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Functionalized Polymers by Noncatalytic Addition−Fragmentation Chain Transfer: Modeling and Simulation of End-Group Functionality and Molecular Weight Distribution for High-Conversion Reactions in a Batch Process

W. K. Busfield,*,† Ilyas Dawood,‡ and A. F. Johnson‡

School of Science, Griffith University, Nathan, Queensland 4111, Australia, and IRC in Polymer Science, School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

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ABSTRACT: Kinetic models of free radically initiated polymerizations involving chain transfer by the noncatalytic addition−fragmentation mechanism have been simulated with the aim of finding the effect of conversion on the molecular weight, molecular weight distribution, and the efficiency with which specific end-group-functionalized polymers are produced. The specific situations explored are those where (i) the magnitude of the chain transfer constant is varied in processes where the rate of initiation is moderate and termination takes place exclusively by combination or exclusively by disproportionation and (ii) the magnitude of the initiation rate is varied for processes where there is considerable chain transfer occurring and termination is exclusively by combination. These systems have been examined in detail because they relate to likely practical systems for the synthesis of well-tailored telechelic polymers. The results show that there are situations where it is possible to produce the functionalized polymers of interest with high efficiency but not with the concurrent control of the molecular weight distribution of the product.

Introduction

There is considerable interest in the production of architecturally designed functionalized polymers. One method showing much promise is that of chain transfer by the addition−fragmentation mechanism in free radically initiated polymerization of vinyl monomers. A large range of chain transfer agents have been explored including allylic sulfides[1] and sulfones,[2] methacrylate macromonomers,[3] vinyl ethers,[4] hydroxamine esters,[5] and ketene acetals,[6] with generally encouraging results; i.e., products with the desired end groups have been made with some degree of control over the mean molecular weight (MW) of the products. The examples fall into two groups; one leads to vinyl end groups in the fragmentation process,[1−3] which may either copolymerize and form grafts or undergo further addition−fragmentation with growing polymer radicals, thus acting as catalytic chain transfer agents as the reaction proceeds. There is a comprehensive review describing the kinetics and MW trends in these systems.[7] Fragmentation of the other group of chain transfer agents[4−6] leads to end groups that are inert in the system and take no further part in the reaction. These noncatalytic addition−fragmentation chain transfer agents are the subject of this paper. It is clear that, even in this group, unless the chain transfer constant of the transfer agent has the ideal value of unity, the instantaneous MW of the polymer will drift with conversion, leading to a broadening of molecular weight distribution (MWD). Also, conventional radical initiation reactions will inevitably lead to the incorporation into the product of initiator fragments or other groups derived in the initiation process. Thus, the fraction of target functionalized-polymer molecules produced may be significantly less than unity, especially in the cases where the chain transfer constants are very large and the conversion is high, or where the initiation rates are very fast.

The aim here is to use modeling and computer simulation techniques to explore the synthetic routes to polymers with specific end groups in free radical polymerizations with chain transfer. Particular attention has been given to the efficiency of selected high-conversion batch processes together with the impact of the chemistry on the MW and MWD of the products. In these studies, the commonly accepted reaction mechanisms for radically initiated polymerization have been adopted and it has also been assumed that the batch reactor conditions are ideal in every way. These assumptions have made it possible to develop algorithms for MW and MWD predictions for different reaction input conditions including rate constants and initial concentrations. A longer term objective is to compare model predictions with real experimental results, which will make it possible, should it be needed, to extend the models to take into account nonidealities in both the chemistry and physical conditions within a reactor and still produce polymers with the desired MW, MWD, and functionality.

Reaction Mechanism

All steps in a chain polymerization process influence the nature of the polymer produced but the mechanism of termination processes have a particularly strong influence on the analyses described here. For convenience, the two cases of termination by combination and termination by disproportionation have been treated separately below.

The reaction scheme that forms the basis of the calculations carried out is as follows:

$$\mathrm{I} \xrightarrow{k_\mathrm{i}} 2\mathrm{R}^\bullet \qquad \mathrm{d}[\mathrm{I}]/\mathrm{d}t = -k_\mathrm{i}[\mathrm{I}] \tag{1}$$

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† Griffith University.
‡ University of Leeds.

