathrm{ClC(CH_3)_2C_6H_4C(CH_3)_2Cl}$, raises new problems. The initiation, the addition of the first monomer molecule to one of its functional groups, results in incorporation of both groups into the formed polymer and requires distinction between a functional group of a free initiator and that attached to a polymer. Hence, the treatment has to be modified.

Two kinds of bifunctional initiators are visualized. Either the reactivity of one of the functional groups is independent of the fate of the other or ionization of one group affects the reactivity of the other one. In the extreme case ionization of one end group may hinder entirely ionization of the other, e.g., due to a positive charge developed in the resulting species. The second group becomes ionizable only after addition of the first monomer molecule to the ionized end. In either case one has to distinguish between the original bifunctional initiator, denoted by I, its monoionized ion I^+, the polymer P^+ with a single arm resulting from addition of at least one monomer molecule to I^+, polymer P^{2+} produced from P^+ by ionization of the second end group of the attached initiator, and the living polymer with both arms propagating, denoted by P^{2+}.

The un-ionized initiator and its monoion are assumed to be in equilibrium. Denoting by $K_1' = K_1[\mathrm{BCl_3}]$ the equilibrium constant of ionization of the initiator's end group and by I_t the total concentration of the initiator in whatever form, one gets

$$I^+ = \alpha' I_t \text{ with } \alpha' = 2K_1'/(1 + 2K_1')$$

The one-arm polymers are in equilibrium with their dormant polymers, e.g.

ClIn–C$^+$ (denoted P^+) with ClIn–CCl (denoted $P_n^{\ +}$)

as well as

$^+$In–C$^+$ (denoted P^{2+}) with $^+$In–CCl (denoted $P_n^{\ 2+}$)

and similar equilibrium is established between active and dormant two-arm polymers, e.g.

C$^+$–In–C$^+$ (denoted $P_2^{\ 2+}$) with ClC–In–C$^+$ (denoted $P_2^{\ +}$) and with ClC–In–CCl (denoted $P_2^{\ 0}$)

Denoting by $K_2[\mathrm{BCl_3}] = K_2'$ the dormant-to-active polymers equilibrium constant and by P_1 and P_2 the total concentrations of one-arm and of two-arm polymers, respectively, one finds

$$P^+ + P^{2+} = \beta P_1, \quad \text{with } \beta = K_2'/(1 + K_2')$$

$$P_t^{\ 2+} = P^{2+} + P_n^{\ 2+} = \alpha P_1, \quad \text{with } \alpha = K_1'/(1 + K_1')$$

$$2P_2^{\ 2+} + P_2^{\ +} = \gamma P_2, \quad \text{with } \gamma = 2\beta$$

A stoichiometric relation yields $P_2 = I_{t0} - I_t - P_1$, where I_{t0} denotes the initial concentration of the initiator. The kinetics of this polymerization is described by the scheme

$$\mathrm{I} + \mathrm{BCl_3} \Leftrightarrow \mathrm{I}^+ + \mathrm{BCl_4}^-; \ 2K_1$$

$$\mathrm{I}^+ + \mathrm{M} \rightarrow \mathrm{P}^+ \text{ or } (\mathrm{IM}^+); \ k_i$$

$$\mathrm{P}^+ + \mathrm{M} \rightarrow \mathrm{P}^+ \text{ or } (\mathrm{I\text{-}M}^+); \ k_p$$

$$\mathrm{P}^+ \text{ or } \mathrm{P}_n^{\ +} + \mathrm{BCl_3} \Leftrightarrow \mathrm{P}^{2+} \text{ or } \mathrm{P}_n^{\ 2+} + \mathrm{BCl_4}^-; \ K_1$$

$$\mathrm{P}^{2+} \text{ or } \mathrm{P}_n^{\ 2+} + \mathrm{M} \rightarrow \mathrm{P}_2^{\ 2+} \text{ or } \mathrm{P}_2^{\ +}; \ k_i$$

$$\mathrm{P}^{2+} \text{ or } \mathrm{P}^+ + \mathrm{M} \rightarrow \mathrm{P}^{2+} \text{ or } \mathrm{P}^+; \ k_p$$

$$\mathrm{P}_2^{\ 2+} \text{ or } \mathrm{P}_2^{\ +} + \mathrm{M} \rightarrow \mathrm{P}_2^{\ 2+} \text{ or } \mathrm{P}_2^{\ +}; \ 2k_p \text{ or } k_p$$

which leads to the following differential equations:

$$\mathrm{d}I_t/\mathrm{d}t = -k_i I^+ M = -k_i \alpha' I_t M \tag{14}$$

$$\mathrm{d}P_1/\mathrm{d}t = k_i(I^+ - P_t^{\ 2+})M = k_i(\alpha' I_t - \alpha P_1)M \tag{15}$$

$$\mathrm{d}M/\mathrm{d}t = -k_i(I^+ + P_t^{\ 2+})M - k_p(P^+ + P^{2+} + P_2^{\ +} + 2P_2^{\ 2+})M = -k_i(\alpha' I_t + \alpha P_1)M - k_p(\beta P_1 + 2\beta P_2)M \tag{16}$$

