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A Kinetic Theory on Cationic Polymerization with Termination by Combination with a Negative Fragment

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ABSTRACT: The cationic polymerization with instantaneous initiation and termination by combination with a negative fragment, which is the product formed during initiation reaction with some component of the polymerization system, has been studied by means of a non-steady-state method. The molecular weight distribution function and a series of important molecular parameters of the polymer generated from mono-, bi-, and multifunctional initiators are rigorously derived. The theoretical results obtained are applicable to any ionic polymerization with second-order termination. A procedure is described for calculating the molecular weight distribution curve and the values of the various molecular parameters directly from the polymerization conditions.

Introduction

As we know, chain termination has an important effect upon the molecular weight distribution and other molecular parameters of the polymer formed in a polymerization system. Important work on chain termination has been done by Overberger,[1] Pepper,[2] Plesch,[3] and Szwarc,[4] etc. Generally speaking, chain termination is second order with respect to the propagating chains in free radical polymerization but first order with respect to the growing chains in ionic polymerization. The reason for this is that initiation of ionic polymerization usually leads to ion pairs, and termination arising from collapse of an ion pair is a first-order reaction. Formation of the free ions is feasible only if their combination into inactive product does not take place at every collision; otherwise the two oppositely charged species have no chance to separate after being formed. The termination in systems involving free ions is, of course, a second-order reaction.[3,4] There are, indeed, several cationic polymerization systems with termination involving counterions, such as the polymerization of the oxetane initiated by $SnCl_4$,[6] etc. It has also been reported that in a few sufficiently pure cationic polymerization systems, in which concentrations of water and other terminating agents are less than 10^{-7}–10^{-10} mol/L, termination of a propagating cationic chain occurs by combination with a negative fragment Y^-. Y^- is formed during an initiation reaction.[7-11]

$$...M^+ + Y^- \xrightarrow{k_t} ...M\text{-}Y$$

For many ionic polymerization systems with termination and transfer, such as monomer transfer,[12-19] monomer termination,[20-22] spontaneous termination,[22,23] impurity termination,[25,26] impurity transfer,[27] spontaneous transfer,[28] etc., the influences of termination and transfer on molecular weight distributions of the resultant polymers have been theoretically studied by means of non-steady-state analysis. For cationic polymerization systems with termination by combination with a negative fragment, the concentration of which is equal to that of the propagating species, $\sum N_n^+$, i.e., $Y^- = \sum N_n^+$, the termination rate should be

$$R_t = k_t(Y^-)\sum N_n^+ = k_t(\sum N_n^+)^2 \qquad (1)$$

if other terminations are absent.[3,4,7] Such a case is quite

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different from the usual ionic polymerization in that termination rate is second order in the growing chains. The second-order dependence is then the same as observed in free-radical chain polymerization.[29,30] In this paper, we tackle this problem and derive the expressions for the molecule weight distribution function and some important molecular parameters of the resultant polymer.

For cationic polymerization, there have been a number of reports on polymerization systems initiated by bifunctional and multifunctional initiators or polymer chains possessing active groups[8,31-35] in addition to those initiated by monofunctional initiators. It is therefore also important to explore the cases of bifunctional and multifunctional cationic polymerizations with counteranion termination.

Theory

I. Case of Monofunctional Initiation. In the following, I, M, N_n^+, and N_n' represent the concentrations of the initiator, monomer, growing n-mer, and terminated n-mer, respectively, and k_p and k_t are the rate constants for chain propagation and for chain termination. In order to simplify the mathematical derivation, initiation is assumed to be instantaneous. For polymerization with instantaneous initiation and termination by combination with a negative fragment, the chemical equations may be written as

$$I + M \xrightarrow{\text{fast}} N_1^+ + Y^-$$

$$N^+_{n-1} + M \xrightarrow{k_p} N_n^+ \qquad (n \geq 2)$$

$$N_n^+ + Y^- \xrightarrow{k_t} N_n' \qquad (n \geq 1)$$

The corresponding kinetic differential equations are as follows:

$$dN_1^+/dt = -k_p M N_1^+ - k_t Y^- N_1^+ \tag{2}$$

$$dN_n^+/dt = k_p M(N_{n-1}^+ - N_n^+) - k_t Y^- N_n^+ \qquad (n \geq 2) \tag{3}$$

$$dN_n'/dt = k_t Y^- N_n^+ \qquad (n \geq 1) \tag{4}$$

$$dM/dt = -k_p M \sum_{n=1}^{\infty} N_n^+ \tag{5}$$

$$d\sum_{n=1}^{\infty} N_n^+/dt = -k_t Y^- \sum_{n=1}^{\infty} N_n^+ \tag{6}$$

The initial conditions are

$$N_1^+|_{t=0} = I_0 \qquad Y^-|_{t=0} = I_0 \qquad N_{n\geq 2}^+|_{t=0} = 0$$
$$N_n'|_{t=0} = 0 \qquad M|_{t=0} = M_0 - I_0$$

where I_0 and M_0 are respectively the initial concentrations of initiator and monomer added to the polymerization system. Introducing a parametric variable x,