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$$R^\bullet + M \xrightarrow{k_p} P_1^\bullet \qquad d[R^\bullet]/dt = -2fk_i[I] \tag{2}$$

$$P_n^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet \qquad d[M]/dt = -\,k_p[M][P_n^\bullet] \tag{3}$$

$$P_n^\bullet + S \xrightarrow{k_{TR}} P_nX + S^\bullet \qquad d[S]/dt = -k_{TR}[S][P_n^\bullet] \tag{4}$$

$$S^\bullet + M \xrightarrow{k_p} P_1^\bullet$$

$$\text{(i)}\quad P_n^\bullet + P_m^\bullet \xrightarrow{k_{TC}} P_{n+m} \quad d[P_n^\bullet]/dt = -2k_{TC}[P_n^\bullet]^2 \tag{5}$$

$$\text{(ii)}\quad P_n^\bullet + P_m^\bullet \xrightarrow{k_{TD}} P_n + P_m \qquad d[P_n^\bullet]/dt = -2k_{TD}[P_n^\bullet]^2 \tag{6}$$

where k_i, k_p, k_{TR}, k_{TC}, and k_{TD} are rate constants for initiation, propagation, transfer, and termination by combination (i) and disproportionation (ii), respectively, f is the initiator efficiency, and I, M, and S are initiator, monomer and transfer agent, respectively. With reasonable kinetic chain lengths, the termination rate quickly becomes equal to the initiation rate, i.e.,

$$2k_T[P_n^\bullet]^2 = 2fk_i[I] \qquad \text{or} \qquad [P_n^\bullet] = (fk_i[I]/k_T)^{1/2} \tag{7}$$

Molecular Weight

The instantaneous number average degree of polymerization, h, is given by the ratio of the rate of monomer loss to the rate of dead polymer formation and can be formalized for each of the situations of interest here:

(i) Termination by combination (eq 5)

$$h_c = k_p[M][P_n^\bullet]/(k_{TR}[S][P_n^\bullet] + k_{TD}[P_n^\bullet]^2) = (\alpha + \beta)^{-1} \tag{8}$$

where the subscript c denotes termination by combination and $c = k_{TR}/k_p$ = chain transfer constant, and $\alpha = c[S]/[M]$; $\beta = (fk_ik_T[I])^{1/2}/(k_p[M])$.

(ii) Termination by disproportionation (eq 6)

$$h_d = k_p[M][P_n^\bullet]/(k_{TR}[S][P_n^\bullet] + 2k_{TD}[P_n^\bullet]^2) = (\alpha + 2\beta)^{-1} \tag{9}$$

where the subscript d denotes termination by disproportionation.

The instantaneous weight average degree of polymerization, w, is given by the following eqs, which are derived from those given by Peebles[8] for the case of invariant monomer concentration together with a constant rate of initiation and chain transfer to monomer and/or solvent.

(i) Termination by combination

$$w_c = 2(\alpha + 3\beta)/(\alpha + 2\beta)^2 \tag{10}$$

(ii) Termination by disproportionation

$$w_d = (2 + \alpha + 2\beta)/(\alpha + 2\beta) \tag{11}$$

The instantaneous MWs are easily derived by multiplying the appropriate degrees of polymerization (eqs 8−11) by the molecular weight of the monomer. The instantaneous polydispersity index, PDI, is given by eqs 12 and 13.

$$(\mathrm{PDI})_c = 2(\alpha + 3\beta)(\alpha + \beta)/(\alpha + 2\beta)^2 \tag{12}$$

$$(\mathrm{PDI})_d = 2 + \alpha + 2\beta \tag{13}$$

Equations for the instantaneous weight fractions of polymer, $w(r)$, as a function of chain length, r, have also been derived from the eqs given by Peebles[8] under the same conditions as those used for the derivation of w_c and w_d. They are

(i) Termination by combination

$$w(r)_c = r(\alpha + 2\beta)[\alpha + (r - 1)\beta(\alpha + 2\beta)]/(1 + \alpha + 2\beta)^r \tag{14}$$

(ii) Termination by disproportionation

$$w(r)_d = r(\alpha + 2\beta)^2/(1 + \alpha + 2\beta)^{r+1} \tag{15}$$

The cumulative number average degree of polymerization, g, after polymerization to a specific conversion can also be derived by counting end groups, since all the end groups are derived from initiator loss, transfer agent loss, or termination (by disproportionation) and these are given below for the different modes of termination.

(i) Termination by combination

$$g_c = ([M]_0 - [M])/\{f([I]_0 - [I]) + ([S]_0 - [S])\} \tag{16}$$

(ii) Termination by disproportionation

$$g_d = ([M]_0 - [M])/\{2f([I]_0 - [I]) + ([S]_0 - [S])\} \tag{17}$$

The subscript zero designates initial conditions in the above eqs.

