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Significance of Reversibility of Initiation and of Equilibrium between Growing and Dormant Polymers in Cationic Polymerization

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ABSTRACT: We examined reversibility of initiation of cationic polymerization leading to dormant polymers and exchange between the dormant and growing polymers. Interesting systems arise from initiation caused by proton transfer. Mathematical treatment of such systems was accomplished for polymerization involving a minute but constant concentration of monomer maintained by its continual replenishment. The results, supported by computer calculations, showed that the amount of polymerized monomer is proportional to duration time of polymerization, while the number of formed polymer molecules increases proportionally to the square root of time, provided that the reaction progresses for a sufficiently long time. Moreover, computer calculations revealed that the equilibrium between dormant and growing n-mers is eventually established; i.e., as the reaction progresses, higher and higher n-mers attain the equilibrium state between their dormant and growing forms. The following assumptions were introduced in the mathematical model used in the computations: (1) The rate constants of reversible initiation and reinitiation are the same for the reaction involving monomer or a polymer terminated by a C═C bond (a dormant polymer, P_n). (2) The rate constant of irreversible propagation is the same for activated monomer (HM^+,A^-) or growing polymer (HR_n^+,A^-). (3) Termination is absent; i.e., the sum of concentration of the initiation acid (HA), activated monomer (HM^+,A^-), and growing polymers (HR_n^+,A^-) is constant all the time. (4) The minute concentration of the monomer is kept constant by its replenishment. Nevertheless the volume of the polymerizing solution is treated as constant. Analysis of the proposed model for long times leads to DP_n proportional to the square root of time and the ratio $DP_w/DP_n \to 4/3$, provided that the equilibria are established between the growing and dormant polymers. Computer calculation of the ratio DP_w/DP_n showed, however, that the ratio has a complicated dependence on time and eventually overshoots $4/3$ after a long time.

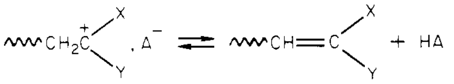
A recent interesting series of papers by Kennedy et al.[1] drew our attention to the problem of reversible chain transfer in cationic polymerization. We are concerned with systems in which the monomer concentration is kept constant by replenishing it as the reaction proceeds. Two kinds of transfer will be discussed: (a) chain transfer to monomer and (b) spontaneous chain transfer resulting in regeneration of initiator. Chain transfer to solvent or polymer, if it occurs at all, will not be treated.

Chain transfer to monomer is the most frequently reported transfer in cationic polymerization. It results from a bimolecular reaction between growing carbenium ions and a monomer. Its rate, like that of propagation, is proportional to monomer concentration; hence, the number-average degree of polymerization, DP_n, of the resulting polymers is independent of the monomer concentration, provided that such a transfer is the only reaction terminating the growth of polymer molecules. This indeed is often the case.

In cationic polymerization of olefins, chain transfer to monomer, i.e., proton transfer from a growing carbenium ion to a monomer yielding a protonated monomer and a "dormant" polymer terminated by a C═C bond, could be reversible since the protonated monomer may act as an acid while the dormant olefin would behave as a base. Moreover, a dormant polymer may acquire a proton from a growing carbocation, "reviving" the former and terminating the latter.

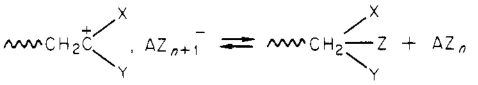
Although such a reversibility is feasible, at least in principle, and gains significance with increasing concentration ratio of dormant polymers to monomer, its participation in the overall process is questionable. Proton transfer from a growing polymer to a dormant polymer has to compete with an alternative bimolecular reaction of these two species, namely, propagation in which the dormant polymer olefin acts as a macromer. The latter reaction should yield branched polymers and, like propagation involving monomer, it should be much faster than transfer. Since this kind of branching is not observed, one concludes that the reverse of proton transfer is too slow to be of importance even in a system in which the ratio [dormant polymers]/[M] ≫ 1.

Unimolecular transfer may be reversible:



$$\sim\!\sim\!\sim CH_2\overset{X}{\underset{Y}{\overset{+}{C}}}\ ,A^- \rightleftharpoons \sim\!\sim\!\sim CH{=}\overset{X}{\underset{Y}{C}} + HA \qquad (I)$$

and the regenerated acid may initiate a new polymer chain. The nature of the unsaturation (i.e., endo or exo) will depend on the substituents α to the carbenium center. The alternative reaction



$$\sim\!\sim\!\sim CH_2\overset{X}{\underset{Y}{\overset{+}{C}}}\ ,AZ_{n+1}^- \rightleftharpoons \sim\!\sim\!\sim CH_2\overset{X}{\underset{Y}{C}}{-}Z + AZ_n \qquad (II)$$

reversibly converts a growing polymer into a dormant one. In reaction II, Z is usually a halogen and AZ_n a boron or transition-metal halide often present in excess and therefore favoring the reverse reaction but not the creation of a new polymeric chain.