$$x = k_p \int_0^t \sum_{n=1}^{\infty} N_n^+ \, dt \tag{7}$$

or

$$dx/dt = k_p \sum_{n=1}^{\infty} N_n^+ \tag{8}$$

and putting $a = k_t/k_p$, $K = (M_0 - I_0)/I_0$, and $Y^- = \sum_{n=1}^{\infty} N_n^+$, we get from eq 5 and 6

$$M = (M_0 - I_0)e^{-x} \tag{9}$$

$$\sum_{n=1}^{\infty} N_n^+ = I_0 e^{-ax} \tag{10}$$

Further, by the above relationships, eq 2–4 can be easily transformed into a set of differential equations

$$dN_1^+/dx = -(a - Ke^{(a-1)x})N_1^+ \tag{11}$$

$$dN_n^+/dx = Ke^{(a-1)x}N_{n-1}^+ - (a + Ke^{(a-1)x})N_n^+ \qquad (n \geq 2) \tag{12}$$

$$dN_n'/dx = aN_n^+ \qquad (n \geq 1) \tag{13}$$

which are identical with those of free radical polymerization with termination by disproportionation.[29] Thus, the molecular weight distribution functions for the growing and terminated chains are the same as those reported, i.e.,

$$N_n^+ = \frac{I_0}{(n-1)!}\left(\frac{K}{a-1}(e^{(a-1)x} - 1)\right)^{n-1} \times \exp\left[-ax + \frac{K}{a-1}(1 - e^{(a-1)x})\right] \tag{14}$$

$$N_n' = \frac{aI_0}{(n-1)!}\left(\frac{K}{a-1}\right)^{n-1} \int_0^x (e^{(a-1)x} - 1)^{n-1} \times \exp\left[-ax + \frac{K}{a-1}(1 - e^{(a-1)x})\right] dx \tag{15}$$

and all the other molecular parameters, such as number- and weight-average degrees of polymerization and their ratio etc., have the identical expressions given in our previous paper.[29] If monomer chain transfer occurs in the cationic polymerization treated here, the molecular weight distribution and other molecular parameters of the resulting polymer could be derived, which are the same as those given in the paper[30] in which we studied the free radical polymerization with disproportionation termination and monomer chain transfer. All the formulas listed could be directly used without any change. Therefore, in this paper, we study mainly the polymerization systems initiated by bifunctional and multifunctional initiators.

II. Case of Bifunctional Initiation. Now, we shall carry out most of the relevant derivations in detail for the cationic polymerizations initiated by a bifunctional initiator, in which termination by combination with a negative fragment occurs. We adopt the following nomenclature for polymers with different functionalties: N_n^{2+}, bifunctional n-mer, in which both sites are active; N_n^+, monofunctional n-mer, in which one of the propagating sites has been terminated; and N_n', n-mer with no propagating sites, i.e., both of the propagating sites have been terminated. The chemical equations are as follows:

$$I + M \xrightarrow{\text{fast}} N^{2+} + 2Y^-$$

$$N_{n-1}^{2+} + M \xrightarrow{2k_p} N_n^{2+} \qquad (n \geq 3)$$

$$N_n^{2+} + Y^- \xrightarrow{2k_t} N_n' \qquad (n \geq 2)$$

$$N_{n-1}^+ + M \xrightarrow{k_p} N_n^+ \qquad (n \geq 3)$$

$$N_n^+ + Y^- \xrightarrow{k_t} N_n' \qquad (n \geq 2)$$

The kinetic differential equations derived from the above reaction scheme are

$$dN_2^{2+}/dt = -2k_p M N_2^{2+} - 2k_t Y^- N_2^{2+} \tag{16}$$

$$dN_n^{2+}/dt = 2k_p M(N_{n-1}^{2+} - N_n^{2+}) - 2k_t Y^- N_n^{2+} \qquad (n \geq 3) \tag{17}$$

$$dN_2^+/dt = -k_p M N_2^+ + 2k_t Y^- N_2^{2+} - k_t Y^- N_2^+ \tag{18}$$

$$\mathrm{d}N_n^+/\mathrm{d}t = k_pM(N_{n-1}^+ - N_n^+) + 2k_tY^-N_n^{2+} - k_tY^-N_n^+ \qquad (n \geq 3) \tag{19}$$

$$\mathrm{d}N_n'/\mathrm{d}t = k_tY^-N_n^+ \qquad (n \geq 2) \tag{20}$$

$$\mathrm{d}M/\mathrm{d}t = -k_pM(2\sum_{n=2}^{\infty}N_n^{2+} + \sum_{n=2}^{\infty}N_n^+) \tag{21}$$

where the concentration of the counteranion Y^- is identical with the total concentration of the propagating sites, that is,

$$Y^- = 2\sum_{n=2}^{\infty}N_n^{2+} + \sum_{n=2}^{\infty}N_n^+ \tag{22}$$

The corresponding initial conditions are as follows:

$$N_2^{2+}|_{t=0} = I_0 \qquad N_{n\geq3}^{2+}|_{t=0} = 0 \qquad N_n^+|_{t=0} = 0$$
$$N_n'|_{t=0} = 0 \qquad M|_{t=0} = M_0 - 2I_0 \qquad Y^-|_{t=0} = 2I_0$$