Efficiency of Target Molecule Production

The target polymer molecules are shown as SM_nX in the reaction mechanism where S and X represent end groups derived solely from the chain transfer agent. Other molecules produced when termination is by combination are IM_nI, IM_nX, SM_nI, and SM_nS. For this particular case, the following analysis holds:

If, in any given increment of monomer conversion, −dM, the numbers of moles of these polymers produced are dn_1, dn_2, dn_3, dn_4, respectively, and the target molecules are given by dn_5, then a series of eqs can be set up that allows the efficiency of target polymer production to be found for that increment of conversion, i.e., $dn_5/\sum_{a=1}^{5} d_{n_a}$.

These equations are

$$-d[I] = (2dn_1 + dn_2 + dn_3)/2f \tag{18}$$

$$-d[S] = dn_2 + dn_5 \tag{19}$$

$$= dn_3 + 2dn_4 + dn_5 \tag{20}$$

$$dn_2/dn_5 = (2fd[I])/d[S] \tag{21}$$

$$-d[M]/h_c = \sum_{a=1}^{5} d_{n_a} \tag{22}$$

To obtain eq 21, it is necessary to assume that the ratio of growing free radicals terminating in S to those terminating in I ($[SM_n^\bullet]/[IM_n^\bullet]$) is equal to the ratio of the rates of formation of the initial radicals, ($(d[S^\bullet]/dt)/(d[I^\bullet]/dt)$), i.e., that growth and transfer of the growing radicals are independent of the nonradical end group. Elimination leads to the equation that defines the desired fraction of target molecules, χ_c

$$\chi_c = dn_5/\sum_{a=1}^{5} d_{n_a} = (1 - h_c f d[I]/d[M])/(1 + 2f d[I]/d[S]) = (1 - h_c\beta)/(1 + 2\beta/\alpha) \qquad (23)$$

For the case of termination by disproportionation, the nontarget polymer molecules in this case are IM_nE_1, IM_nE_2, IM_nX, SM_nE_1, and SM_nE_2 where E_1 and E_2 are the end groups derived from disproportionation termination. A similar set of relationships to that arrived at for the case of combination termination gives, on elimination, the expression for the fraction of target molecules, SM_nX, in this specific case (eq 24).

$$\chi_d = (1 - 2h_d f d[I]/d[M])/(1 + 2f d[I]/d[S]) = (1 - 2h_d\beta)/(1 + 2\beta/\alpha) \qquad (24)$$

Simulation

Although it is conventional to use time, t, as the independent variable in the simulation of kinetic models, it is more convenient in pursuing the objectives in this work to use the conversion as the independent variable. The conversion, P, is defined as the fraction of reaction from zero time to the point at which the desired total conversion has been reached:

$$P = ([M]_0 - [M])/([M]_0 - [M]_f) \qquad (25)$$

If, for example, it is required to study the changes up to 70% conversion with an initial monomer concentration of 1 mol L^{-1}, $[M]_0$ is set at 1 mol L^{-1} and $[M]_f$ is set at 0.3 mol L^{-1}.

The input data include the kinetic constants (k_i, k_T, k_p, and c), initial concentrations ($[I]_0$, $[M]_0$, and $[S]_0$), initiator efficiency (f), and the final monomer concentration, $[M]_f$. Three differential equations are set up to generate values of [I], [S], and time, t, as a function of conversion (eqs 26−28),

$$d[I]/d[P] = -\beta([M]_0 - [M]_f)/f \qquad (26)$$

$$d[S]/d[P] = -\alpha([M]_0 - [M]_f) \qquad (27)$$

$$dt/d[P] = k_T([M]_0 - [M]_f)/(\beta k_p^2) \qquad (28)$$

where [M] is derived from data input to eq 25.

Further eqs are set up to generate values of t, h, w, g, α, β, and χ as a function of conversion. The values of the key parameters are plotted directly from the computer calculations, e.g., h and g vs P or P vs t, or compiled in a data file at prechosen intervals of conversion, e.g., 5% intervals (as in the examples presented here). The value of P is ramped from 0 to 1 at constant prechosen intervals in the computations; in this work it was increased at 1% intervals.

Generation of MWDs

Weight fractions, $w(r)$, are calculated using eqs 14 or 15, for each value of r from 1 to a prechosen upper limit (e.g., 500 or 1000 depending on the expected MWs) and for each conversion increment. A plot is made of the total weight fraction for each value of r, summed over the conversion range from $P = 0-1$ and divided by the number of increments, m (e.g., $m = 21$ if 5% increments are used), versus the MWD of the final polymer.