Under conventional polymerization conditions, contribution of the reverse of transfer or exchange to the overall reaction is insignificant since the concentration of monomer exceeds that of dormant polymers by a large factor. However, in systems where the monomer is continually replenished, its concentration may be exceedingly low, and then the reverse of transfer or exchange might be appreciable. Mathematical treatment of the reversible spontaneous transfer described by reaction I and taking place under the above conditions, i.e., at a low stationary concentration of monomer, is outlined below. In fact, this reaction seems to account for some puzzling features of cationic polymerization, namely, for the low DP_w/DP_n often reported by various investigators.[2]

The Model

The model is shown in Scheme I. Here, HA denotes an acid that initiates polymerization; M, the monomer;

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Scheme I

$$\mathrm{HA} + \mathrm{M} \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \mathrm{HM}^+,\mathrm{A}^- \qquad \text{reversible initiation} \qquad \text{(a)}$$

$$\mathrm{HA} + \mathrm{P}_n \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \mathrm{HR}_n{}^+,\mathrm{A}^- \qquad \text{reversible conversion of a dormant polymer into a growing one and } \textit{spontaneous} \text{ decomposition of a growing polymer} \qquad \text{(b)}$$

$$\left.\begin{aligned} \mathrm{HM}^+,\mathrm{A}^- + \mathrm{M} &\xrightarrow{k_p} \mathrm{HR}_2{}^+,\mathrm{A}^- \\ \mathrm{HR}_n{}^+,\mathrm{A}^- + \mathrm{M} &\xrightarrow{k_p} \mathrm{HR}_{n+1}{}^+,\mathrm{A}^- \end{aligned}\right\} \quad \text{irreversible propagation}$$

$\mathrm{HM}^+,\mathrm{A}^-$, the product of their interaction; $\mathrm{HR}_n{}^+,\mathrm{A}^-$, a growing polymer; and P_n, a dormant polymer terminated by C═C bond and therefore capable of being reactivated.

A constant concentration of monomer is maintained in each run by continuously replenishing it as the polymerization proceeds. Moreover, by keeping $[\mathrm{M}] \gg [\mathrm{M}]_e$ (the concentration of the monomer while in equilibrium with its growing polymer), one ensures the irreversibility of steps c and d. We assume equal reactivity for the dormant polymer, P_n, and for the monomer in reactions a and b and again in reactions c and d. Nothing essential is sacrificed by these assumptions, which simplify the algebra. Termination is assumed to be absent and hence

$$[\mathrm{HA}] + [\mathrm{HM}^+,\mathrm{A}^-] + \sum_2^\infty[\mathrm{HR}_n{}^+,\mathrm{A}^-] = [\mathrm{HA}]_0 = I_0$$

where I_0 is the initial concentration of acid.

It is advantageous to introduce dimensionless variables, namely, $t' = k_p[\mathrm{M}]t$ for time, and define the concentrations in units of I_0; i.e., $[\mathrm{M}]/I_0 = m$, $[\mathrm{HM}^+,\mathrm{A}^-]/I_0 = x$, $[\mathrm{HA}]/I_0 = y$, $\sum[\mathrm{P}_n]/I_0 = z$, and $\sum_2^\infty[\mathrm{HR}_n{}^+,\mathrm{A}^-]/I_0 = 1 - x - y$. One unit of t' corresponds to the average time of addition of one molecule of monomer to a growing polymer. In this notation the unimolecular rate constant, k_{-i}, is converted into the dimensionless primed one by dividing it by $k_p[\mathrm{M}]$, while the conversion of the bimolecular rate constant, k_i, requires its multiplication by $I_0/k_p[\mathrm{M}]$; i.e., $k_i' = k_iI_0/k_p[\mathrm{M}]$, $k_{-i}' = k_{-i}/k_p[\mathrm{M}]$, and $k_p' = 1/m$.

The kinetics of the studied polymerization is described then by the following differential equations:

$$\mathrm{d}y/\mathrm{d}t' = k_{-i}'(1 - y) - k_i'(m + z)y \tag{1}$$

$$\mathrm{d}x/\mathrm{d}t' = k_i'my - (k_{-i}' + 1)x \tag{2}$$

$$\mathrm{d}z/\mathrm{d}t' = k_{-i}'(1 - x - y) - k_i'yz \tag{3}$$

$$\mathrm{d}\mathbf{A}/\mathrm{d}t' = 1 - y + k_i'my - k_{-i}'x \tag{4}$$

A denotes the total amount of monomer supplied to the system up to time t'. At $t' = 0$, $x = 0$, $y = 1$, $z = 0$, and $\mathbf{A} = 0$. For $t' \to \infty$, $x \to 0$, $y \to 0$, and $z \to \infty$ while $yz \to K_i'^{-1}$ and $K_i' = k_i'/k_{-i}'$. In the notation adopted here, the relation $\lim_{t'\to\infty}(yz) = 1/K_i'$ could be written in the form $\lim_{t'\to\infty}(yz)/\sum[\mathrm{HR}_n{}^+,\mathrm{A}^-] = 1/K_1'$ since $\lim_{t'\to\infty}\sum[\mathrm{R}_n{}^+,\mathrm{A}^-] = 1$.

Numerical solutions of the above differential equations for some chosen values of k_1' and k_{-1}' were obtained by using the method of Gear;[3] other methods were used only to check the numerical results.[4] The results will be discussed in a latter part of this report; we shall consider first the molecular weight distribution of the resulting product and then the solution of the above equations in the approximation of steady state of x and y.

Molecular Weight Distribution

Integration of eq 4 leads in our notation to

$$\mathbf{A} = t' + (k_i'm - 1)\int_0^{t'} y\,\mathrm{d}t' - k_{-1}'\int_0^{t'} x\,\mathrm{d}t'$$

and the total amount of monomeric segments in all the polymers, growing and dormant but excluding the activated monomer x, is given by

$$\mathbf{M}_1 = \sum_2^\infty n([\mathrm{HR}_n{}^+,\mathrm{A}^-] + [\mathrm{P}_n])/I_0 = \mathbf{A} - x$$

As shown in Appendix I, the time derivative of the second moment, $I_0\mathbf{M}_2$, is

$$I_0\,\mathrm{d}\mathbf{M}_2/\mathrm{d}t' = \mathrm{d}\{\sum_2^\infty n^2([\mathrm{HR}_n{}^+,\mathrm{A}^-] + [\mathrm{P}_n])\}/\mathrm{d}t' = 4[\mathrm{HM}^+,\mathrm{A}^-] + 2\sum_2^\infty n[\mathrm{HR}_n{}^+,\mathrm{A}^-] + \sum_2^\infty[\mathrm{HR}_n{}^+,\mathrm{A}^-]$$

