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Theoretical Study of Living Polymerization Reactions Involving a Transfer Agent

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ABSTRACT: In the present paper, a theoretical study is made of the effect of a transfer agent on the molecular size distribution in living polymers, assuming an infinitely fast initiation and instantaneous reinitiation after the transfer reaction. Expressions for the number-average and weight-average chain lengths are obtained for three cases: (a) both the monomer and the transfer agent remain at constant concentration, (b) only the concentration of the transfer agent is kept constant, and (c) both concentrations vary with time. The last one is the usual situation, but the circumstances under which approximate solutions corresponding to constant concentration of transfer agent could be safely used are discussed in detail.

In living polymerization, when initiation is instantaneous and transfer is absent, the resulting material has a narrow Poisson distribution[1] of chain lengths. Broadening of the distribution can be due to different factors such as impurities, transfer to monomer, slow initiation, depropagation, etc. Szwarc and Litt[2] and also Coleman et al.[3] have studied the molecular weight distribution for ionic polymerizations in which there exist termination reactions, either spontaneous or due to impurities. Similarly, Orofino and Wenger[4] and Figini[5] studied such systems with bifunctional initiators. Many workers[6-8] have considered mathematically the effect on the molecular weight distribution of a slow initiation. In those ionic polymerizations in which two species contributing to the chain growth can coexist, the polydispersity ratio increases, as shown by Szwarc and Hermans,[9] Coleman and Fox,[10] and Figini.[11] Still another factor which can affect the distribution is reversibility of the propagation step, mathematical study of which was carried out by Brown and Szwarc[12] and by Miyake and Stockmayer.[13] More recently, Nanda and Jain[14,15] have studied the distribution of molecular weights in ionic polymerizations with spontaneous transfer and transfer to monomer.

So far, however, no study is known, at least to these authors, of the distribution in ionic polymerizations in which there exists a transfer reaction involving a species present in the mixture or formed in the initiation step and in which, at the same time, an instantaneous reinitiation takes place. Rozenberg and co-workers[16] have experimentally studied the polymerization of tetrahydrofurane with trialkyloxonium salts, including water as transfer agent, and observed that the polymerization rate remains constant while the polydispersity index increases with the transfer agent concentration. It therefore seemed worthwhile to discuss this problem, and we report here the averages obtained for different cases from an appropriate kinetic scheme. We hope the results will be useful for checking against experimental findings and for providing increased understanding of the factors governing a living polymerization.

Kinetic Scheme and the Averages

The kinetic scheme we considered is analogous to those in ref 4 and 5, the only difference being the inclusion of a transfer agent in the corresponding step. It involves three stages: initiation:

$$\mathrm{I} + \mathrm{M} \xrightarrow{k_i} \mathrm{N}_1^*$$

propagation:

$$\mathrm{N}_i^* + \mathrm{M} \xrightarrow{k_p} \mathrm{N}_{i+1}^*$$

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transfer:

$$\mathrm{N}_i^* + \mathrm{T} \xrightarrow{k_t} \mathrm{N}_i + \mathrm{I}$$

Here I, M, N*, T, and $\mathrm{N_i}$ denote the initiator, monomer, living (or active) i-mer, transfer agent, and dead (or inactive) i-mer, respectively; k_i, k_P, and k_t represent the rate constants for initiation, propagation, and transfer. In the following we assume that $k_\mathrm{i} \to \infty$, and therefore the total amount of initiator is converted immediately into active (living) propagating centers. As a consequence, after chain transfer the infinitely fast initiation step results in practically instantaneous rebirth of an active chain, so that the following condition must be fulfilled at any time

$$\sum_{i=1}^{\infty} N_i^* = I_0 \tag{1}$$

where I_0 is the amount of initiator added to start the reaction.