The overall number average degree of polymerization, $\bar{h}$, is obtained by averaging the inverse value of h calculated for each increment by eq 8 or 9 (eq 29).

$$h = m/\sum_{P=0}^{1}(h)^{-1} \qquad (29)$$

The final weight average degree of polymerization, $\bar{w}$, is obtained by averaging w calculated for each increment by eq 10 or 11 (eq 30).

$$\bar{w} = \sum_{P=0}^{1} w/m \qquad (30)$$

The polydispersity index of the final polymer is then given by $\bar{w}/\bar{h}$.

Fraction of Target Polymer Molecules

The overall fraction of target molecules, $\bar{\chi}$, is given by the total number of target polymer molecules, divided by the total number of polymer molecules which leads to

$$\bar{\chi} = \frac{g}{m}\sum_{P=0}^{1}(\chi/h) \qquad (31)$$

It should be noted that χ, g, w, and h all have different values for the cases of termination by combination and by disproportionation.

Influence of Chain Transfer Constant with a Moderate Rate of Initiation

(i) Termination by Combination. To illustrate the influence of conversion on the MW, MWD, and the efficiency of target end-group production in the functionalized polymer molecules, χ, a typical set of values of input constants and initial concentrations have been used, as shown in Table 1. A roughly similar MW was targeted by keeping the product $c[S]_0$ to a constant value of 0.025 for three cases that might be described as having high, ideal, and low values of c.

The trend in the instantaneous value of h and cumulative degrees of polymerization (g) up to a conversion of 80% for the three cases of chain transfer coupled with termination by combination are illustrated in Figure 1. The fact that there is a negligible drift of MW with conversion for the ideal case of $c = 1$ is well-illustrated in Figure 1B and the large drift of h with conversion when c is either greater or less than 1 is equally clear in Figure 1A,C, respectively. For example, h increases by a factor of 6 from 0 to 40% conversion ($P = 0-0.5$) when $c = 5$ and decreases by 30% from 0 to 40% conversion when $c = 0.1$. Deviations of the cumulative degree of polymerization (g) are, of course, significantly less. A comparison of the deviations of h (Figure 1A−C) with the conversion of the chain transfer agent (dashed line) and monomer for each case (Figure 1D−F) readily explains the reason for the observed changes: The ratio [S]/[M] has decreased almost 10-fold