Table III[a]

$\beta k_p = 200$ M^{-1} s^{-1}, $\alpha k_i = 1.0$ M^{-1} s^{-1}, $I_{t0} = 0.001$ M (0.002 for Monofunctional Initiator), $M_0 = 0.1$ M, $K_1' = 1 \times 10^{-2}$, and $K_2' = 1 \times 10^{-3}$

	monofunctional		bifunctional		
t, s	I/I_0	M/M_0	I_t/I_{t0}	P_1/I_{t0}	M/M_0
1	0.9055	0.9790	0.8199	0.1713	0.9790
2	0.8231	0.9253	0.6774	0.2912	0.9253
3	0.7531	0.8484	0.5672	0.3719	0.8484
5	0.6472	0.6638	0.4189	0.4567	0.6638
10	0.5159	0.2792	0.2661	0.4995	0.2792
15	0.4724	0.1002	0.2232	0.4985	0.1002
20	0.4581	0.0341	0.2099	0.4965	0.0341
50	0.4510	0.0046	0.2034	0.4952	0.0046
100	0.4510	0.0000	0.2034	0.4952	0.0000

[a] Inspection of this table demonstrates that the polymerization proceeds with the same rate for the monofunctional initiator as for the bifunctional initiator (see the respective M/M_0's). This is the result of minuteness of K_1' and K_2'; virtually the same amount of functional groups is active in both systems. Note $2I_t/I_{t0} + P_1/I_{t0} = 2I/I_0$; the fractions of I^+, P^+, P^{2+}, and $P_n^{\ 2+}$ are all very small. However, the "bookkeeping" for the residual initiator is different. All the residual initiator is accounted for by I in the monofunctional case, while some of it is in the form of P_1 in the bifunctional system. Therefore, $I_t/I_{t0} < I/I_0$.

Table IV[a]

$\beta k_p = 200$ M^{-1} s^{-1}, $\alpha k_i = 1.0$ M^{-1} s^{-1}, $I_{t0} = 0.001$ M (0.002 for Monofunctional Initiator), $M_0 = 0.1$ M, $\alpha = \alpha' = \beta = 1$, and $\gamma = 2$

	monofunctional		bifunctional		
t, s	I/I_0	M/M_0	I_t/I_{t0}	P_1/I_{t0}	M/M_0
1	0.9055	0.9790	0.9052	0.0902	0.9891
2	0.8231	0.9253	0.8210	0.1619	0.9593
3	0.7531	0.8484	0.7476	0.2175	0.9130
5	0.6472	0.6638	0.6304	0.2909	0.7858
10	0.5159	0.2792	0.4661	0.3558	0.4312
15	0.4724	0.1002	0.4008	0.3665	0.1968
20	0.4581	0.0341	0.3751	0.3678	0.0829
50	0.4510	0.0046	0.3584	0.3678	0.0035
100	0.4510	0.0000	0.3583	0.3677	0.0000

[a] The relations $\alpha = \alpha' = 1$, $\beta = 1$, and $\gamma = 2$ mean all the initiator available at any time t is in the form of its monoion I^+, all the one-arm polymers P_1 are in the form P^{2+}, and all the two-arm polymers P_2 are in the form $P_2^{\ 2+}$, respectively. Polymerization involving a bifunctional initiator is slower than that induced by monofunctional one because some of the functional groups of the former, but not of the latter, are inhibited.

These equations were solved for typical values of rate constants, namely, $\alpha k_i = 1.0$ and $\beta k_p = 200$ (both in M^{-1} s^{-1}), and for the initial conditions $I_t = 0.001$ M and $M_0 = 0.1$ M. The computations were performed twice: once for reasonably low values of $K_1' = 1 \times 10^{-2}$ and $K_2' = 1 \times 10^{-3}$ and then for nonrealistic, but interesting, high values of K_1' and K_2' which ascertain complete ionization of one group of the bifunctional initiator, as well as of the polymers. The results are collected in Tables III and IV. For the sake of comparison the computations were performed also for the monofunctional initiator by using the same constants but $I_0 = 0.002$ (to keep the concentration of the active groups of the monoinitiator the same as in the bifunctional case). These results are included in the pertinent tables.