The last sum in our notation is $(1 - x - y)I_0$. To evaluate $\sum_2^\infty[\mathrm{HR}_n{}^+,\mathrm{A}^-]$ we introduce an approximation stating that the equilibrium (b)

$$\mathrm{HA} + \mathrm{P}_n \rightleftarrows \mathrm{HR}_n{}^+,\mathrm{A}^-, \qquad K_i = K_i'/I_0 \tag{b}$$

is maintained all the time. Hence

$$\sum_2^\infty n([\mathrm{HR}_n{}^+,\mathrm{A}^-] + [\mathrm{P}_n]) = (1 + 1/K_i'y)\sum_2^\infty n[\mathrm{HR}_n{}^+,\mathrm{A}^-] = (\mathbf{A} - x)I_0$$

and

$$(1/I_0)\sum_2^\infty n[\mathrm{HR}_n{}^+,\mathrm{A}^-] = (\mathbf{A} - x)/(1 + 1/K_i'y)$$

Therefore

$$\mathrm{d}\mathbf{M}_2/\mathrm{d}t' = 4x + 2(\mathbf{A} - x)/(1 + 1/K_i'y) + 1 - x - y$$

This allows one to calculate the ratio $\mathrm{DP_w/DP_n}$ subject to the above approximation, namely

$$\mathrm{DP_w/DP_n} = \mathbf{M}_2(1 + z - x - y)/\mathbf{M}_1{}^2$$

Solution for Steady-State Approximation, $\mathrm{d}x/\mathrm{d}t' = 0$ and $\mathrm{d}y/\mathrm{d}t' = 0$

In the stationary-state approximation

$$\mathrm{d}y/\mathrm{d}t' = k_{-i}'(1 - y) - k_i'(m + z)y = 0 \tag{1'}$$

and

$$\mathrm{d}x/\mathrm{d}t' = k_i'my - (k_{-i}' + 1)x = 0 \tag{2'}$$

Subtracting eq 1′ and 2′ from eq 3, we get

$$\mathrm{d}z/\mathrm{d}t' = x \tag{3'}$$

From (1′)

$$y = k_{-i}'/(k_{-i}' + k_i'm + k_i'z)$$

while from eq 2′

$$x = k_i'my/(k_{-i}' + 1)$$

Hence

$$\mathrm{d}z/\mathrm{d}t' = \{k_i'm/(1 + k_{-i})\}k_{-i}'/(k_{-i}' + k_i'm + k_i'z)$$

or

$$\mathrm{d}z/\mathrm{d}t' = \{k_{-i}'m/(1 + k_{-i}')\}/(m + 1/K_i' + z), \qquad K_i' = k_i'/k_{-i}'$$

Introducing the abbreviation $C_1 = k_{-1}'m/(1 + k_{-i}')$ and $C_2 = m + 1/K_i'$, we find

$$\mathrm{d}z/\mathrm{d}t' = C_1/(C_2 + z)$$

and on integration

$$C_2z + (1/2)z^2 = C_1t'$$

i.e.

$$z = -C_2 + \{C_2{}^2 + 2C_1t\}^{1/2}$$

Table I
log DP_n vs. Time for Chosen Values k_i' and k_{-i}' and Constant Monomer Concentration $m = 1$

k_i', k_{-i}'	tolerance	2	4	8	20	40	80	100	400	10^3	4×10^3	10^4	4×10^4	10^5
0.2, 0.002	1×10^{-5}	0.445	0.58	0.80	1.21	1.53	1.83	1.915	2.39	2.65	2.99	3.19	3.50	3.68
0.05, 0.005	1×10^{-5}	0.44	0.57	0.76	1.10	1.4	1.71	1.80	2.24	2.47	2.79	3.00	3.32	3.49, 3.48^a
0.2, 0.02	2×10^{-5}	0.445	0.58	0.79	1.14	1.39	1.59	1.65	1.99	2.20	2.50	2.69, 2.73^b	2.95, 2.92^b	3.07, 2.97^b
10, 0.1	1×10^{-5}	0.50	0.64	0.91	1.03	1.15	1.33	1.38	1.60	1.84	2.15	2.39	2.60	2.77
0.2, 0.2	1×10^{-5}	0.44	0.54	0.68	0.87	1.015	1.165	1.21	1.52	1.73	2.03	2.21	2.50	2.69
10, 1.0	1×10^{-5}	0.43	0.51	0.60	0.75	0.87	0.99	1.04	1.32	1.52	1.80	1.98		

[a] For tolerance 2×10^{-5}. [b] For tolerance 1×10^{-4}.

Table II
Comparison of $(C_1/C_{1,\mathrm{std}})^{1/2}$ with $(DP_n)_{\mathrm{std}}/(DP_n)$ for $m = 1$[a]

				$(DP_n)_{\mathrm{std}}/(DP_n)$		
k'_i	k'_{-i}	$10^2(C_1)^{1/2}$	$(C_1/C_{1,\mathrm{std}})^{1/2}$	$t' = 10^4$	$t' = 4 \times 10^4$	$t' = 10^5$
0.2	0.002	4.47	(1.00)	(1.00)	(1.00)	(1.00)
0.005	0.005	7.05	1.58	1.55	1.51	1.55
0.2	0.02	14.0	3.13	3.16	3.55	4.07
10	0.1	30.2	6.76	6.31	7.94	8.13
0.2	0.2	40.8	9.13	9.55	10.0	9.77
10	1.0	70.7	15.8	16.2		

[a] $C_1 = k_{-i}'m/(1 + k_{-i}')$; the DP_n values are given in Table I.