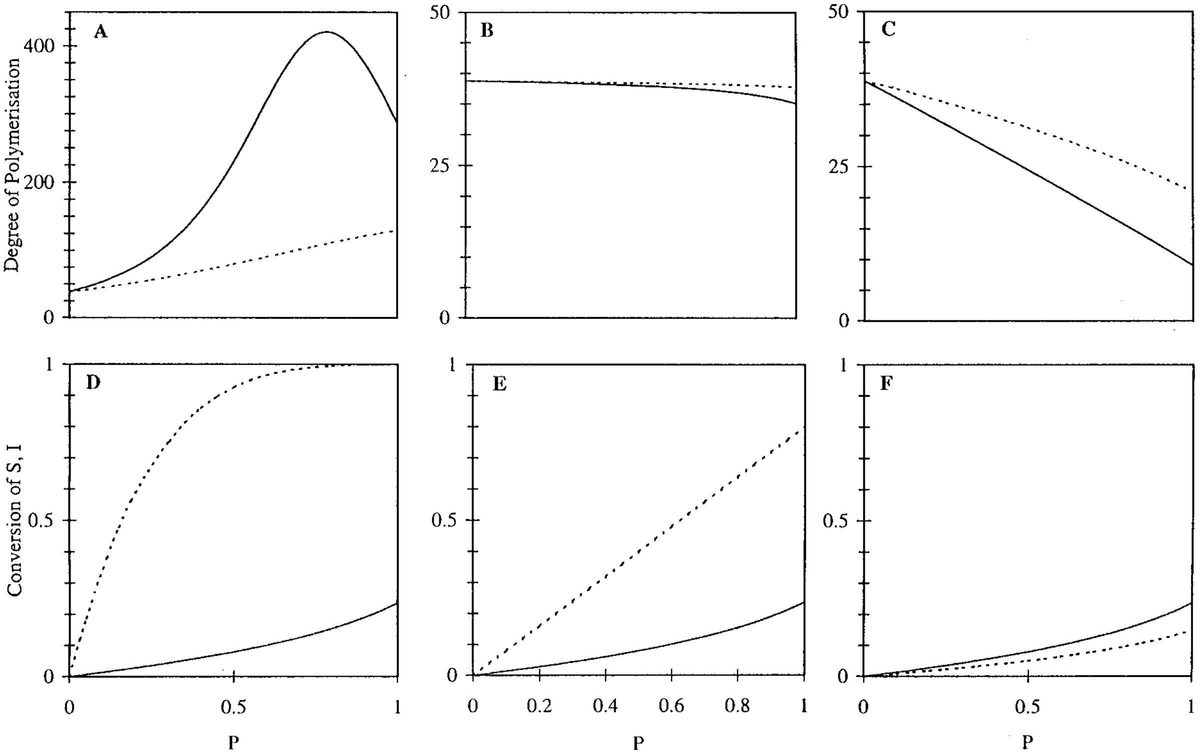

Figure 1. Effect of conversion up to 80% ($P = 1$) on instantaneous (full line) and cumulative (dashed line) number average degrees of polymerization for chain transfer constants $c = 5$ (A), 1 (B), and 0.1 (C), and on the conversion of initiator (full line) and chain transfer agent (dashed line) for chain transfer constants, $c = 5$ (D), 1 (E), and 0.1 (F). Termination by combination.

Table 1. Kinetic Constants and Initial Concentrations Used for Simulation Experiments (C = Combination, D = Disproportionation; All Symbols Defined in the Text)

simulation code	k_p, L mol^{-1} s^{-1}	k_T, L mol^{-1} s^{-1}	f	k_i, s^{-1}	c	$[M]_0$, mol L^{-1}	$[I]_0$, mol L^{-1}	$[S]_0$, mol L^{-1}	termn mode
A_1	200	10^6	1	5×10^{-6}	5	1	5×10^{-3}	5×10^{-3}	C
B_1	200	10^6	1	5×10^{-6}	1	1	5×10^{-3}	2.5×10^{-2}	C
C_1	200	10^6	1	5×10^{-6}	0.1	1	5×10^{-3}	2.5×10^{-1}	C
A_2	200	10^6	1	5×10^{-6}	5	1	5×10^{-3}	5×10^{-3}	D
B_2	200	10^6	1	5×10^{-6}	0.1	1	5×10^{-3}	2.5×10^{-1}	D
A_3	200	10^6	1	5×10^{-4}	5	1	2×10^{-2}	5×10^{-3}	C
B_3	200	10^6	1	1×10^{-6}	5	1	1×10^{-3}	5×10^{-3}	C
C_3	200	10^6	1	1×10^{-6}	5	1	5×10^{-2}	5×10^{-3}	C

from the initial value in the case of $c = 5$ and increased from 0.25 to 0.40 in the case of $c = 0.1$.

In the absence of chain transfer a relatively small change in the degree of polymerization with conversion is generally seen as a result of a drift in the monomer-to-initiator ratio. The exception is when $[M]/[I]^{1/2}$ remains constant with conversion (independent of the mode of termination). This condition pertains when $[I]_0 = (k_i k_T)/(4fk_p^2) = 3.125 \times 10^{-5}$ mol L^{-1} for the particular rate constants used in this example. With the more typical value of $[I]_0$ (=0.005 mol L^{-1}), h would steadily decrease with conversion in the absence of chain transfer as the ratio $[M]/[I]^{1/2}$ decreases. This drift can be observed in Figure 1A at conversions greater than 77%, a stage in the reaction when chain transfer has effectively ceased.

In Figure 2 are illustrated the monomer conversions with time for the different chain transfer situations considered (the rate of monomer conversion is not affected by the extent of chain transfer, everything else being equal).

The data required to calculate weight fractions up to final conversions of 20, 40, 60, and 80% are readily obtained during the simulation process. In each case, numerical values of these data at 5% intervals of P were used to calculate $w(r)$ values (eq 14) for each increment of conversion and each value of r. The sum of $w(r)$ values for each value of r over the conversion range, P

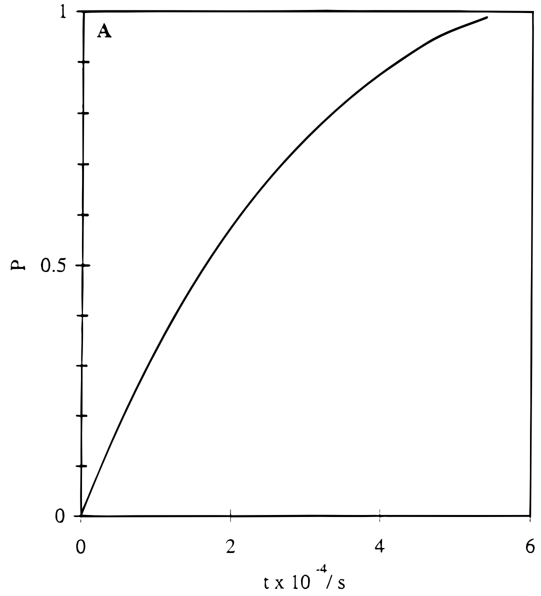

Figure 2. Monomer conversion up to 80% ($P = 1$) with time for simulations A_1, B_1, and C_1.