For a very low degree of ionization the polymerization proceeds with the same rate in both cases. This is the consequence of minuteness of K_1' and K_2'. However, the ratio I_t/I_{t0} is smaller than I/I_0, because two functional groups are removed in each initiation step involving the bifunctional initiator. This effect is compensated by initiation due to one-arm polymers and therefore does not affect propagation. The plot of $R = I_t/I_{t0} - 1 - \ln(I_t/I_{t0})$ vs $\sum M$ is not linear; it is strongly convex as shown

Table V[a]
βk_p = 200 M^{-1} s^{-1}, αk_i = 1.0 M^{-1} s^{-1}, M_0 = 0.1 M, and I_0 = 0.002 M

	k_1' = 1.0 s^{-1}; k_2 = 10 s^{-1}; τ = 0.09 s			k_1' = 0.2 s^{-1}; k_2 = 2.0 s^{-1}; τ = 0.45 s			k_1' = 0.05 s^{-1}; k_2 = 0.5 s^{-1}; τ = 2 s		
t, s	I/I_0	I^+/I_n	M/M_0	I/I_0	I^+/I_n	M/M_0	I/I_0	I^+/I_n	M/M_0
1.0	0.919	0.0917	0.982	0.931	0.0675	0.984	0.939	0.0490	0.985
2.0	0.848	0.0921	0.936	0.874	0.0691	0.945	0.902	0.0382	0.953
3.0	0.786	0.0926	0.868	0.824	0.0702	0.889	0.873	0.0332	0.911
5.0	0.687	0.0939	0.700	0.738	0.0736	0.743	0.821	0.0381	0.804
10	0.554	0.0971	0.319	0.604	0.0844	0.377	0.719	0.0485	0.503
15	0.505	0.0989	0.123	0.545	0.0927	0.159	0.652	0.0629	0.266
20	0.488	0.0996	0.044	0.521	0.0970	0.062	0.613	0.0771	0.126
30	0.479	0.0999	0.006	0.508	0.0996	0.009	0.584	0.0941	0.025
50	0.478	0.100	0.000	0.506	0.0999	0.002	0.577	0.0998	0.008
75	0.478	0.100	0.000	0.506	0.1000	0.000	0.576	0.1000	0.000
100	0.478	0.100	0.000	0.506	0.1000	0.000	0.576	0.1000	0.000

[a] The initial conditions are I^+/I_0 = 0.0909 and I_n/I_0 = 0.9090; i.e., the ion and the neutral initiator are at equilibrium at the onset of polymerization.

below, but the outcome of polymerization is independent of the mode of monomer addition. For example, under conditions stated in Table III the final ratio of I_t/I_{t0} after two consecutive additions of monomer (ΔM = 0.1 M) is 0.091 94, and it is still 0.091 94 after one batch addition of 0.2 M. The ratios P_1/I_{t0} also are identical, namely 0.4226. Five-fold additions of 0.1 M each leads to I_t/I_{t0} = 0.014 22, the same as obtained in a single addition of 0.5 M. This confirms the general law proved in ref 5. In an equilibrated system with initiation and propagation first order in monomer, albeit more complex in initiator, the mode of monomer addition is immaterial.

The same conclusions transpire from Table IV. Double addition of 0.1 M gives I_t/T_{t0} = 0.2250, the same as addition of 0.2 M. Five-fold addition leads to the ratio of 0.080 08—again the same as by a single addition of 0.5 M.

The results of incremental monomer addition tested by the previously described procedure are given below:

no. of increments	1st	2nd	3rd	4th	5th
	For Conditions See Table III				
R	0.7959	1.479	2.106	2.698	3.267
$R/\sum M$	0.7959	0.7393	0.7019	0.6746	0.6535
	For Conditions See Table IV				
R	0.3847	0.7167	1.026	1.320	1.605
$R/\sum M$	0.3847	0.3583	0.3419	0.3300	0.3209

Plots R vs $\sum M$ of bifunctional initiator are convex for both sets of data. Computations based on the results obtained for the monofunctional initiator gave, as expected, constant values for $R/\sum M$, namely, 0.2474 ± 0.0001; i.e., for monofunctional initiator the plot of R vs $\sum M$ is linear.