From eq 16 and 17, we obtain

$$\mathrm{d}\sum_{n=2}^{\infty}N_n^{2+}/\mathrm{d}t = -2k_tY^-\sum_{n=2}^{\infty}N_n^{2+} \tag{23}$$

Similarly, from eq 4 and 5, we get,

$$\mathrm{d}\sum_{n=2}^{\infty}N_n^+/\mathrm{d}t = 2k_tY^-\sum_{n=2}^{\infty}N_n^{2+} - k_tY^-\sum_{n=2}^{\infty}N_n^+ \tag{24}$$

Putting

$$x = k_p\int_0^t Y^-\,\mathrm{d}t \tag{25}$$

or

$$\mathrm{d}x/\mathrm{d}t = k_pY^- \tag{26}$$

Equations 21, 23, and 24 can be transformed as follows:

$$\mathrm{d}M/\mathrm{d}x = -M \tag{27}$$

$$\mathrm{d}\sum_{n=2}^{\infty}N_n^{2+}/\mathrm{d}x = -2a\sum_{n=2}^{\infty}N_n^{2+} \tag{28}$$

$$\mathrm{d}\sum_{n=2}^{\infty}N_n^+/\mathrm{d}x = 2a\sum_{n=2}^{\infty}N_n^{2+} - a\sum_{n=2}^{\infty}N_n^+ \tag{29}$$

Solving eq 27–29 and setting the initial conditions

$$M|_{x=0} = M_0 - 2I_0 \qquad \sum_{n=2}^{\infty}N_n^{2+}|_{x=0} = I_0 \qquad \sum_{n=2}^{\infty}N_n^+|_{x=0} = 0$$

we get

$$M = (M_0 - 2I_0)e^{-x} \tag{30}$$

$$\sum_{n=2}^{\infty}N_n^{2+} = I_0e^{-2ax} \tag{31}$$

$$\sum_{n=2}^{\infty}N_n^+ = 2I_0e^{-ax}(1 - e^{-ax}) \tag{32}$$

From eq 31 and 32, we obtain the expression for the concentration of the negative fragments

$$Y^- = 2I_0e^{-ax} \tag{33}$$

Obviously,

$$M/Y^- = K_2e^{(a-1)x} \tag{34}$$

where, $K_2 = (M_0 - 2I_0)/2I_0$. By means of the above results, it is easy to change eq 16–20 into a set of linear differential equations which can be solved:

$$\mathrm{d}N_2^{2+}/\mathrm{d}x = -2K_2e^{(a-1)x}N_2^{2+} - 2aN_2^{2+} \tag{35}$$

$$\mathrm{d}N_n^{2+}/\mathrm{d}x = 2K_2e^{(a-1)x}N_{n-1}^{2+} - 2(a + K_2e^{(a-1)x})N_n^{2+} \qquad (n \geq 3) \tag{36}$$

$$\mathrm{d}N_2^+/\mathrm{d}x = 2aN_2^{2+} - (a + K_2e^{(a-1)x})N_2^{2+} \tag{37}$$

$$\mathrm{d}N_n^+/\mathrm{d}x = K_2e^{(a-1)x}N_{n-1}^+ + 2aN_n^{2+} - (a + K_2e^{(a-1)x})N_n^+ \qquad (n \geq 3) \tag{38}$$

$$\mathrm{d}N_n'/\mathrm{d}x = aN_n^+ \qquad (n \geq 2) \tag{39}$$

The corresponding initial conditions become

$$N_2^{2+}|_{x=0} = I_0$$
$$N_{n\geq3}^{2+}|_{x=0} = N_n^+|_{x=0} = N_n'|_{x=0} = 0$$

From eq 35 and 36, the molecular weight distribution function for the polymer with two propagating sites is derived.

$$N_n^{2+} = I_0\frac{(2U)^{n-2}}{(n-2)!}\exp(-2ax - 2U) \tag{40}$$

where

$$U = \frac{K_2}{a-1}(e^{(a-1)x} - 1) \tag{41}$$

Inserting eq 40 into eq 37 and 38, we obtain the molecular weight distribution function for the polymer with one propagating site and one terminated site.

$$N_n^+ = \frac{2aI_0e^{-ax-U}}{(n-2)!}\sum_{i=0}^{n-2}\binom{n-2}{i}U^{n-i-2}\int_0^x U^ie^{-ax-U}\,\mathrm{d}x \tag{42}$$

Furthermore, the molecular weight distribution function for the terminated polymer is deduced.

$$N_n' = \frac{2a^2I_0}{(n-2)!}\sum_{i=0}^{n-2}\binom{n-2}{i}\int_0^x\left(U^{n-i-2}e^{-ax-U}\int_0^x U^ie^{-ax-U}\,\mathrm{d}x\right)\mathrm{d}x \tag{43}$$

Evidently, the molecular weight distribution functions for the total system is

$$N_n = N_n^{2+} + N_n^+ + N_n' \tag{44}$$

The above molecular weight distribution functions for different kinds of polymer chains are derived in the case of $a \neq 1$ or $k_t \neq k_p$. If $a = 1$, the method of derivation of the molecular weight distribution functions is identical with that given in the previous papers.[29,30] Since there is a limit,

$$\lim_{a\to1} U = K_2x \tag{45}$$

substituting K_2x for U in the above formulas yields the molecular weight distribution functions that are suitable for the case of $a = 1$.