Table 2. Average MW and Fraction of Target Molecules at 20% and 80% Conversion in the Simulation Experiments (C = Combination, D = Disproportionation; All Symbols Defined in the Text)

				$\bar{n}$		$\bar{w}$		PDI		$\bar{\chi}$
simulation code	initiation rate	transfer rate	termn. mode	20%	80%	20%	80%	20%	80%	80%
A_1	mod	fast	C	57	125	120	390	2.1	3.1	0.70
B_1	mod	ideal	C	39	38	77	75	2.0	2.0	0.84
C_1	mod	slow	C	35	20	70	49	2.0	2.4	0.94
A_2	mod	fast	D	54	105	115	296	2.1	2.8	0.59
B_2	mod	slow	D	34	20	69	48	2.0	2.4	0.91
A_3	fast	fast	C	30	35	53	58	1.8	1.6	0.07
B_3	slow	fast	C	59	148	126	1011	2.1	6.8	0.94
C_3	mod	fast	C	55	115	117	300	2.1	2.6	0.60

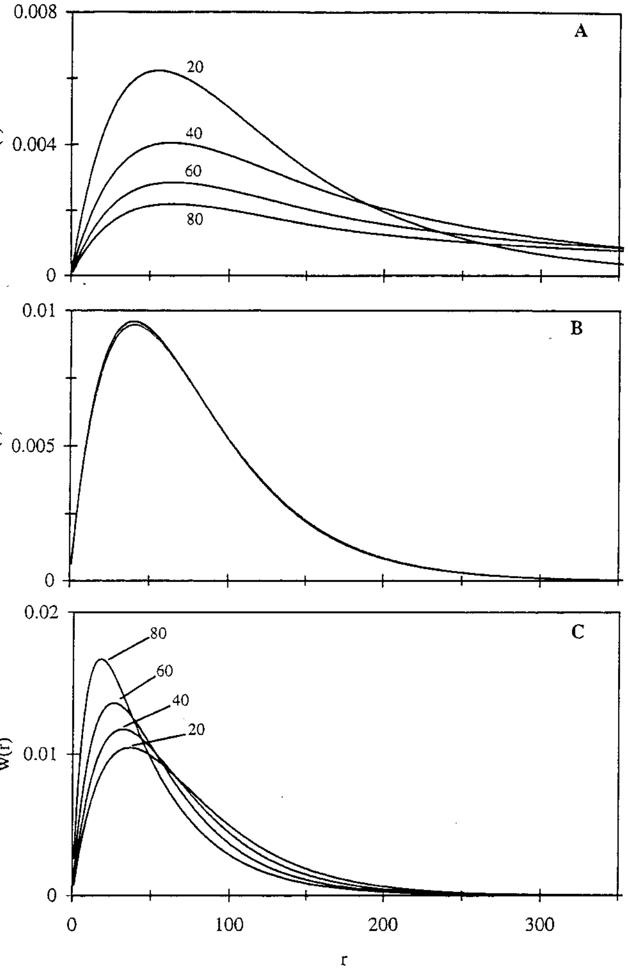

Figure 3. MWDs of polymers produced at 20, 40, 60, and 80% conversion with chain transfer constants $c = 5$ (A), 1 (B), and 0.1 (C). Termination by combination. Note: curves virtually overlap in B.

= 0−1, divided by 21 and plotted against r gives the MWDs shown in Figure 3. The same simulated data were also used to calculate $\bar{n}$ and $\bar{w}$ from eqs 29 and 30. The results obtained together with the polydispersity index of each polymer are given in Table 2.

When the chain transfer constant is large, the broadening of the MWD with conversion is very marked (Figure 3A). It is interesting to note that the numerical values of the polydispersity index at 20 and 80% conversion (Table 2) give little indication of the extent of the broadening. Another point of interest is that the number average degree of polymerization, $\bar{n}$, at 80% conversion lies well above the maximum on the MWD and not close to the maximum as commonly assumed.

The behavior observed for the ideal case when $c = 1$ is illustrated in Figure 3B where the MWDs at all conversions overlap completely, within computational errors, as might be expected. In addition, the PDIs are close to the most probable value of 2.0 up to high conversion, as is also expected for polymers with a reasonable degree of polymerization.