Perturbation of the Equilibria between the Dormant and Active Initiators. Initiation perturbs the equilibrium established between the inactive initiator and the active carbenium ions by removing the latter through their reaction with the monomer. Thus the concentration of carbenium ions is reduced, and the rates of initiation and polymerization are slowed down. Propagation does not perturb the equilibrium between ionized and un-ionized growing polymers. Hence, only the perturbation involving the initiating species needs to be considered in quantitative treatment. Let us start with a discussion of monofunctional initiator. Kinetics of the perturbed polymerization is described by three equations

$$\mathrm{d}I^+/\mathrm{d}t = -(k_iM + k_2)I^+ + k_1'I_n \tag{17}$$

$$\mathrm{d}M/\mathrm{d}t = -k_iI^+M - k_p(I_0 - I^+ - I_n)M \tag{18}$$

$$\mathrm{d}I_n/\mathrm{d}t = k_2I^+ - k_1'I_n \tag{19}$$

where $k_1' = k_1[BCl_3]$ and k_2 refer to the forward and backward conversion of the neutral initiator into carbenium ions, with other symbols retaining their previously defined meaning. For comparison with the previous results the values of αk_i = 1.0 and βk_p = 200 M^{-1} s^{-1} are retained, in conjunction with the concentrations I_0 = 0.002 M and M_0 = 0.1 M. Such polymerization is virtually completed in about 30 s. The computations were performed for K_1' = 0.0909, i.e., α = 0.1 and therefore k_1'/k_2 = 0.1. The characteristic time of initiation is $1/k_iM_0$, and for the chosen constants it is 1 s. To observe appreciable perturbation of polymerization, the relaxation time of ionization, $\tau = 1/(k_1' + k_2)$, has to be comparable to or larger than 1 s. The following values were chosen therefore for k_1' and k_2: 1.0 and 10 (τ = 0.09 s), 0.2 and 2 (τ = 0.45 s), and 0.05 and 0.5 (τ = 1.8 s). The results of computations are collected in table V.

Inspection of Table V reveals a progressive slowing down of polymerization with increasing relaxation time of ionization (compare the M/M_0' in Table V and the values for the monofunctional initiator in Tables III or IV computed for an equilibrated system, i.e., for extremely short relaxation time). The perturbation reduces the ratio I^+/I_n at early stages of the reaction, although the equilibrium is eventually reestablished after disappearance of the monomer. It is assumed in the computations that the initiator is at equilibrium with its ionized form at the onset of polymerization. It takes time to perturb the equilibrium, and at the longest relaxation time of 2 s this requires a few seconds, causing an initial decrease and then an increase of I^+/I_n.

The effect of incremental monomer addition was tested again by using the previously described procedure. The results are collected in Table VI. The lim I/I_0 increases progressively from its value of 0.4510 found for the equilibrated system as the relaxation time increases. This is in accord with the following general rule: the slower the initiation, the lower the initiator consumption. The diagnostic $R/\sum M$ increases with the number of increments, only very slightly for τ = 0.009 s but quite substantially for τ = 2 s, leading to a somewhat concave plot of R vs $\sum M$. This might be another explanation of Kennedy's observations.

Perturbation of polymerization involving bifunctional initiator is more complex. Whether the initiator is free or attached to the polymer, the equilibrium between its un-ionized and ionized groups is perturbed. This calls for distinction between the following species: the un-ionized initiator I, its monoion I^+, the one-arm polymer P^+ resulting from I^+, the product of dissociation of the active group attached to its initiator moiety denoted by P^{2+}, and the two-arm polymer P_2. The initial concentration

Table VI
Monofunctional Initiator. Perturbed Equilibrium

no. of additions	1st	2nd	3rd	4th	5th
	$k_1' = 1.0$, $k_2 = 10.0$, and $\tau = 0.09$ s				
lim I/I_0	0.4781	0.3324	0.2449	0.1855	0.1429
R	0.2160	0.4338	0.6519	0.8702	1.0886
$R/\sum M$	0.2160	0.2169	0.2173	0.2176	0.2177
	$k_1' = 0.2$, $k_2 = 2.0$, and $\tau = 0.45$ s				
lim I/I_0	0.5064	0.3622	0.2736	0.2124	0.1674
R	0.1931	0.3778	0.5698	0.7615	0.9550
$R/\sum M$	0.1868	0.1889	0.1899	0.1904	0.1910
	$k_1' = 0.05$, $k_2 = 0.5$, and $\tau = 1.8$ s				
lim I/I_0	0.5764	0.4352	0.3445	0.2792	0.2295
R	0.1274	0.2671	0.4101	0.5550	0.7013
$R/\sum M$	0.1274	0.1336	0.1367	0.1388	0.1403