Furthermore, we can begin counting time from the very moment at which the whole of the initiator has been depleted,[17] and we have the initial conditions

$$M_0 = M_\mathrm{in} - I_0;\ (N_1^*)_0 = I_0;\ (N_i^*)_0 = 0,\ i \geq 2;\ (N_i)_0 = 0,\ i \geq 1 \tag{2}$$

where M_in is the total amount of monomer which is present before the initiator is added.

The differential rate equations corresponding to the above kinetic scheme are

$$\begin{gathered} \mathrm{d}N_1^*/\mathrm{d}t = -(k_\mathrm{P}M + k_\mathrm{t}T)N_1^* + k_\mathrm{t}TI_0 \\ \mathrm{d}N_i^*/\mathrm{d}t = -(k_\mathrm{P}M + k_\mathrm{t}T)N_i^* + k_\mathrm{P}MN_{i-1}^*,\ i \geq 2 \\ \mathrm{d}N_i/\mathrm{d}t = k_\mathrm{t}TN_i^*,\ i \geq 1 \end{gathered} \tag{3}$$

With instantaneous reinitiation following the transfer step, the monomer depletion rate is given by

$$\mathrm{d}M/\mathrm{d}t = -(k_\mathrm{P}M + k_\mathrm{t}T)I_0 \tag{4}$$

while for the transfer agent we have

$$\mathrm{d}T/\mathrm{d}t = -k_\mathrm{t}TI_0 \tag{5}$$

The following situations can now be considered: (a) both T and M remain constant; (b) M disappears with time while T is kept constant; and (c) both M and T are variable. The fourth possible case (M constant and T variable) is not so interesting for reasons made clear below but could be treated similarly. The invariance of M would seem to be a purely academic case, but it can be attained quite easily both in research and industrial processes if the reactor is fed with M at the initial depletion rate, which in turn is obtainable without difficulty for any given initial concentration of monomer. The transfer agent, on the other hand, is present at an initial concentration usually much smaller than that of monomer in order to make $k_\mathrm{P}M \gg k_\mathrm{t}T$, because this situation favors chain growth. At such small concentrations, the slow depletion of T makes the changes in its concentration almost unobservable, and therefore it is a good *approximation* to consider T as a constant. For these reasons it is not practically interesting to keep T constant and allow M to vary, because after some time $k_\mathrm{P}M$ and $k_\mathrm{t}T$ would be of the same order of magnitude which is unfavorable to chain growth.

The number-average and weight-average chain lengths are defined as

$$i_\mathrm{n} = \frac{\sum_i i(N_i + N_i^*)}{\sum_i (N_i + N_i^*)} \qquad i_\mathrm{w} = \frac{\sum_i i^2(N_i + N_i^*)}{\sum_i i(N_i + N_i^*)} \tag{6}$$

In order to find expressions for these averages (and others of higher order that could be defined), we used the same procedure as Nanda and Jain.[4] Defining the generating functions

$$G = \sum_i N_i y^i; \qquad G^* = \sum_i N_i^* y^i \tag{7}$$

and using the differential rate eq 3, one obtains at once

$$\mathrm{d}G/\mathrm{d}t = k_\mathrm{t}TG^* \tag{8}$$

and

$$\mathrm{d}G^*/\mathrm{d}t = -\{(1 - y)k_\mathrm{P}M + k_\mathrm{t}T\}G^* + k_\mathrm{t}TI_0y \tag{9}$$

By applying the operator $y\ \mathrm{d}/\mathrm{d}y$ successively to eq 8 and 9, we obtained a set of general equations which must hold for any value of y. In particular, putting $y = 1$ the following useful results are obtained after application of the initial conditions in (2):

$$\sum_i i(N_i + N_i^*) = I_0\left\{1 + \int_0^t (k_\mathrm{P}M + k_\mathrm{t}T)\ \mathrm{d}t\right\} \tag{10}$$

$$\sum_i i^2(N_i + N_i^*) = \sum_i i(N_i + N_i^*) + \int_0^t 2k_\mathrm{P}M(\sum_i iN_i^*)\ \mathrm{d}t \tag{11}$$

$$\mathrm{d}(\sum_i iN_i^*)/\mathrm{d}t + k_\mathrm{t}T\sum_i iN_i^* = (k_\mathrm{P}M + k_\mathrm{t}T)I_0 \tag{12}$$

Upon integration of the last equation in (3)

$$\sum_i N_i = I_0\int_0^t k_\mathrm{t}T\ \mathrm{d}t \tag{13}$$

Note that eq 12 is a linear differential equation which can be easily integrated using the standard formula.