At long time, when $2C_1t' \gg C_2^2$, a further simplification is permisible, namely

$$z \approx (2C_1t')^{1/2}$$

and for $k_{-i} \ll 1$

$$z \approx (2k_{-i}'mt')^{1/2}$$

Molecular Weight Distribution at Long Time

Since x and y tend to zero as time increases while K_i'/y tends to z, one deduces for a long time

$$\mathbf{M}_1 \approx \mathbf{A} \approx t'$$

and

$$d\mathbf{M}_2/dt' \approx 2\mathbf{A}/(1 + z) + 1$$

provided that the equilibrium between growing and dormant polymers is maintained.

In view of $z \approx (2C_1t')^{1/2}$ the integration with the initial value 0 for $\mathbf{M}_2$ gives

$$\mathbf{M}_2 = (4/3)(t')^{3/2}/(2C_1)^{1/2} + t' \approx (4/3)(t')^{3/2}/(2C_1)^{1/2}$$

Hence

$$DP_n = \mathbf{M}_1/(1 + z) \approx (t'/2C_1)^{1/2}$$

and for $k_{-i}' \ll 1$, $DP_n \approx (t'/2k_{-i}'m)^{1/2}$ while $DP_w = \mathbf{M}_2/\mathbf{M}_1$ is given within this approximation by $(4/3)(t'/2C_1)^{1/2}$. Therefore $DP_w/DP_n \approx \mathbf{M}_2z/\mathbf{M}_1^2$ tends to $^4/_3$ as $t' \to \infty$

In conclusion, in the limit of long time the DP_n seems to increase proportionally to the square root of time and inversely proportionally to the square root of C_1. Interestingly, DP_n is virtually unaffected by k_i, provided that $C_1t' \gg C_2^2$. The results of computer calculations, shown below, justify these conclusions.

Computer Calculation

The results of computer calculations for some chosen values of k_i' and k_{-i}' but constant $m = 1$ are shown in Figure 1 as plots of log z vs. log t'. In addition, the values of log (DP_n) for various time values are listed in Table I. The choice of the constants k_i' and k_{-i}' was dictated by the desire to investigate their effects on the results of computation.

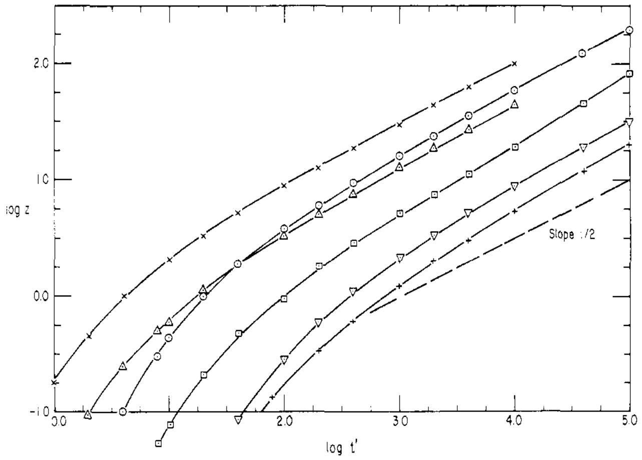


Figure 1. Double-logarithmic plot of $z = \sum P_n$ vs. t' calculated from eq 1-4. Note the approach of the lines to straight lines of slope $^1/_2$. k_i' and k_{-i}': (×) for 10, 1; (○) for 0.2, 0.2; (△) for 10, 0.1; (□) for 0.2, 0.02; (▽) for 0.05, 0.005; (+) for 0.2, 0.002.

The reliability of the computed data was checked by repeating some calculations with the aid of an alternative program and using another computer. The agreement was perfect for $t' \leq 10^4$ but some deviations were observed at $t' = 10^5$. Similarly, variations of the tolerance parameter led to some deviations at $t' > 10^4$ but did not affect the results for $t' \leq 10^4$ (see Table I).[5]

The data of x, y, z, $\mathbf{A}$, and DP_n as well as dz/dt' showed that the stationary-state approximation is valid for $t' >$ 200 or 300 (depending on the values of k_i' and k_{-i}'); i.e., dz/dt' differs then by less than 1% from the value of x.

The most gratifying results are shown in Table II. The constants $(C_1)^{1/2}$ and the respective relative values $(DP_n)_{\mathrm{stdd}}/(DP_n)$ are collected in that table, the results obtained for $k_{-i}' = 0.002$ (the lowest chosen value of k_{-i}') being considered as the standard. According to our deviation $(C_1/C_{1,\mathrm{std}})^{1/2}$ should be equal to $(DP_n)_{\mathrm{stdd}}/(DP_n)$. This relation is well fulfilled for $t' = 10^4$ but some deviations are noted for longer t' or larger k_{-i}'. The accumulation of errors in computer calculations makes them less reliable at too long times.

Unfortunately, the approximation asserting the maintenance of the equilibrium (b) is not fulfilled at the early

Table III
Comparison of the Ratio $R_N = DP_w/DP_n$ Given by the Approximate Equations with Cutoff at $N = 20$, $N = 50$, and $N = 500$ and the Difference $(R_{500} - R_{50})/R_{500}$ in Percent

	t'									
	0.5	1.0	1.5	2.0	3.0	5.0	8.0	10	16	20
R_{20}	1.040	1.076	1.107	1.133	1.173	1.215	1.229	1.227	1.207	1.186 (?)
R_{50}	1.040	1.076	1.107	1.133	1.173	1.215	1.229	1.227	1.217	1.218
R_{500}	1.045	1.078	1.108	1.134	1.174	1.215	1.229	1.227	1.217	1.218
$(R_{500} - R_{50})/R_{500}$, %	+0.5	+0.2	+0.1	+0.1	+1	0	0	0	0	0
	t'									
	25	30	40	50	90	200	300	400	450	500
R_{50}	1.227	1.242	1.286	1.292 (?)						
R_{500}	1.223	1.241	1.276	1.309	1.403	1.484	1.505	1.509	1.509	1.509 (?)
$(R_{500} - R_{50})/R_{500}$, %	−0.3	−0.01	−0.8							