Table VII
Bifunctional Initiator. Perturbed Equilibrium ($\alpha k_i = 1.0$, $\beta k_p = 200$, $k_1 = 0.05$, $k_2 = 0.5$, $\alpha = 0.1$, $I_0 = 0.001$, and $M_0 = 0.1$)

t, s	I/I_0	I^+/I_0	P^+/I_0	P^{2+}/I_0	M/M_0
1	0.9198	0.0491	0.0305	0.0004	0.9974
2	0.8581	0.0568	0.0822	0.0017	0.9853
3	0.8035	0.0562	0.1334	0.0034	0.9623
5	0.7069	0.0522	0.2211	0.0068	0.8874
10	0.5253	0.0476	0.3596	0.0148	0.6094
15	0.4124	0.0483	0.4202	0.0229	0.3458
20	0.3477	0.0508	0.4413	0.0307	0.1732
25	0.3137	0.0533	0.4465	0.0367	0.0807
30	0.2970	0.0549	0.4469	0.0406	0.0362
40	0.2858	0.0563	0.4462	0.0437	0.0070
50	0.2836	0.0566	0.4459	0.0444	0.0013
70	0.2831	0.0566	0.4458	0.0446	4×10^{-6}
100	0.2831	0.0566	0.4458	0.0446	3×10^{-7}

of the bifunctional initiator is equal to $I_0 = I + I^+ + P^+ + P^{2+} + P_2$.

Kinetics of such polymerization is given by the differential equations

$$dI/dt = -2k_1 I + k_2 I^+ \tag{20}$$

$$dI^+/dt = 2k_1 I - (k_2 + k_i M)I^+ \tag{21}$$

$$dP^+/dt = k_i I^+ M + k_2 P^{2+} - k_1 P^+ \tag{22}$$

$$dP^{2+}/dt = k_1 P^+ - (k_2 + k_i M)P^{2+} \tag{23}$$

$$dM/dt = -\{k_i(I^+ + P^+) + k_p(2I_0 - 2I - 2I^+ - P^+ - P^{2+})\}M \tag{24}$$

To compare the results of their solution with those obtained for monofunctional initiators, the I_0 is taken as 0.001 M; i.e., the concentration of the active groups is kept the same as in previous calculations, namely 0.002 mol/L.

The results of computations collected in Table VII illustrate the increasing complexity of the system. They were obtained for relatively long relaxation time, i.e., for large perturbation. The initiator was assumed to be not yet ionized at the onset of polymerization, and hence the concentration of the monoions, I^+, had to be built up during the first 2 s. Thereafter, it abates because the supply, due to ionization of the initiator, diminishes with decreasing initiator concentration. However, at about 10 s after the onset of polymerization the drainage resulting from the reaction with monomer is reduced due to large monomer depletion. This allows for an increase in monoions concentration, which continues with the progress of the reaction until its limiting value is reached. Here is an example of the sophistication of that system.

Comparison of the data of Table VII with those of Table V shows how much slower the polymerization induced by the bifunctional initiator is than that involving a monofunctional one at the same concentration of the initiating groups. The limiting ratio (We are concerned with the fraction of initiator molecules remaining at completion of polymerization and not with the fraction of residual functional groups. Both, the residual I and I^+ are not incorporated into polymers.) $(I + I^+)/I_0 = 0.340$ is lower than that in the monofunctional case—a result justified previously. For five incremental monomer additions (ΔM = 0.1 M) $R = (I + I^+)/I_0 - 1 - \ln (I + I^+)/I_0$ was calculated to be R = 0.3609, 0.6707, 0.9576, 1.2299, 1.4920, respectively, i.e., $R/\sum M$ = 0.3609, 0.3354, 0.3192, 0.3075, 0.2984, indicating again a convex shape of the plot of R vs $\sum M$.

The large degree of perturbation is indicated by the ratios I/I^+ and P^+/P^{2+}. They are 5 and 10, respectively, for equilibrated systems, while the data of Table VII show them to be substantially large at early stages of polymerization. However, they reach the equilibrium values at completion of the reaction when the monomer disappears, as required by theory.

Chain Transfer to the Initiator. Another kind of perturbation of the equilibrium results from the reaction of living polymers with the dormant initiator. This irreversible reaction, although similar to chain transfer to initiator, differs from it considerably. In classic chain transfer a growing polymer is terminated and growth of a new polymer ensues. In systems discussed here the equilibrium between the dormant and active initiators is perturbed, but the growth of the polymers is not terminated because their activity is assumed to be regenerated by BCl_3.

The transfer discussed here involves the dormant initiators only. Hence, it is insignificant at high degrees of ionization, i.e., at concentrations of BCl_3 resulting in K' of 100 or more. Moreover, it should not affect polymerization, or perturb the equilibrium between the ionized and un-ionized initiator, when $(k_1 + k_2)/I_0$ is at least 10 times greater than the effective rate constant βk_{tr}. For a relatively long relaxation time of 2 s and I_0 = 0.002 M the $(k_1 + k_2)/I_0$ amounts to 250. Therefore, a value of βk_{tr} = 200 M^{-1} s^{-1} was chosen in the subsequent computations to ensure substantial perturbation of the ionization equilibrium.