Next we consider separately the three cases mentioned earlier.

T and *M* Remain Constant

This particular case is so simple that eq 3 can be solved directly to obtain analytical formulas for both N_i and N_i^* as a function of time and of index i. The formulas are quite involved, showing that N_i and N_i^* depend on time in a very complicated manner. However, in the limit $t \to \infty$, one obtains

$$N_i^* = I_0\,(1 - P)P^{i-1}; \qquad N_i = k_\mathrm{t}T_0N_i^*t \tag{14}$$

where

$$P = k_\mathrm{P}M_0/(k_\mathrm{P}M_0 + k_\mathrm{t}T_0) = \text{constant} < 1 \tag{15}$$

For t large enough, the concentrations of the inactive chains are proportional to the time of reaction, a result which comes directly from the last equation in (3) when all N_i^*'s remain constant. Therefore, this limit corresponds to the stationary state for active chains, and, in fact, the results of eq 14 could be obtained by solving eq 3 with that approximation.

When $k_\mathrm{P}M_0 \gg k_\mathrm{t}T_0$ or, in other words, when the propagation step is very fast in comparison with the transfer, we have $P \simeq 1$ and $N_1^* \simeq 0$. This means that practically the entire initiator N_1^* ($=I_0$) has been transformed into N_i^* ($i > 1$), and the polymerization yields very long inactive chains. On the contrary, if the transfer is very fast vs. the propagation step, that is to say, if $k_\mathrm{t}T_0 \gg k_\mathrm{P}M_0$, then $P \simeq 0$ and $N_1^* \simeq I_0$, and therefore very short chains are obtained.

Concerning the averages, eq 10–13, when solved for this particular case, give:

$$i_\mathrm{n} = (1 + St)/(1 + k_\mathrm{t}T_0t) \tag{16}$$

and

$$i_w = \{1 + S(1 + 2R)t + 2R^2[\exp(-k_tT_0t) - 1]\}/(1 + St) \tag{17}$$

where $S = k_PM_0 + k_tT_0$ and $R = k_PM_0/k_tT_0$. It can be seen that both i_n and i_w increase with time, eventually reaching, for long enough t (this value being correspondingly smaller as k_tT_0 is larger), the limiting values

$$\begin{aligned} i_n^\infty &= 1 + R = 1/(1-P) \\ i_w^\infty &= 1 + 2R = (1 + P)/(1 - P) \end{aligned} \tag{18}$$

These values depend only upon R, and so any desired average could be obtained in any desired time by conveniently varying R, the ratio between propagation and transfer rates.

An interesting result can be obtained when one considers the derivative $\mathrm{d}i_n/\mathrm{d}t = k_PM_0/(1 + k_tT_0t)^2$. As k_PM_0 is constant, from the slope of the curve i_n vs. t at two different times k_tT_0 can be obtained as well as (since T_0 is known) k_t. Then, from a particular i_n value, S and therefore k_P could be evaluated. If upon substitution of these values in the equation for i_w we regain the experimental results, the consistency of the proposed mechanism can be ascertained. In this way, working at constant M_0 and T_0 can be very useful for obtaining the propagation and transfer rate constants, which can then be used in the more general cases treated below.