For eq 40 and 42, we find the first-order statistical moments of N_n^{2+} and N_n^+:

$$\sum_{n=2}^{\infty}nN_n^{2+} = 2I_0e^{-2ax}\left[1 + \frac{K_2}{a-1}(e^{(a-1)x} - 1)\right] \tag{46}$$

$$\sum_{n=2}^{\infty}nN_n^+ = 2I_0e^{-ax}\left[2 + K_2 - \frac{K_2}{a-1} + 2\left(\frac{K_2}{a-1} - 1\right)^{-ax} + \frac{(a+1)K_2e^{-x}}{a-1} + \frac{K_2e^{(a-1)x}}{a-1}\right] \tag{47}$$

The various statistical moments of the terminated polymers formed in the reaction system may easily be derived by the aid of the following equation:

$$\sum_{n=2}^{\infty} n^s N_n' = a \int_0^x \sum_{n=2}^{\infty} n^s N_n^+ \, dx \qquad s = 0, 1, 2 \tag{48}$$

Consequently, we have

$$\sum_{n=2}^{\infty} N_n' = I_0(1 - e^{-ax})^2 \tag{49}$$

$$\sum_{n=2}^{\infty} n N_n' = 2I_0\left[1 + K_2 - e^{-ax}\left[2 + K_2 - \frac{K_2}{a-1} + \left(\frac{K_2}{a-1} - 1\right)e^{-ax} - \frac{aK_2}{a-1}(e^{-x} - e^{(a-1)x})\right]\right] \tag{50}$$

From the above formulas, the moments of the total polymers formed in the reaction system are derived.

$$\sum_{n=2}^{\infty} N_n = I_0 \tag{51}$$

$$\sum_{n=2}^{\infty} n N_n = 2I_0(1 + K_2 - K_2 e^{-x}) \tag{52}$$

Equations 51 and 52 are in accord with the following constraint conditions:

$$\sum_{n=2}^{\infty} (N_n^{2+} + N_n^+ + N_n') = I_0 \tag{53}$$

$$\sum_{n=2}^{\infty} n(N_n^{2+} + N_n^+ + N_n') = M_0 - M \tag{54}$$

which demonstrate that the results obtained are correct. Though we could also derive the second-order statistical moments of N_n^{2+}, N_n^+, and N_n', we need only that of the total polymers. Equations 35–39 result in the following equation:

$$\mathrm{d}\sum_{n=2}^{\infty} n^2 N_n/\mathrm{d}x = K_2 e^{(a-1)x}\left[2\sum_{n=2}^{\infty} (2n + 1)N_n^{2+} + \sum_{n=2}^{\infty} (2n + 1)N_n^+\right] \tag{55}$$

It is easy to get

$$\mathrm{d}\sum_{n=2}^{\infty} n^2 N_n/\mathrm{d}x = 2I_0\left[2 + K_2\left[\left(5 + 2K_2 - \frac{2K_2}{a-1}\right) \times (1 - e^{-x}) + \frac{2K_2}{(a-1)(a-2)}(e^{(a-2)x} - 1) + K_2(e^{-2x} - 1)\right]\right] \tag{56}$$

Hence, the number- and weight-average degrees of polymerization of the total polymers formed in the reaction system are respectively

$$\bar{P}_n = 2[1 + K_2(1 - e^{-x})] \tag{57}$$

$$\bar{P}_\mathrm{w} = \left[2 + K_2\left[\left(5 + K_2 - \frac{2K_2}{a-1}\right)(1 - e^{-x}) + K_2(e^{-2x} - 1) + \frac{2K_2}{(a-1)(a-2)}(e^{(a-2)x} - 1)\right]\right] \Big/ [1 + K_2(1 - e^{-x})] \tag{58}$$

The respective molecular fractions of polymer chains with two propagating sites, one propagating site, and no propagating site are as follows:

$$f_n^{2+} = e^{-2ax} \tag{59}$$

$$f_n^+ = 2e^{-ax}(1 - e^{-ax}) \tag{60}$$

$$f_n' = 1 - f_n^{2+} - f_n^+ \tag{61}$$

Table I
Several Molecular Parameters for $a = 1$ and $a = 2$

cases	params	expressions
$a = 1$	$\bar{P}_\mathrm{w}$	$[2 + K_2[(5 + 2K_2)(1 - e^{-x}) + K_2[1 + e^{-x}(e^{-x} - 1 - x)]]]/[1 + K_2(1 - e^{-x})]$
	f_w^{2+}	$(1 + K_2 x)/[[1 + K_2(1 - e^{-x})]e^{2x}]$
	f_w^+	$[K_2(1 + x) + 2(1 - e^{-x}) - K_2 e^{-x}(1 + 2x)]/[[1 + K_2(1 - e^{-x})]e^{-x}]$
$a = 2$	$\bar{P}_\mathrm{w}$	$[2 + K_2[5(1 - e^{-x}) + K_2(e^{-2x} - 1) + 2K_2 x]]/[1 + K_2(1 - e^{-x})]$