Such computations require modifications of eqs 17–19 when dealing with monofunctional initiator and of eqs 20–24 needed for treatment of bifunctional initiators. A term $k_{tr}(I_0 - I^+ - I_n)I_n$ accounting for the reaction of living polymers with the the dormant initiator has to be added to the right side of eq 17 and subtracted from the right side of eq 19. A similar term $2k_{tr}I(2I_0 - 2I - 2I^+ - P^+ - P^{2+})$ accounting for the reaction of living polymers with the neutral bifunctional initiator has to be subtracted from the right side of eq 20 and added to the right side of eq 21, while the term $k_{tr}P^+(2I_0 - 2I - 2I^+ - P^+ - P^{2+})$ accounting for the reaction of living polymers with the un-ionized initiator's groups attached to the one-arm polymers has to be subtracted from the right side of eq 22 and added to the right side of eq 23.

The results of these computations for a relatively long relaxation time are listed in Table VIII. Its inspection and comparison with the findings obtained for the transfer-free polymerization (see M/M_0's in Tables V and VIII) reveals increasing acceleration of propagation arising from the increase in the concentration of the ionized initiator caused by stronger perturbation of the ionization equilibrium as gauged by the ratio I^+/I_n. Although small at early stages of the reaction, it reaches its stationary value of $(k_1 + \beta k_{tr}(I_0 - \lim (I_n + I_0)))/k_2$ at completion of polymerization. Note, the perturbation resulting from the reaction induced by living polymers affects the I^+/I_n even

Table VIII[a]
Monofunctional Initiator. Effects of Relaxation Time and of Transfer to Initiator ($\alpha = 0.1$, $\alpha k_i = 1.0$, $\beta k_p = 200$, $\beta k_{tr} = 200$, $k_1' = 0.05$, $k_2 = 0.5$, $I_0 = 0.002$, and $M_0 = 0.1$)

t, s	I_n/I_0	I^+/I_0	I^+/I_n	M/M_0
1	0.8838	0.0517	0.058	0.9847
2	0.8354	0.0514	0.061	0.9492
3	0.7779	0.0584	0.075	0.8972
5	0.6496	0.0759	0.117	0.7515
10	0.3687	0.1098	0.298	0.3297
15	0.2432	0.1215	0.498	0.1004
20	0.2062	0.1246	0.602	0.0267
30	0.1941	0.1247	0.641	0.0017
50	0.1933	0.1248	0.645	7×10^{-5}
100	0.1933	0.1248	0.645	

[a] The initial conditions are $I^+/I_0 = 0.0909$ and $I_n/I_0 = 0.9090$; i.e., the ions and the neutral initiator are at equilibrium at the onset of polymerization. For the initial conditions $I_n/I_0 = 1.000$ and $I^+/I_0 = 0.000$ the results at 100 s are $I_n/I_0 = 0.1954$ and $I^+/I_0 = 0.1257$, a minute difference from the previous fittings.

after cessetion of polymerization, contrary to the perturbation caused by the initiation.

Let it be stressed that all these large perturbations of ionization equilibrium and the appreciable acceleration of propagation result not only from the large magnitude of k_{tr} but more substantially from the long relaxation time of the ionization process. Computations with the same value of k_{tr} but performed for a relaxation time of 0.09 s show only small changes in the rates of propagation and in the I^+/I_n as seen from the data listed below:

t (s) after the onset of polymerizn		5	10	20
no transfer	M/M_0	0.700	0.319	0.044
$\beta k_{tr} = 200$		0.699	0.307	0.039
no transfer	I^+/I_n	0.094	0.097	0.100
$\beta k_{tr} = 200$		0.106	0.115	0.121

These remarks become more significant on inspection of Table IX, summarizing the results of incremental monomer addition. For short relaxation times and even for the large βk_{tr} of 200 the diagnostic $R/\sum M$ remains constant on consecutive monomer increments; i.e., the plot of R vs $\sum M$ is virtually linear, while it is strongly concave for the longer relaxation time of 1.8 s.

Examination of polymerization induced by bifunctional initiators shows the previously noted features. Consumption of monomer is somewhat slower than in the monofunctional case while incorporation of the initiator into the polymer is faster. The tendency for a convex plot of R vs $\sum M$ is reduced by participation of the transfer in the overall process. In fact, for the standard conditions used in this work such a plot is convex for a relaxation time of 0.09 s but concave for a time of 1.8 s. This is shown by the data listed in Table X.