Table IV
Comparison of M_1 Computed from Eq 13 and $M_1 = M_0(DP_n)$ for $N = 500$

	t'								
	0.5	1.0	2.0	4.0	8.0	10	20	40	90
eq 13	0.0464	0.1605	0.5353	1.627	4.454	6.200	15.23	34.06	81.78
$M_0(DP_n)$	0.0450	0.1619	0.5439	1.673	4.706	6.429	15.77	35.15	84.12
Δ, %	−3	+1	+1	+3	+6	+4	+3.5	+3	+3

	t'					
	110	200	300	400	450	500
eq 13	101.02	188.21	285.66	383.51	432.54	481.62
$M_0(DP_n)$	103.97	193.30	293.81	394.84	445.08	495.26
Δ, %	+3	+3	+3	+3	+3	+3

stages of polymerization, rendering the computation of DP_w unreliable. In fact, the question of whether the equilibrium between growing and dormant polymers is established is examined in the following section.

Testing the Assumption of Equilibrium between Growing and Dormant Polymers

To examine the relation between growing and dormant n-mers and to get a more realistic assessment of DP_w, the following system of $2N + 2$ simultaneous differential equations was solved by computer, using the same procedures as before:

$$dy/dt' = k_{-i}'(1 - y) - k_i'(m + \sum_2^N P_n)y \tag{5}$$

$$dx/dt' = k_i'my - (k_{-i}' + 1)x \tag{6}$$

$$dR_2/dt' = x - R_2 + k_i'P_2y - k_{-i}'R_2 \tag{7}$$

$$dP_2/dt' = k_{-i}'R_2 - k_i'P_2y \tag{8}$$

for n from 3 to N

$$dR_n/dt' = R_{n-1} - R_n + k_i'P_ny - k_{-i}'R_n \tag{9}$$

for n from 3 to $N + 1$

$$dP_n/dt' = k_{-i}'R_n - k_i'P_ny \tag{10}$$

and

$$dR_{n+1}/dt' = R_N + k_i'P_{N+1}y - k_{-i}'R_{N+1} \tag{11}$$

The dimensionless notation utilized in the former treatment is again adopted, while the dimensionless concentrations of HR_n^+,A^- and of P_n are denoted by R_n and P_n, respectively; i.e., $[HR_n^+,A^-]/I_0 = R_n$ and $[P_n]/I_0 = P_n$.

The last equation represents a cutoff of the polymerization; the last R_{N+1}-mer is formed from a growing R_N-mer but it does not grow further. Introduction of this equation is required to make soluble the above system of simultaneous equations. Numerical computations were performed for only one set of kinetic coefficients, namely, $m = 1$, $k_i' = 0.2$, and $k_{-i}' = 0.02$. The computations were performed for three values of the cutoff parameter N, namely, 20, 50, and 500.

In each calculation the computer displays the values of x, y, R_2, R_3, R_4, R_N, R_{N+1}, P_2, P_3, P_4, P_N, and P_{N+1} for various times, t'. Moreover, it computes for each time the moments

$$\mathbf{M}_0 = \sum_2^{N+1} (R_n + P_n) \tag{12a}$$

$$\mathbf{M}_1 = \sum_2^{N+1} n(R_n + P_n) \tag{12b}$$

$$\mathbf{M}_2 = \sum_2^{N+1} n^2(R_n + P_n) \tag{12c}$$

as well as the $DP_n = \mathbf{M}_1/\mathbf{M}_0$, $DP_w = \mathbf{M}_2/\mathbf{M}_1$, and the ratio DP_w/DP_n denoted by R_N.

To evaluate the effect of the cutoff equation, we compare in Table III the values of R_N's corresponding to the same times but calculated for $N = 20$, $N = 50$, and $N = 500$, respectively. The comparison is satisfactory for times $t' < N$. At $t' = N$ the accumulation of $(N + 1)$-mers becomes significant, and this distorts the results. Thus, for $N = 20$ and $N = 50$ the relevant 21-mers and 51-mers form ~15% and ~8%, respectively, of all the polymers. However, for $N = 500$ the relevant 501-mers from only 0.01% of all the polymers, making the pertinent results reliable even at $t' = 500$.

A further test of the reliability of the calculation is shown by Table IV. The first moment $\mathbf{M}_1 = \mathbf{M}_0(DP_n)$ may be alternatively calculated from the equation

$$d\mathbf{M}_1/dt' = 1 + x - y \tag{13}$$

representing the rate of consumption of the monomer by all the growing polymers (the $+x$ term arises since the

Table V
Comparison of DP_n Calculated from the Exact Equations, $DP_n(\infty)$, with the One Obtained from the Approximate Equations with Cutoff at $N = 500$, $DP_n(500)$[a]

	t'									
	0.5	1.0	2.0	4.0	10	20	50	90	200	400
$DP_n(\infty)$	2.174	2.365	2.788	3.749	7.396	13.815	28.61	42.09	67.1	97.9
$DP_n(500)$	2.180	2.366	2.788	3.770	7.358	13.815	28.76	42.21	67.5	98.4
% of Δ[b]	−0.3	−0.04	0	−0.6	+0.5	0	−0.5	−0.3	−0.6	−0.5

[a] $k_i' = 0.2$, $k_{-i}' = 0.02$. [b] $\Delta = [DP_n(\infty) - DP_n(500)]/DP_n(\infty)$.