M Changes while *T* is Constant

For reasons to be discussed, this can be an interesting and important case in practice. Equation 4 is a linear differential equation which, integrated in the usual way for T constant, gives

$$M = (M_0 + k_tT_0/k_P)\exp(-k_PI_0t) - k_tT_0/k_P \tag{19}$$

with M_0 defined in eq 2. Accordingly, the time τ at which the whole of the monomer has been consumed is given by

$$(t)_{M=0} = \tau = (k_PI_0)^{-1}\ln(1 + k_PM_0/k_tT_0) \tag{20}$$

With the same procedure used in the preceding section, the following results are obtained:

$$\sum_i i(N_i + N_i^*) = M_{\text{in}} - M \tag{21}$$

as should be expected, for the difference in the right-hand side represents the total amount of monomer consumed in the reaction, which must be either in active or inactive chains, and

$$\sum_i N_i = k_tT_0I_0t \tag{22}$$

as before, showing that the total amount of inactive chains is proportional to the reaction time, as long as the initial concentration of transfer agent remains constant.

Obviously the results obtained in this case for the averages are the same as those of Nanda and Jain[4] if the spontaneous transfer rate constant is replaced by its present counterpart k_tT_0. Defining as in ref 4

$$\alpha = k_tT_0/k_PM_0\ (=1/R), \qquad \beta = M_0/I_0, \qquad Y = (M_0 - M)/M_0 \tag{23}$$

one gets:

$$i_n = (1 + Y\beta)\Big/\left[1 - \alpha\beta\ln\left(1 - \frac{Y}{1 + \alpha}\right)\right] \tag{24}$$

and

$$i_w = 1 + [(1 + Y\beta)(\alpha\beta - 1)]^{-1}\left[Y\beta^2(1 + \alpha) \times \left(2 - \frac{Y}{1 + \alpha}\right) - 2Y\alpha\beta^2 + 2(1 + \beta)\left\{1 - \left(1 - \frac{Y}{1 + \alpha}\right)^{\alpha\beta}\right\} - 2\beta(1 + \beta)(1 + \alpha) \times (1 + \alpha\beta)^{-1}\left\{1 - \left(1 - \frac{Y}{1 + \alpha}\right)^{1+\alpha\beta}\right\}\right] \tag{25}$$

The limiting values at time τ, $(i_n)_\tau$ and $(i_w)_\tau$, when the whole of the monomer has been depleted, are easily obtained from the above equations by putting $Y = 1$.

Both *M* and *T* Change with Time

It is obvious that with the kinetic scheme considered here T must vary with time, but the preceding case can be thought of as the limiting situation in which $k_PM \gg k_tT$, and this situation can always be obtained, in principle, by using a very big ratio of M_0/T_0. Even so, an inherent error is introduced, for when the monomer has been almost totally consumed the inequality can no longer hold. Therefore, if such an error is to be removed the depletion of the transfer agent must be considered along with that of the monomer, and when this is done one finds, as will be shown below, that the actual condition for T being considered as a constant is $k_P \gg k_t$.

Upon integration of eq 5, the concentration of the transfer agent as a function of time is given by

$$T = T_0\exp(-k_tI_0t) \tag{26}$$

where T_0 is the initial concentration. When this result is introduced in eq 4 and the latter is integrated, the following relation for M is obtained:

$$M = \{M_0 + T_0/r\}\exp(-k_PI_0t) - T_0/r\exp(-k_tI_0t) \tag{27}$$

where $r = (k_P - k_t)/k_t$. Therefore the time τ at which the monomer concentration has reduced to zero is

$$\tau = \frac{1}{(k_P - k_t)I_0}\ln\left\{1 + \frac{M_0}{T_0}r\right\} \tag{28}$$

where we have assumed only the case $r > 0$, that is to say, $k_P > k_t$.[18] There are two limiting values: if $r \rightarrow 0$,

$$\tau = \frac{M_0}{k_tI_0T_0} \tag{29a}$$

if $r \rightarrow \infty$,

$$\tau = \frac{1}{k_PI_0}\ln\frac{k_PM_0}{k_tT_0} \tag{29b}$$

The last result is the same as that obtained from eq 20 (when T is considered constant at T_0) for the particular case $k_P \gg k_t$, since in this case the transfer agent disappears so slowly vs. the monomer that its concentration can be considered constant at the initial value.