Hypothetical Autoaccelerated Polymerization. Some workers in the field expected autoaccelerated polymerization arising from chain transfer to initiator and formation of a new living polymer without terminating the previous one. No system exhibiting this behavior has been described in the literature. Nevertheless, let us consider its hypothetical kinetics. The expected scheme involves the steps

$$\mathrm{I} + \mathrm{M} \rightarrow \mathrm{P}, \quad k_i$$

$$\mathrm{P} + \mathrm{M} \rightarrow \mathrm{P}, \quad k_p$$

$$\mathrm{P} + \mathrm{I} \rightarrow 2\mathrm{P}, \quad k_{tr}$$

The last step leads to ultimate consumption of the initiator; even after cessation of polymerization the initiator continues to be consumed. Provided that the time between consecutive monomer additions is sufficiently long, virtually all the initiator disappears after the first incremental monomer addition, and thereafter subsequent additions lead to conventional living polymer propagation. Accepting the rate constants and initial conditions used in the previous calculations, one finds by numerical computations only minor effects on the rate of monomer consumptions for k_{tr} not exceeding 20% of k_p.

Table IX[a]
Monofunctional Initiator. Effects of Relaxation Time for Polymerization Perturbed by Transfer to Initiator ($\alpha = 0.1$, $\alpha k_i = 1.0$, $\beta k_p = 200$, $\beta k_{tr} = 200$, $I_0 = 0.002$, and $M_0 = 0.1$)

increments	lim $(I_n + I^+)/I_0$	lim I_n/I^+	R	$R/\sum M$
	$k_1' = 2$, $k_2 = 20$, and $\tau = 0.045$ s			
1st	0.4610	9.03	0.2354	0.2354
2nd	0.3095	8.78	0.4824	0.2412
3rd	0.2200	8.65	0.7343	0.2448
4th	0.1606	8.56	0.9892	0.2473
5th	0.1192	8.50	1.241	0.2481
	$k_1' = 1$, $k_2 = 10$, and $\tau = 0.091$ s			
1st	0.4254	8.19	0.2456	0.2456
2nd	0.2963	7.80	0.5127	0.2564
3rd	0.2051	7.61	0.7894	0.2631
4th	0.1457	7.47	1.072	0.2680
5th	0.1051	7.37	1.358	0.2717
	$k_1' = 0.2$, $k_2 = 2.0$, and $\tau = 0.45$ s			
1st	0.4007	4.55	0.3152	0.3152
2nd	0.2206	3.91	0.7319	0.3659
3rd	0.1271	3.64	1.1902	0.3967
4th	0.0746	3.51	1.6706	0.4177
5th	0.0442	3.43	2.1634	0.4327
	$k_1' = 0.05$, $k_2 = 0.5$, and $\tau = 1.8$ s			
1st	0.3211	1.55	0.4572	0.4572
2nd	0.1171	1.24	1.262	0.6307
3rd	0.0439	1.16	2.171	0.7235
4th	0.0166	1.13	3.116	0.7789
5th	0.0063	1.11	4.073	0.8147

[a] In these computations the initial values of I_0 and I_0^+ are taken as 0.002 and 0.0, respectively; i.e., the equilibrium was not established at the onset of polymerization. For equilibrium established at the onset of polymerization, i.e., for $I_0 = 0.001\,818$ and $I_0^+ = 0.000\,18\,8$, negligibly different results are derived; e.g., for the most perturbed run ($k_1 = 0.05$ and $k_2 = 0.5$) the following values were obtained; namely, 0.3181 for the limiting $(I + I^+)/I_0$, 1.55 for I/I^+, and 0.4635 for R, all pertaining to completion of polymerization after the first monomer addition. The deviations are even smaller in the subsequent increments.

Concluding Remarks

The computations presented in this paper provide answers to some questions concerning the system investigated here.

(1) How does the incremental monomer addition affect the outcome of living polymerization resulting from initiation and propagation, which are first order in monomer? It was shown earlier[5] that this mode of monomer addition does not affect the outcome of polymerization nor the molecular weight distribution of the resulting polymer for a constant total amount of added monomer, provided that all the species participating in the process are in equilibrium with each other and that the properties of the medium in which polymerization takes place remain constant and not changed by each incremental monomer addition. These conclusions are confirmed by the computations and remain valid even in polymerization induced by bifunctional initiator for which ionization of one functional group renders the other inactive until monomer is added to the former one. Although such a system behaves in a complex manner, the mode of monomer addition still does not affect the process.