Table VI
Apparent Equilibrium Constant[a] $K_n' = R_n^+/P_ny$

	t'									
	5	10	20	40	70	110	200	300	400	450	500
$n = 2$	36	22.0	14.8	12.4	11.4	10.9	10.4	10.28	10.11	10.08	10.03
$n = 3$	59	26.5	15.4	12.3	11.3	10.9	10.4	10.16	10.08	10.06	10.03
$n = 4$	77	32.7	16.2	12.2	11.2	10.7	10.3	10.13	10.06	10.04	10.02
$n = 102$								13.7	12.3	11.9	11.8
$n = 202$								34	18.9	17.3	16.1
$n = 302$									39	28	24

[a] Cutoff for $N = 500$.

conversion of HM^+,A^- into dimer HR_2^+,A^- introduces two monomeric segments into $\sum_2^{N+1} nR_n$). The comparison is satisfactory for $N = 500$, and the deviations of the two computed values are even smaller for $N = 20$ and $N = 50$, provided that the calculations pertain to $t' < N$.

Finally, we compare in Table V the values of DP_n derived from the solution of the exact equations (1)–(4) with the values derived from the approximate set of equations (5)–(11) for the cutoff $N = 500$. The results are satisfactory, confirming their reliability.

The time dependence of concentrations of R_2, R_3, and P_2 are shown in Figure 2. As expected, the concentrations of growing polymers are represented by the initially sigmoidal curves, each passing through a maximum, and thereafter tend to 0 at longer times. The maxima become lower the higher the n and appear then at later times as exemplified by the behavior of R_2 and R_3. Although $[R_n] > [R_{n+1}]$ at early times, the reverse is true at sufficiently long times. On the other hand, the concentrations of dormant polymers slowly rise in sigmoidal fashion to constant asymptotic values, as exemplified by the behavior of P_2.[6]

After establishing the reliability of the computer calculations, we investigated whether the assumption concerned with the establishment of equilibrium between the growing R_n-mers and the dormant P_n-mers is justified. The ratio $K_n = R_n/P_n$ was calculated, therefore, as a function of t' for $n = 2$, 3, and 4, i.e., dimers, trimers, and tetramers. The results, collected in Table VI and displayed in Figure 3, show that K_n's rapidly and asymptotically approach their equilibrium value of 10. At $t' \sim 100$ the deviations from equilibrium are $\sim$1%, and at $t' = 500$ they are smaller than 0.5%. Moreover, the K_n's approach the asymptote from above; i.e., at no time does the concentration of dormant polymers exceed their expected equilibrium value corresponding to the pertinent R_n's and y. However, the concentrations of P_n reach a constant asymptotic value because the ratios R_n/y become constant at a sufficiently long time, although R_n and y tend to 0.

As expected, large deviations from the state of equilibrium are observed at early times; for any fixed early time the deviations are larger for tetramers than for trimers and for dimers. However, the respective curves, $K_n(t')$, are steeper for larger mers than for smaller ones, and at sufficiently long times the approach to the asymptote is closer for the larger than for the smaller mers.

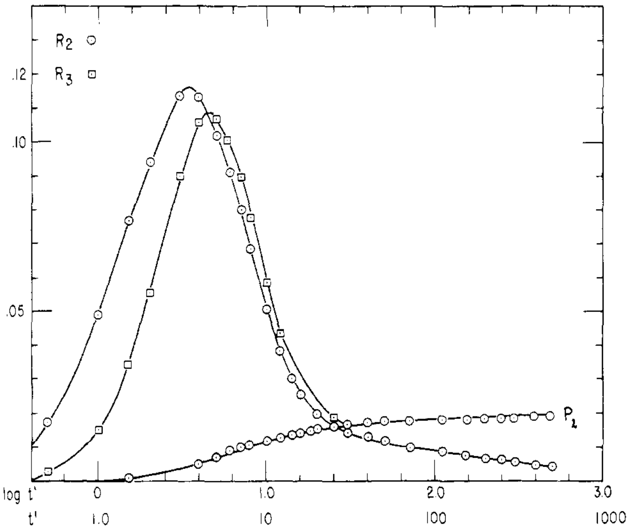


Figure 2. Concentrations of growing dimers, R_2, and trimers, R_3, as well as the dormant dimers, P_2, as functions of log t'. Calculated from 5 to 11 with $k_i' = 0.2$ and $k_{-i}' = 0.02$.

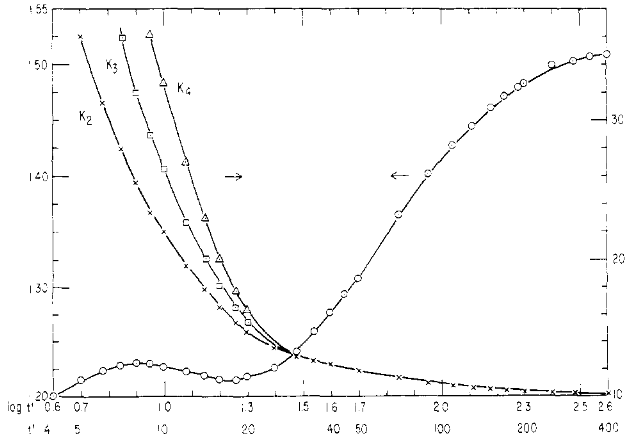


Figure 3. Apparent equilibrium constant $K_n = P_ny/R_n$ as functions of log t' for $n = 2$, 3, and 4. Note the rapid approach of K_n's to their equilibrium value of 10. Plot of DP_w/DP_n as a function of log t'. Note the unexpected hump. The computed data were obtained on the basis $k_i' = 0.2$ and $k_{-i}' = 0.02$.