These equations represent the functionality distribution of the polymers generated. The average functionality is

$$\bar{r} = 2e^{-ax} \tag{62}$$

The respective weight fractions of the above three kinds of polymer chains are

$$f_\mathrm{w}^{2+} = \frac{1 + \dfrac{K_2}{a-1}(e^{(a-1)x} - 1)}{[1 + K_2(1 - e^{-x})]e^{2ax}} \tag{63}$$

$$f_\mathrm{w}^+ = \left[2 + K_2 - \frac{K_2}{a-1} + 2\left(\frac{K_2}{a-1} - 1\right)e^{-ax} - \frac{a+1}{a-1}K_2 e^{-x} + \frac{K_2}{a-1}e^{(a-1)x}\right] \Big/ [[1 + K_2(1 - e^{-x})]e^{-ax}] \tag{64}$$

$$f_n' = 1 - f_\mathrm{w}^{2+} - f_\mathrm{w}^+ \tag{65}$$

When $a = 1$ or $a = 2$, the aforementioned statistical moments can no longer be used, since both the numerator and denominator in the formulas are equal to zero. Therefore, the expressions for $\bar{P}_\mathrm{w}$, f_w^{2+}, f_w^+, etc. need to be derived according to L'Hospital's rule.[36] The results are listed in Table I.

III. Case of Multifunctional Initiation. The cationic polymerization with termination by combination with a negative fragment has been treated for both monofunctional and bifunctional initiations. It is of interest to extent the aforementioned treatment to that initiated by a multifunctional initiator, and derive the expressions for some important molecular parameters. In the following derivation, we designate the functionality of initiator as f and the concentration of the species with r growing sites, i.e., $f - r$ growing sites have been terminated, and n monomer units as $N_n^{(r)}$. Because the initiation is assumed to be accomplished instantaneously, the reaction scheme of the multifunctional cationic polymerization with termination by combination with a negative fragment can be extracted from Figure 1.

The set of kinetic equations corresponding to this reaction scheme is as follows:

$$\mathrm{d}N_f^{(f)}/\mathrm{d}t = -fk_\mathrm{p}MN_f^{(f)} - fk_\mathrm{t}Y^-N_f^{(f)} \tag{66}$$

$$\mathrm{d}N_n^{(f)}/\mathrm{d}t = fk_\mathrm{p}M(N_{n-1}^{(f)} - N_n^{(f)}) - fk_\mathrm{t}Y^-N_n^{(f)} \qquad (n \geq f + 1) \tag{67}$$

$$\mathrm{d}N_f^{(r)}/\mathrm{d}t = -rk_\mathrm{p}MN_f^{(r)} + (r + 1)k_\mathrm{t}Y^-N_f^{(r+1)} - rk_\mathrm{t}Y^-N_f^{(r)} \qquad (0 \leq r \leq f - 1) \tag{68}$$

$$\mathrm{d}N_n^{(r)}/\mathrm{d}t = rk_\mathrm{p}M(N_{n-1}^{(r)} - N_n^{(r)}) + (r + 1)k_\mathrm{t}Y^-N_n^{(r+1)} - rk_\mathrm{t}Y^-N_n^{(r)} \qquad (n \geq f + 1, 0 \leq r \leq f - 1) \tag{69}$$

$$\sum_{n=f}^{\infty} N_n^{(f)}/\mathrm{d}t = -fk_\mathrm{t}Y^- \sum_{n=f}^{\infty} N_n^{(f)} \tag{70}$$

$$\sum_{n=f}^{\infty} N_n^{(\gamma)}/\mathrm{d}t = (r+1)k_\mathrm{t}Y^- \sum_{n=f}^{\infty} N_n^{(\gamma+1)} - rk_\mathrm{t}Y^- \sum_{n=f}^{\infty} N_n^{(\gamma)} \qquad (0 \le r \le f-1) \quad (71)$$

$$\mathrm{d}M/\mathrm{d}t = -k_\mathrm{p}M\sum_{r=1}^{f} r \sum_{n=f}^{\infty} N_n^{(r)} \qquad (72)$$

The initial conditions of these differential equations are

$$N_f^{(f)}|_{t=0} = I_0 \qquad M|_{t=0} = M_0 - fI_0 \qquad N_n^{(r)}|_{t=0} = 0$$
$$(0 \le r \le f,\ r \neq f)$$

It is obvious that the polymerization system must undergo the following conservative condition:

$$Y^- = \sum_{r=1}^{f} r \sum_{n=f}^{\infty} N_n^{(r)} \qquad (73)$$

By the aid of eq 25 and the above derivation method, we can obtain the following results from eq 70–73:

$$Y^- = fI_0e^{-ax} \qquad (74)$$

$$M = (M_0 - fI_0)e^{-x} \qquad (75)$$

Then, eq 66–69 can be transformed into the following:

$$\mathrm{d}N_f^{(f)}/\mathrm{d}x = -f(a + K_fe^{(a-1)x})N_f^{(f)} \qquad (76)$$

$$\mathrm{d}N_n^{(f)}/\mathrm{d}x = fK_fe^{(a-1)x}N_{n-1}^{(f)} - f(a + K_fe^{(a-1)x})N_n^{(f)} \qquad (n \ge f+1) \quad (77)$$