By using once again the general procedure outlined before, we obtain:

$$\sum_i i(N_i + N_i^*) = M_{\text{in}} - M \tag{30}$$

as expected for reasons already given, and

$$\sum_i N_i = T_0\{1 - \exp(-k_tI_0t)\} = T_0 - T \tag{31}$$

a result which could also be expected by direct inspection of the kinetic mechanism.

The last equation tells us that the sum of concentrations of inactive chains goes asymptotically T_0. However, if k_t (or actually k_tI_0) is very small, an expansion of the exponential gives the same result as the assumption of T remaining constant at T_0. That is because in such a case the actual reaction times are relatively short and we are at the beginning of a curve which can be considered as a straight line passing through the origin. As k_t increases $\sum_i N_i$ more quickly goes toward T_0, and the assumption of T being constant is less valid.

With the above results, the number-average chain length is therefore

$$i_n = (M_{in} - M)/(I_0 + T_0 - T) \tag{32}$$

and, upon substitution of the T value at τ, one gets

$$(i_n)_\tau = M_{in}\Big/\left[I_0 + T_0\left\{1 - \left(1 + \frac{M_0}{T_0}r\right)^{-1/r}\right\}\right] \tag{33}$$

We can consider again two limiting values: if $r \rightarrow 0$,

$$(i_n)_\tau = M_{in}/[I_0 + T_0\{1 - \exp(-M_0/T_0)\}] \tag{34a}$$

if $r \rightarrow \infty$,

$$(i_n)_\tau = M_{in}/I_0 \tag{34b}$$

The last one is the same as that obtained under the assumption of T constant if $k_P \gg k_t$. On the other hand, if $M_0 \gg T_0$, as is usual in practice, the former reduces to $(i_n)_\tau = M_{in}/(I_0 + T_0)$, and if T_0 and I_0 are of the same order of magnitude, the number-average chain length reduces by a factor of 2 with respect to the limit $r \rightarrow \infty$. In any case, we see that the number-average chain length increases, as expected, with the difference $k_P - k_t$. Of course, no limit is actually found, but for "true" polymerizations, that is to say, for reactions which really give rise to sufficiently long chains, we must expect to be close to the second limiting value. Accordingly, the r value, which can be quite easily obtained from the experimental value for (i_n) and eq 33 by a trial and error procedure, is expected to have quite a high value.

As for the weight-average chain length, the integral appearing in eq 11 is very involved. However, it can be solved exactly if r happens to be an integer by defining a new variable $x = \exp(-k_t I_0 t) = T/T_0$. If the value of r is high, the error introduced by taking the nearest integer is expected to be much smaller than the experimental errors associated with the actual determination of i_w. Under that assumption ($r \simeq m$ = integer), one obtains

$$i_w = 1 + A/(M_{in} - M) \tag{35}$$

where

$$\begin{aligned} A = \int_0^t 2k_P M \sum_i iN_i^* \, dt = 2\frac{m+1}{m^2}T_0(1 - T/T_0) - \\ \frac{2}{m}(M_0 + T_0/m)[1 - (T/T_0)^{m+1}] + \\ a\left[\frac{1}{I_0}(M_0 + T_0/m)\{\exp(T_0/I_0)\varphi_2 - \exp(T/I_0)\varphi_3\} - \right. \\ \left. \frac{1}{m}\{\exp(T_0/I_0) - \exp(T/I_0)\}\right] - \\ b[(T_0/I_0)\varphi_4/m - (M_0 + T_0/m)\varphi_5/I_0] \end{aligned} \tag{36}$$