The equilibrium is not attained for large N's at $t' = N$. Thus, $K_{20} = 55$ at $t' = 20$, $K_{50} = 80$ at $t' = 50$, and $K_{500} =$

100 at $t' = 500$. These deviations from the equilibrium are responsible for the larger than expected value of DP_w/DP_n, which apparently tends to ~1.51 at very long times. This result is revealed by inspection of Table III and Figure 3. The latter shows an unexpected behavior of DP_w/DP_n—the respective function has a hump at $t' \sim 8$. We have no explanation for this peculiarity of the system, but undoubtedly it is real and not an artifact of calculation, since a similar hump appears in a curve resulting from the calculation limited to cutoff = 50.

In conclusion, the amount of consumed monomer in polymerizing systems involving reversible addition of initiator to monomer ([M] = constant) or to dormant polymers is proportional to the duration time of the reaction while the number of formed polymers increases as the sqaure root of the duration time. These relations apply at sufficiently long times of polymerization. Under those conditions, the number-average degree of polymerization rises proportionally to the square root of the duration time, whereas the increase of the weight-average degree of polymerization is more complex. Our calculations appear to indicate that the ratio DP_w/DP_n tends to a constant value of ~1.51, albeit the value $^4/_3$ is expected for systems in which equilibrium is established between the growing R_n-mers and dormant P_n-mers. Indeed, the equilibrium is rapidly established for lower mers but not for the higher ones formed in the last periods of polymerization; i.e., for large n, P_n is smaller than its equilibrium value. Interestingly, as the equilibrium is established, P_n's tend to constant values, although the amounts of R_n and of the initiator decay to zero.

It should be recalled that the solution of eq 1–4 reveals the approach of $(\sum R_n)/(\sum P_n)y$ to K_i' as $t' \rightarrow \infty$ since $\sum R_n$ tends then to 1.[7] This implies an approach to a state of equilibrium involving all the growing polymers on one hand and all the dormant ones and the initiator on the other. Such a relation does not necessarily imply an eventual establishment of equilibrium between R_n, P_n, and y for each n. However, since we demonstrated the approach to equilibrium for lower n-mers, it is tempting to suppose that as $t' \rightarrow \infty$ the highest n-mers, which are not yet at equilibrium, become a negligible fraction of all the polymers and then their presence only negligibly affects DP_n and DP_w. Accepting this reasoning, one might anticipate the limit of DP_w/DP_n to be $^4/_3$ at $t' \rightarrow \infty$, and hence the curve shown in Figure 3 should pass through a flat maximum of ~1.51 and eventually approach the limiting value of 1.33.

Some numerical results obtained by computer support this conclusion. The following amounts of n-mers, growing and dormant, were calculated at $t' = 500$ for the cutoff of 500.

n	2	3	4	102	202	302	402	total
$10^2(R_n + P_n)$	2.40	2.40	2.40	2.08	0.94	0.21	0.02	438

For a constant population of all n-mers, the ratio $DP_w/DP_n = {}^4/_3$ and the above results indicate a virtually constant population from $n = 2$ to $n = 102$. Together they amount to more than 50% of all the formed polymeric molecules.

Further tests of these conclusions require computations involving at least 100 000 variables—a task too costly for our limited resources.

Appendix I

Introduce the notation $r_n = [HR_n^+,A^-]/I_0$ and $p_n = [P_n]/I_0$.

$$dr_2/dt' = x - r_2 + k_i'yp_2 - k_{-i}'r_2;$$

$$dp_2/dt' = k_{-i}'r_2 - k_i'yp_2$$

$$dr_3/dt' = r_2 - r_3 + k_i'yp_3 - k_{-i}'r_3;$$

$$dp_3/dt' = k_{-i}'r_3 - k_i'yp_3$$

$$dr_n/dt' = r_{n-1} - r_n + k_i'yp_n - k_{-i}'r_n;$$

$$dp_n/dt' = k_{-i}'r_n - k_iyp_n$$

Therefore

$$d(r_2 + p_2)/dt' = x - r_2$$

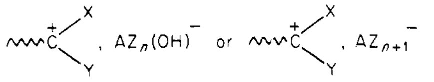
$$d(r_3 + p_3)/dt' = r_2 - r_3$$

$$d(r_n + p_n)/dt' = r_{n-1} - r_n$$

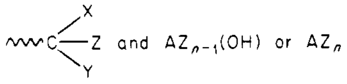
Multiplying each equation by the respective n^2 and adding them together, we get

$$\sum_2^\infty n^2\, d(r_n + p_n)/dt' = 4x + 2\sum_2^\infty nr_n + \sum_2^\infty r_n$$

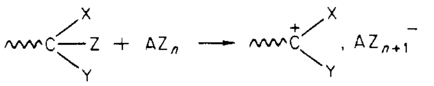
Transfer Involving AZ_{n+1}^- Counterions. Polymerizations induced by Friedel–Crafts reagents, AZ_n, require catalysts for initiation. For example, a trace of water allows for proton transfer to monomer, yielding $AZ_n(OH)^-$ and a protonated monomer. The transfer results in such systems from reactions exemplified by



yielding



In most of the investigated systems the concentration of AZ_n greatly exceeds that of the cocatalysts; hence the reverse of the transfer is caused by the reaction



There are two important differences between these systems and those discussed previously.

(1) The regenerated AZ_n may revive the terminated polymers possessing the C–Z terminal bond but cannot interact with the monomer after quantitative utilization of the cocatalyst. Hence, the genuine initiation could be completed in the early stages of polymerization.

(2) The concentration of AZ_n is independent of the concentration of the initiating species.

Treatment of such reactions is analogous to those involving living and dormant polymers. The early stages yield polymers mostly terminated by halogen transfer. If a monomer is still available, a revival process allows for further growth, and this process narrows the original molecular weight distribution.