$$\mathrm{d}N_f^{(r)}/\mathrm{d}x = -r(a + K_fe^{(a-1)x})N_f^{(r)} + a(r+1)N_f^{(r+1)} \qquad (0 \le r \le f-1) \quad (78)$$

$$\frac{\mathrm{d}N_n^{(r)}}{\mathrm{d}x} = rK_fe^{(a-1)x}N_{n-1}^{(r)} - r(a + K_fe^{(a-1)x})N_n^{(r)} + a(r+1)N_n^{(r+1)} \qquad (n \ge f+1,\ 0 \le r \le f-1) \quad (79)$$

where $K_f = (M_0 - fI_0)/fI_0$. The corresponding initial conditions are

$$N_f^{(f)}|_{x=0} = I_0 \qquad N_n^{(r)}|_{x=0} = 0 \qquad (0 \le r \le f,\ n \ge f)$$

From the theoretical point of view, a general expression for $N_n^{(r)}$ could be derived by solving the above set of differential equations, but the derivation and the results would be rather complicated. Even so, we can still obtain some statistical moments of the polymer formed.

Equations 78 and 79 result in

$$\mathrm{d}\sum_{n=f}^{\infty} N_n^{(r)}/\mathrm{d}x = a(r+1)\sum_{n=f}^{\infty} N_n^{(r+1)} - ar\sum_{n=f}^{\infty} N_n^{(r)} \qquad (0 \le r \le f-1) \quad (80)$$

By means of eq 76, 77, and 80, the following moment is deduced:

$$\sum_{n=f}^{\infty} N_n^{(r)} = I_0\binom{f}{r}e^{-rax}(1 - e^{-ax})^{f-r} \qquad (0 \le r \le f) \quad (81)$$

From eq 59–62, we obtain

$$\mathrm{d}\sum_{n=f}^{\infty} n^sN_n/\mathrm{d}x = K_fe^{(a-1)x}\sum_{r=0}^{f} r \sum_{n=f+1}^{\infty} n^sN_{n-1}^{(r+1)} - (a + K_fe^{(a-1)x})\sum_{r=0}^{\infty} r \sum_{n=f}^{\infty} n^sN_n^{(r)} + a\sum_{r=0}^{f-1}(r+1)\sum_{n=f}^{\infty} n^sN_n^{(r+1)} \qquad (s = 0, 1, 2) \quad (82)$$

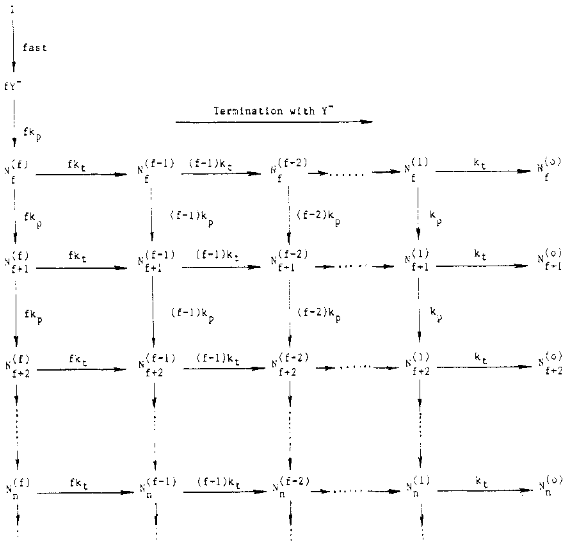

Figure 1. Reaction scheme of multifunctional cationic polymerization with termination by combination with a negative fragment which is either a solvated electron or the product of the displaced electron formed during initiation reaction with some component of the reaction system.

The statistical moments of the total polymers formed in the reaction system may be derived from eq 82. They are

$$\sum_{n=f}^{\infty} N_n = I_0 \qquad (83)$$

$$\sum_{n=f}^{\infty} nN_n = fI_0[1 + K_f(1 - e^{-x})] \qquad (84)$$

$$\sum_{n=f}^{\infty} n^2N_n = fI_0\left[f + K_f\left[\frac{2K_f}{(a-1)(a-2)}(e^{(a-2)x} - 1) + K_f(f-1) \times (e^{-2x} - 1) + \left[1 + 2f + 2K_f(f-1) - \frac{2K_f}{a-1}\right](1 - e^{-x})\right]\right] \qquad (85)$$

Hence, the number- and weight-average degrees of polymerization of the total polymers are respectively

$$\bar{P}_n = f[1 + K_f(1 - e^{-x})] \qquad (86)$$

$$\bar{P}_\mathrm{w} = \left[f + K_f\left[\frac{2K_f}{(a-1)(a-2)}(e^{(a-2)x} - 1) + K_f(f-1) \times (e^{-2x} - 1) + \left[1 + 2f + 2K_f(f-1) - \frac{2K_f}{a-1}\right] \times (1 - e^{-x})\right]\right] \Big/ [1 + K_f(1 - e^{-x})] \qquad (87)$$