In this equation the following definitions have been used:

$$a = 2(m+1)^2 \exp(-T_0/I_0)\left[\frac{1}{m}I_0 - (M_0 + T_0/m)\varphi_1\right]$$

$$b = 2(m+1)^2(M_0 + T_0/m)$$

$$\varphi_1 = \sum_{j=0}^{m} \frac{m!}{(m-j)!}(I_0/T_0)^{j+1}$$

$$\varphi_2 = \sum_{j=0}^{m} (-1)^j \frac{m!}{(m-j)!}(I_0/T_0)^{j+1}$$

$$\varphi_3 = \sum_{j=0}^{m} (-1)^j \frac{m!}{(m-j)!}(I_0/T_0)^{j+1}(T/T_0)^{m-j}$$

$$\varphi_4 = \sum_{j=0}^{m} \frac{m!}{(m-j)!}(I_0/T_0)^{j+1}\frac{1}{m-j+1}[1 - (T/T_0)^{m-j+1}]$$

$$\varphi_5 = \sum_{j=0}^{m} \frac{m!}{(m-j)!}(I_0/T_0)^{j+1}\frac{1}{2m-j+1}[1 - (T/T_0)^{2m-j+1}]$$

The limiting value when the whole of the monomer has been consumed is obtained upon substituting in the above expression the value T_τ, obtained from eq 26 and 28.

For given values of M_{in}, I_0, and T_0, the experimental determination of $(i_n)_\tau$ gives r by using eq 33. If τ is also determined, and eq 28 is used, both k_P and k_t can be estimated. Then using for m the nearest integer to the value found for r, together with the estimated value of k_t, the preceding sums, as well as a and b, can be obtained both as a function of time or for time τ, as said before. The agreement of the theoretically predicted results with the experimental values is an acceptable proof of the reaction proceeding along the kinetic mechanism considered here.

A computer program in FORTRAN language has been written in order to process along these lines the experimental results obtained in living polymerizations in which it is well established that a transfer agent plays an important role. Numerical results will be given in subsequent papers. Usually, in the experimental work the transfer agent and the initiator are used at concentrations several hundred times lower than those of monomer; therefore some simplifications could be introduced in the formula for i_w, for which proper allowance was made in the computer program.

Results and Discussion

After solving in the preceding sections the problem of a living polymerization involving a transfer agent, the obvious question is under what circumstances the approximate results for M changing while T is constant, in which the concentration of the transfer agent was assumed constant at its initial value, can be used. It has already been said that in the limit when $k_P \gg k_t$ the approximation is valid, but there is another factor which decisively influences the actual validity of the assumption that T remains constant. From the exact solution for M and T both changing with time, the following result is obtained for the fraction of transfer agent remaining after the whole of the monomer has been consumed:

$$(T/T_0) = (1 + mM_0/T_0)^{-1/m} \tag{37}$$

Such a quantity is seen to depend not only upon m but also upon the ratio between M_0 ($=M_{in} - I_0$) and the initial amount of transfer agent. In Table I values of (T/T_0) are given for a wide range of values of m and M_0/T_0. The values in Table I show the expected behavior. As the ratio M_0/T_0 increases for a given m, the fraction of transfer agent at the end of the reaction decreases, as more time is needed for the total depletion of monomer. However, the effect is much less important as m increases. If we use as a criterion for the validity of taking T as a constant an error below 5%, the propagation rate constant must be several hundred times bigger than the transfer rate constant in order for the ratio M_0/T_0 to have no practical influence. Moreover, when both m and M_0/T_0 are small, we have $\alpha \gg 1$ in eq 24 and in the limit at total conversion $i_n \simeq 1$. On the contrary, if both m and M_0/T_0 are large,

Table I
Fraction of Transfer Agent Remaining after Total Depletion of Monomer for Different Values of m and M_0/T_0