The last point, although self-evident, may be demonstrated in the following way. Say the polymerization yielded polymers with $(DP_w/DP_n)_0$. The revival process increased their size by a. Hence

$$(DP_w/DP_n)_0 = (\sum n^2P_n)(\sum P_n)/(\sum nP_n)^2$$

while at a later state DP_w/DP_n is given by

$$\{\sum(n + a)^2P_n\}(\sum P_n)/\{\sum(n + a)P_n\}^2 = \{\sum n^2P_n + 2a\sum nP_n + a^2\sum P_n\}(\sum P_n)/\{(\sum nP_n)^2 + 2a(\sum nP_n)(\sum P_n) + a^2(\sum P_n)^2\}$$

Thus

$$DP_w/DP_n = \{(DP_w/DP_n)_0 + \gamma\}/(1 + \gamma)$$

where

$$\gamma = \{2a/(\sum nP_n) + a^2(\sum P_n)/(\sum nP_n)^2\}(\sum P_n)$$

i.e.

$$\mathrm{DP_w}/\mathrm{DP_n} < (\mathrm{DP_w}/\mathrm{DP_n})_0$$

since

$$(\mathrm{DP_w}/\mathrm{DP_n})_0 > 1$$

References and Notes

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(4) Solutions of these equations were obtained by numerical integration with an automatic computer (VAX 11-780). Some difficulty was encountered because the equations are "stiff", that is, the solutions contain a term that varies rapidly with time. This term arises mainly from the first two equations and corresponds to the rapid reaction of initiator with monomer. After a short time this rapidly varying term becomes small, but its presence nevertheless makes the solutions numerically unstable unless very short time increments are used. We tried several methods of integration, of which the most successful was the method of Gear. Variation of the time steps, $\Delta t'$, affects the numerical results by 1–2%.

(5) The tolerance parameters limits the magnitude of the incremental error at each time increment; however, the overall error, being the resultant from all time increments, is much larger and grows with time.

(6) These statements apply to hypothetical systems of constant volume; i.e., the supply of monomer is assumed not to increase the volume of the system. Such an assumption is approximately justified as long as the investigated solutions of monomer and polymers are dilute.

(7) See the remarks after eq 1–4.

Compositional Variation of the Glass Transition

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ABSTRACT: A relation between differential changes of temperature and pressure is obtained for the glass–liquid boundary of random solutions. On integration, this relation yields predictive equations for the compositional variation of glass-transition temperatures and of glass-transition pressures.

Introduction

A thermodynamic theory for the compositional variation of glass-transition temperatures,[1-7] T_g, has provided a unified basis for several topics within the general theme, for both macroscopic[1,5,7-13] and microscopic[2-7,14] composition variables, X_i. The principal equation of this description is obtained by equating the entropy of the glassy and liquid states, respectively S^g and S^l, and taking definite temperature integrals. As outlined below, a more general and transparent theory can be derived from the equality $dS^g = dS^l$ for the glass-transition boundary as a function of pressure, P, temperature, T, and composition. A relation between differential changes of temperature and pressure is thereby obtained for the composition-dependent glass transition. This new equation can be integrated to give, as special cases, an equation for the compositional variation of T_g and an equation for the compositional variation of the transition variable for the isothermal transition (the glass-transition pressure, P_g). A particular advantage of the differential formulation is that for the compositional variation of T_g and P_g, corresponding pure-component properties, T_{g_i} and P_{g_i}, enter as constants of integration.

Theory

For random mixtures the excess entropy of mixing is essentially combinatorial and independent of temperature and pressure. Consequently, at fixed but arbitrary composition, the differential relation $dS^l = dS^g$ for the glass–liquid boundary can be written as

$$\sum X_i \Delta C_{p_i}\, \mathrm{d} \ln T + \sum X_i \Delta C_{T_i}\, \mathrm{d} \ln P = 0 \qquad (1)$$

In eq 1 the ΔC_{p_i} denote pure-component glass-transition increments of heat capacity, the $\Delta C_{T_i} = \Delta(\mathrm{d}S_i/\mathrm{d} \ln P)_T$ denote the isothermal analogues of this property, and $\sum$ denotes the sum over all pure components of the solution. Use of a Maxwell relation gives $\Delta C_{T_i} = -P\Delta(V_i\alpha_i)$, where V_i and α_i are in turn pure-component current volumes and isobaric expansivities, and converts eq 1 to

$$\frac{\mathrm{d} \ln T}{\mathrm{d}P} = \frac{\sum X_i \Delta(V_i\alpha_i)}{\sum X_i \Delta C_{p_i}} \qquad (2)$$

Equation 2 includes the pure-component ($X_i = 1$) Ehrenfest relation[15] as a special case.

To derive an expression for the compositional variation of T_g, consider the indefinite integration of eq 1 at fixed pressure, formally

$$\sum X_i \int \Delta C_{p_i}\, \mathrm{d} \ln T = 0 \qquad (3)$$

A variety of problems has been addressed successfully by the use of temperature-independent ΔC_{p_i},[1-12] for which eq 3 becomes

$$\sum X_i \Delta C_{p_i} (\ln T_g + a_i) = 0 \qquad (4)$$

The constants of integration in eq 4 are obtained from the requirement that at $X_i = 1$, $T_g = T_{g_i}$, to give $a_i = -\ln T_{g_i}$ and

$$\ln T_g = \frac{\sum X_i \Delta C_{p_i} \ln T_{g_i}}{\sum X_i \Delta C_{p_i}} \qquad (5)$$

If the ΔC_{p_i} cannot reasonably be approximated as temperature independent,[16] eq 3 together with the boundary conditions can be used to obtain relations for the composition-dependent isobaric transition other than eq 5.

For the isothermal transition, the relation for the compositional variation of P_g for pressure-independent ΔC_{T_i} is

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