If $a = 1$ or $a = 2$, $\bar{P}_\mathrm{w}$ should be calculated by the following formulas:

$$\bar{P}_\mathrm{w}|_{a=1} = [f + K_f[K_f(f-1)(e^{-2x} - 1) - 2K_fxe^{-x} + (1 + 2f + 2fK_f)(1 - e^{-x})]]/[1 + K_f(1 - e^{-x})] \qquad (88)$$

$$\bar{P}_\mathrm{w}|_{a=2} = \left[f + K_f\left[2K_fx + K_f(f-1)(e^{-2x} - 1) + \left[1 + 2f + 2K_f(f-1) - \frac{2K_f}{a-1}\right] \times (1 - e^{-x})\right]\right] \Big/ [1 + K_f(1 - e^{-x})] \qquad (89)$$

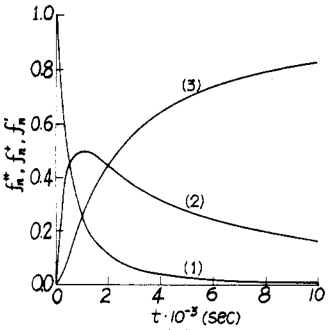

Figure 2. Dependence of the functionality distribution of the polymer on polymerization time, instantaneous initiation, $f = 2$, and the product of I_0 and k_t, $I_0k_t = 5 \times 10^{-3}$ s^{-1}; curves 1–3 correspond to f_n^{2+}, f_n^{+}, and f_n'.

Normalization of eq 81 yields the functionality distribution function of the polymer formed,

$$f_n^{(r)} = \binom{f}{r} e^{-rax}(1 - e^{-ax})^{f-r} \tag{90}$$

from which the average functionality of the total polymer, $\bar{r}$, generated in the reaction system is derived,

$$\bar{r} = fe^{-ax} \tag{91}$$

Obviously, when $f = 1$ and $f = 2$, the results are in accordance with the aforementioned ones.

IV. Determination of the Parametric Variable x. It should be pointed out that the above formulas cannot be utilized practically, until the value of x is determined. The calculation of x can be made by means of the relationship between x and the polymerization conditions. According to eq 84 and the constraint condition

$$\sum_{n=f}^{\infty} \sum_{r=0}^{f} nN_n^{(r)} = M_0 - M \tag{92}$$

we can obtain

$$x = \ln \frac{1 - fI_0/M_0}{1 - y} \tag{93}$$

which makes it possible to calculate x from monomer conversion y. On the other hand, combination of eq 70 and 71 yields

$$\mathrm{d}\sum_{r=1}^{f} r \sum_{n=f}^{\infty} N_n^{(r)}/\mathrm{d}t = -k_t\Big(\sum_{r=1}^{f} r \sum_{n=f}^{\infty} N_n^{(r)}\Big)^2 \tag{94}$$

Solving eq 94 and setting the corresponding initial condition

$$\sum_{r=1}^{f} r \sum_{n=f}^{\infty} N_n^{(r)}|_{t=0} = fI_0$$

result in

$$\sum_{r=1}^{f} r \sum_{n=f}^{\infty} N_n^{(r)} = \frac{fI_0}{1 + fI_0k_tt} \tag{95}$$

Comparison of eq 74 and 95 yields the relationship between x and the reaction time

$$x = (1/a) \ln (1 + fI_0k_tt) \tag{96}$$

It can be seen that eq 93 and 96 are also suitable for the calculation of x in the case of $f = 1$ and $f = 2$.

Results and Discussion

Many sets of polymerization conditions were used for calculation in order to investigate the effects of reaction time, functionality of initiator, initial concentrations of monomer and initiator, and rate constants of propagation and termination on functionality distribution, average functionality, ratio of weight- to number-average degrees of polymerization, and molecular weight distribution of the polymer formed.

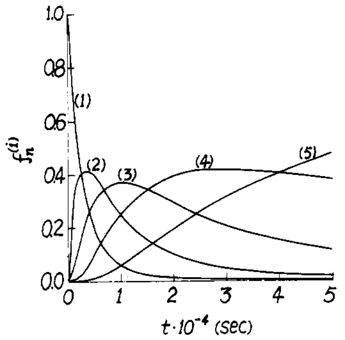

Figure 3. Dependence of the functionality distribution of the polymer on polymerization time, instantaneous initiation, $f = 4$, and the product of I_0 and k_t, $I_0k_t = 10^{-4}$ s^{-1}; curves 1–5 correspond to $f_n^{(4)}$, $f_n^{(3)}$, $f_n^{(2)}$, $f_n^{(1)}$, and $f_n^{(0)}$, respectively.

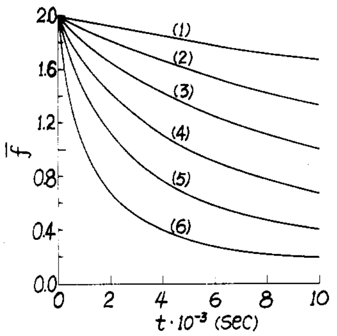

Figure 4. Variation of average functionality of the total polymers with reaction time and instantaneous initiation, $f = 2$; curves 1–6 correspond to the products of I_0 and k_t, $I_0k_t = 10^{-5}$ s^{-1}, 2.5×10^{-5} s^{-1}, 5×10^{-5} s^{-1}, 10^{-4} s^{-1}, 2×10^{-4} s^{-1}, and 5×10^{-4} s^{-1}, respectively.