	$m =$					
M_0/T_0	1	5	20	50	200	1000
1	0.5000	0.6988	0.8588	0.9244	0.9738	0.9931
10	0.0909	0.4555	0.7671	0.8831	0.9627	0.9908
50	0.0200	0.3312	0.7079	0.8551	0.9550	0.9892
100	0.0099	0.2884	0.6838	0.8434	0.9517	0.9886
500	0.0020	0.2091	0.6310	0.8167	0.9441	0.9870
1000	0.0009	0.1821	0.6095	0.8054	0.9408	0.9863

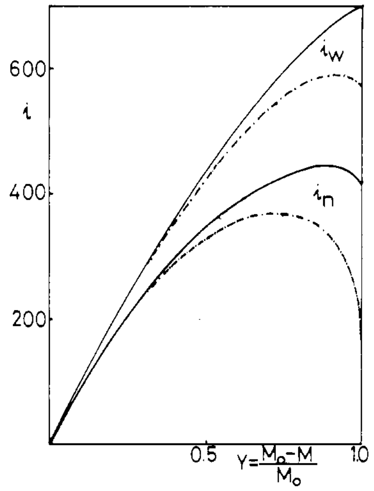

Figure 1. Number-average and weight-average chain lengths as a function of conversion. Full lines refer to the exact solutions; dashed lines correspond to approximate values with T considered constant. The following numerical values were used: $M_{\text{in}} = 10$, $I_0 = 10^{-2}$, $T_0 = 1.5 \times 10^{-2}$ mol dm^{-3}, and $k_p/k_t = 2$.

we obtain the limit $\alpha \ll 1$ and eq 24 predicts, at total conversion, $i_n = 1 + M_0/I_0 \simeq M_0/I_0$. Values of several hundreds for the ratio M_0/T_0 are most frequently used, and in these circumstances it appears clear that only when $m > 200$ can one consider the transfer agent concentration as a constant; otherwise, the formulas given in the section on M changing while T is constant, when used for the analysis of the experimental results, could be misleading. In such cases, which can be quite frequent, use must be made of the exact expressions derived in the preceding section.

So far, the validity of the approximate equations (for T constant) has been discussed only at total conversion of the monomer. It would also be worthwhile, however, to consider the situation through the whole conversion range, mostly for low values of k_P/k_t, when the errors introduced at 100% conversion are quite important. In Figure 1 the approximate and exact values of the number-average and weight-average chain lengths are plotted as a function of the conversion for $k_P/k_t = 2$ ($m = 1$). At conversions below 30%, the approximate formulas (with T assumed constant) yield the same results as the exact ones, but the error increases as the conversion does. Obviously, such an error would decrease with increasing m, and the approximate equations could be safely used even for high conversions when m is large enough, as indicated in the discussion above.

This trend was corroborated by calculations with m up to 6 and different M_0/T_0 ratios. The shape of the curve remains the same, with the maxima displaced toward higher conversions and the curves approaching each other as m increases, while the effect of increasing the M_0/T_0 ratio is to reduce the difference between the exact and the approximate values. The calculations were made using an IBM 1130 system; under the "extended precision" feature, it works with nine significant figures and, as it is necessary to evaluate small differences between very large numbers when the exact equations for the T variable are used to compute i_w, values obtained for this quantity when $m > 6$ were meaningless.

In conclusion, we believe that the comparison between experimental data and the theoretical results obtained in this paper can be very useful for a better understanding of ionic polymerizations in which there exists a transfer reaction.

References and Notes

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(17) If $k_i \rightarrow \infty$, there is no time interval elapsed between the addition of initiator and the start of the reaction. For k_i finite but very much higher than both k_P and k_t, such a time interval should be finite, yet the approximation of instantaneous initiation should still be valid.
(18) When $k_t > k_P$ the time τ is defined only if $k_tT_0/(k_t - k_P)$ is greater than M_0 ($=M_{\text{in}} - I_0$), and this case will not be further considered. In the limit when $k_t \gg k_p$, only N_1 would be obtained.