Table X
Bifunctional Initiator. Polymerization Affected by the Transfer ($\alpha = 0.1$, $\alpha k_i = 1.0$, $\beta k_p = 200$, $\beta k_{tr} = 200$, $I_0 = 0.0025$, $M_0 = 0.1$)

no. of increments	I	I^+	P^+	P^{2+}	$(I + I^+)/I_0$	R	$R/\sum M$
			$k_1 = 1.0\ \mathrm{s}^{-1}$ and $k_2 = 10\ \mathrm{s}^{-1}$				
1st	0.7675	0.2117	1.0077	0.1584	0.3916	0.3291	0.3291
2nd	0.4642	0.1409	1.0437	0.1584	0.2421	0.6606	0.3303
3rd	0.3044	0.0981	0.9783	0.1577	0.1610	0.9872	0.3290
4th	0.2079	0.0699	0.8844	0.1488	0.1111	1.3082	0.3271
5th	0.1455	0.0506	0.7852	0.1364	0.0784	1.624	0.3248
			$k_1 = 0.05\ \mathrm{s}^{-1}$ and $k_2 = 0.5\ \mathrm{s}^{-1}$				
1st	0.1896	0.4269	0.5658	0.6369	0.2466	0.6466	0.6466
2nd	0.0519	0.1642	0.3336	0.5279	0.0864	1.5347	0.7673
3rd	0.0188	0.0683	0.1876	0.3413	0.0348	2.3918	0.7972
4th	0.0076	0.0297	0.1055	0.2053	0.0149	3.220	0.8049

On the other hand, perturbation of the equilibria makes the outcome of polymerization dependent on the mode of monomer addition. Ionization of the functional groups is the subject of perturbation; propagation is treated here as irreversible. Two processes might perturb the ionization equilibrium: the reaction of monomer with the ionized functional groups of initiator or the reaction of living polymers with the initiator's un-ionized groups. The degree of perturbation depends on the relaxation time of ionization and on the rates of the perturbing reactions. To appreciate the problem, consider the results obtained under the conditions described in Table IX.

A rapid reaction of living polymers with un-ionized functional groups of initiator proceeds with a rate constant βk_{tr} assumed to be equal to propagation constant $\beta k_p = 200\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. For a relaxation time of ionization of 0.1 s the fraction of residual initiator left at the end of polymerization of 300 mM of monomer is 0.224, and the ratio I_n/I^+ is 7.62 at that stage. The same polymerization when performed through three incremental additions of 100 mM of monomer leaves 0.205 of initiator unused and the ratio $I_n/I^+ = 7.61$. The respective fractions in batch polymerization of 500 mM of monomer or five increments of 100 mM each are 0.130 and 0.105, and the corresponding ratios of I_n/I^+ are equal to 7.42 and 7.37. However, under otherwise identical conditions but for a longer relaxation time of 1.8 s the results of incremental polymerization differ substantially from those of the batch process. Thus while 4% of initiator is left after three incremental additions of 100 mM of monomer, batch polymerization of 300 mM leaves 21% unutilized. Examination of such data shows progressively greater utilization of initiator in the incremental mode of monomer addition, relative to the batch process, as the relaxation time of ionization becomes longer.

It is instructive to compare the contributions of the transfer and of the spontaneous ionization to generation of the ionic species. Under conditions given in Table IX and for the relaxation time of 0.1 s the reaction of living polymers with initiator contributes only 23% to formation of the ionic species, whereas 77% is contributed by the spontaneous ionization. For a relaxation time of 1.8 s the situation is reversed; the respective contributions are 88% and 12%. The length of relaxation time is a decisive factor.

The above discussion brings us to the next question: how important is the reaction of living polymers with the initiator (chain transfer to initiator) in preparation of telechelic polymers? Such a reaction is precluded when the initiator is fully ionized. Nevertheless, telechelic polymer could be formed when the initiator is bifunctional. Again, such transfer does not affect polymerization when the relaxation time of ionization is sufficiently short, but this does not prevent formation of telechelic polymers by bifunctional initiator. Indeed, it is the bifunctionality of the initiator that is necessary for formation of telechelic polymers; the transfer is rather incidental. It speeds up polymerization when relaxation time of ionization is long, perturbs the ionic equilibrium, and increases the momentary concentration of ionic species. Under such conditions there is some acceleration of polymerization arising from an increase in the concentration of living polymers but it is not the kind of autoacceleration that might lead to uncontrollable reaction. Its participation in the process could be detected by detailed examination of kinetics of the overall polymerization, but not by studies of structure of the resulting polymers. The latter is not affected by the transfer to initiator.

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