Figures 2 and 3 demonstrate the dependence of the functionality distribution of the polymer formed on polymerization time in the case of $f = 2$ and 4, respectively. Figure 4 shows the variation of average functionality of the total polymers with reaction time for bifunctional polymerizations with different products of termination rate constants and initial concentrations of initiator, I_0k_t.

From eq 90, 91, and 96, we know that $f_n^{(r)}$ and $\bar{r}$ are dependent on the ratio $a = k_t/k_p$, the functionality of initiator f, and parametric variable x, while x is related to a, f, t, and the product of k_t and I_0. For given values of a and f, if the product of k_t and I_0 is kept constant, the curves $\bar{r}$ varying with reaction time t are the same; so are the curves of $f_n^{(r)}$. We could conclude that both increasing termination rate and increasing initial concentration of initiator have the same effect on $f_n^{(r)}$ and $\bar{r}$, though other molecular parameters may be quite different.

For a case where $k_p = k_t = 10$ L/mol·s, $M_0 = 1.0$ mol/L, and the product of initiator functionality and initial initiator concentration $fI_0 = 0.001$ mol/L, we have calculated the ratio of weight- to number-average degrees of polymerization for the polymer formed at different times. Figure 5 shows the relationships $\bar{P}_w/\bar{P}_n$ versus t. It can be seen from the figure that the higher the functionality of the initiator is, the more homogeneous is the molecular weight distribution of the total polymers formed.

For bifunctional polymerization, we can calculate numerical results for N_n^{2+}, N_n^{+}, N_n', and N_n from eq 40 and 42–44. For a case where $I_0 = 0.01$ mol/L, $M_0 = 2.0$ mol/L, $k_p = 10.0$ L/mol·s, and $k_t = 12.0$ L/mol·s, we calculated the differential molecular weight distribution curves, as

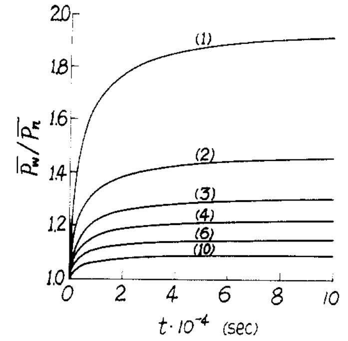

Figure 5. Ratio of weight- to number-average degrees of polymerization $\bar{P}_n/\bar{P}_w$ versus reaction time t, instantaneous initiation, $k_p = k_t = 10$ L/mol·s, $M_0 = 1.0$ mol/L, and the product of initiator functionality and initial concentration of initiator $fI_0 = 0.001$ mol/L; curves 1, 2, 3, 4, 6 and 10 correspond to $f = 1, 2, 3, 4, 6$, and 10, respectively.

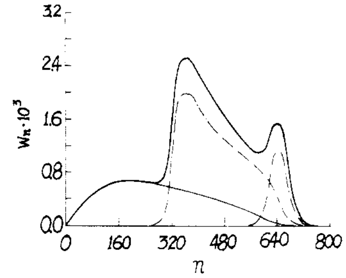

Figure 6. Plot of the molecular weight distribution of the polymer generated in bifunctional cationic polymerization with termination by combination with a negative fragment which was formed during the initiation reaction with some component of the reaction system, instantaneous initiation, $I_0 = 0.01$ mol/L, $M_0 = 2.0$ mol/L, $k_p = 10$ L/mol·s, $k_t = 12$ L/mol·s, and $t = 18$ s: (–··–) W_n^{2+}; (–·–) W_n^+; (—) W_n; (——) W_n.

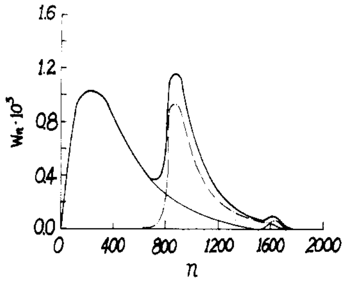

Figure 7. Plot of the molecular weight distribution of the polymer generated in bifunctional cationic polymerization with termination by combination with a negative fragment which was formed during the initiation reaction with some component of the reaction system, $t = 148$ s; other reaction conditions are the same as in Figure 6.

shown in Figures 6 and 7, corresponding to the polymers formed at $t = 18$ s and $t = 148$ s, respectively. In the figures, $W_n^{2+} = nN_n^{2+}/\sum_{n=2}^{\infty} nN_n$, $W_n^+ = nN_n^+/\sum_{n=2}^{\infty} nN_n$, $W_n\infty = nN_n'/\sum_{n=2}^{\infty} nN_n$, and $W_n = W_n^{2+} + W_n^+ + W_n'$. Comparison of these two figures gives us a general idea about the variation of the molecular weight distribution for different kinds of polymers with reaction time.

Finally, it should be noticed that the results obtained in this paper can also be used for the anionic polymerization of ethylene initiated by a soluble dicyclopentadienyltitanium dichloride–dimethylaluminum chloride complex in which the chain termination was reported to be second order in growing ends.[37]

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