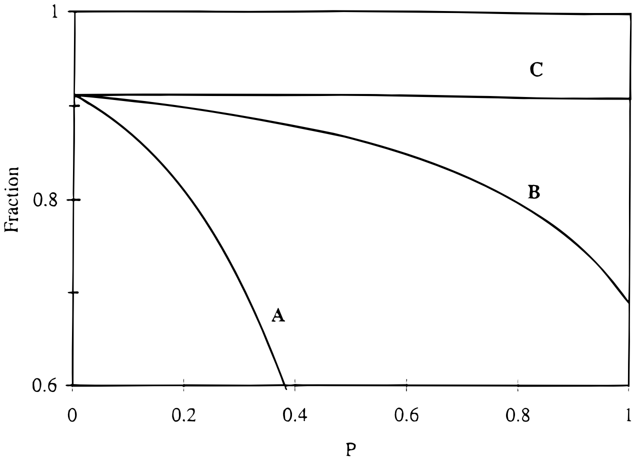

Figure 4. Instantaneous efficiencies of production of target polymer molecules as a function of conversion up to 80% ($P = 1$) with chain transfer constants $c = 5$ (A), 1 (B), and 0.1 (C). Termination by combination.

With a low value of the chain transfer constant, the MWD becomes narrower and the peak maximum decreases with increased conversion, as shown in Figure 3C. In keeping with this observation, the value of $\bar{n}$ decreases significantly, but in contrast and contrary to common expectation, the PDI increases, as shown in Table 2.

Kinetic modeling allows the prediction of the yield of target molecules SM_nX with the aid of eq 23. The fractional yields of target molecules as a function of conversion (maximum 80%, $P = 1$) for each chain transfer case with termination by combination are shown in Figure 4. Initially, slightly over 90% of the polymer molecules produced have the required funtionality irrespective of the magnitude of the chain transfer constant. Only when the chain transfer constant has a low value is this high level of efficiency sustained at higher conversions. Even in the ideal case ($c = 1$), the efficiency level drops significantly with conversion reaching an instantaneous value of 0.7 at $P = 1$ (80% conversion). The decrease is even more catastrophic when the chain transfer constant is larger (Figure 4A) as a result of the rapid loss of transfer agent with conversion. The average fraction of target molecules at 80% conversion, calculated from eq 31 are shown in Table 2. The level attained (84%) appears to be acceptable only because the polymers produced at higher conversions have higher MW values and therefore contribute smaller numbers of polymer molecules to the average fraction.

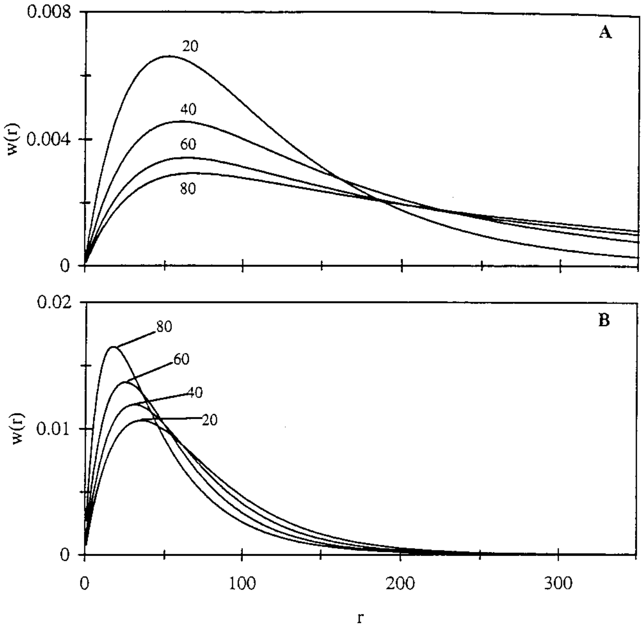

Figure 5. MWDs of polymers produced at 20, 40, 60, and 80% conversion with chain transfer constants $c = 5$ (A) and 0.1 (B). Termination by disproportionation.

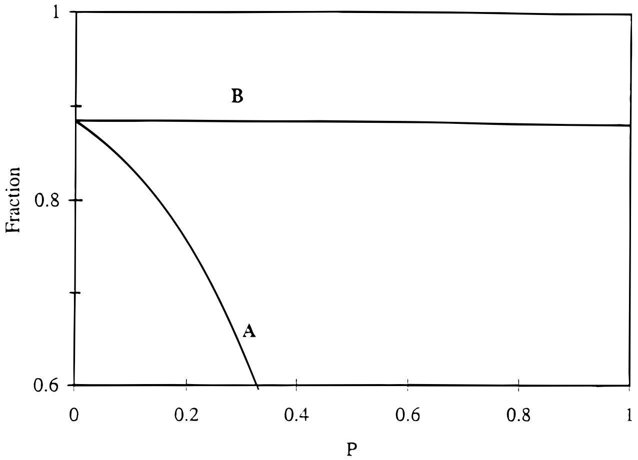

Figure 6. Instantaneous efficiencies of production of target polymer molecules as a function of conversion up to 80% ($P = 1$) with chain transfer constants $c = 5$ (A) and 0.1 (B). Termination by disproportionation.

Clearly, a system with a low chain transfer constant gives the most consistent and highest yield of target polymer molecules over the full conversion range.

(ii) Termination by Disproportionation. The MWs, MWDs, and fractions of target molecules obtained when simulations are carried out with large and small chain transfer constants and in situations where termination is by disproportionation are shown in Figures5 and 6 and Table 2. The other parameters used were the same as those used for the case of termination by combination (Table 1).

Qualitatively, the changes seen with conversion are similar to those described above for the cases where termination is by combination. The main differences are (i) the broadening of the MWD with conversion is slightly less for reactions where the chain transfer constant is large and (ii) the fractions of target molecules produced are less in both cases. These observations can be explained by the fact that more polymer molecules are produced in the case of disproportionation termination.

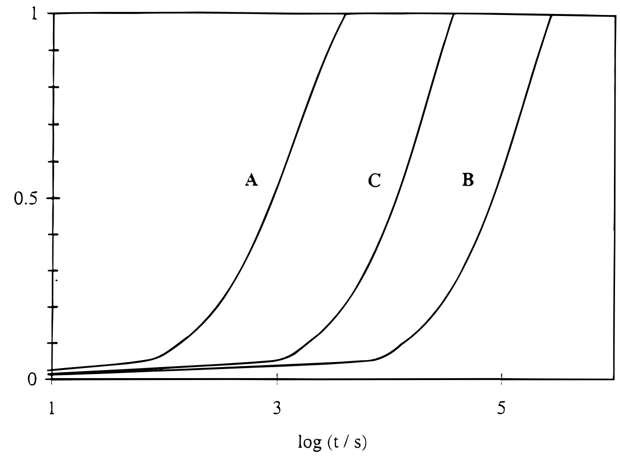

Figure 7. Monomer conversion up to 80% ($P = 1$) with time for simulations A_3 (A), B_3 (B), and C_3 (C).

Influence of Initiation Parameters

The form of eqs obtained for MW, MWD, and χ indicate that initiation parameters will influence the simulation output and calculations made from these data as well as the chain transfer parameters. For this reason, simulations have been carried out with three levels of initiation (see Table 1): fast initiation rate (large k_i, large $[I]_0$; A_3); slow initiation rate (small k_i, small $[I]_0$; B_3) and medium initiation rate (small k_i , large $[I]_0$; C_3). These have only been used for the case where the chain transfer constant is large (see Table 1). The difference in the time scales for the conversion of monomer is illustrated in Figure 7.

The trend in the magnitude of h and g with conversion for each initiation situation is shown in Figure 8. As in the earlier examples, $P = 1$ corresponds to 80% conversion. With a high rate of initiation, the variation in h over the conversion range is quite small. In fact, the whole MWD is only marginally affected by conversion (see Figure 9A). In contrast, the high MW polymers produced as the chain transfer agent concentration decreases when the initiation rate is low (see Figure 8) produce significant broadening of the MWD, as shown in Figure 9B,C. At the slowest initiation rate, the PDI increases from 2.1 at 20% conversion to 6.8 at 80% conversion (see Table 2).

Although a fast initiation rate has the least effect on the MWD at higher conversion, it is also the least useful in producing a reasonable yield of target molecules. The instantaneous fraction of target molecules produced as a function of conversion is shown for each case in Figure 10. With a fast rate of initiation, the maximum value of χ achieved is only 0.27 at zero conversion. Thereafter, it falls to an average value of only 0.07 at 80% conversion (Table 2). In contrast, a very slow rate of initiation results in a high average value of $\bar{\chi}$ of 0.94 at 80% conversion. Even though χ falls rapidly at higher conversion due to decreasing chain transfer (curve B, Figure 10), the polymer chains produced have such large MWs that they have little influence on the average fraction of target molecules. Realistically, however, these high MW molecules would constitute a large fraction of the mass of product and would have nontargeted end groups. Thus, in any practical situation, it

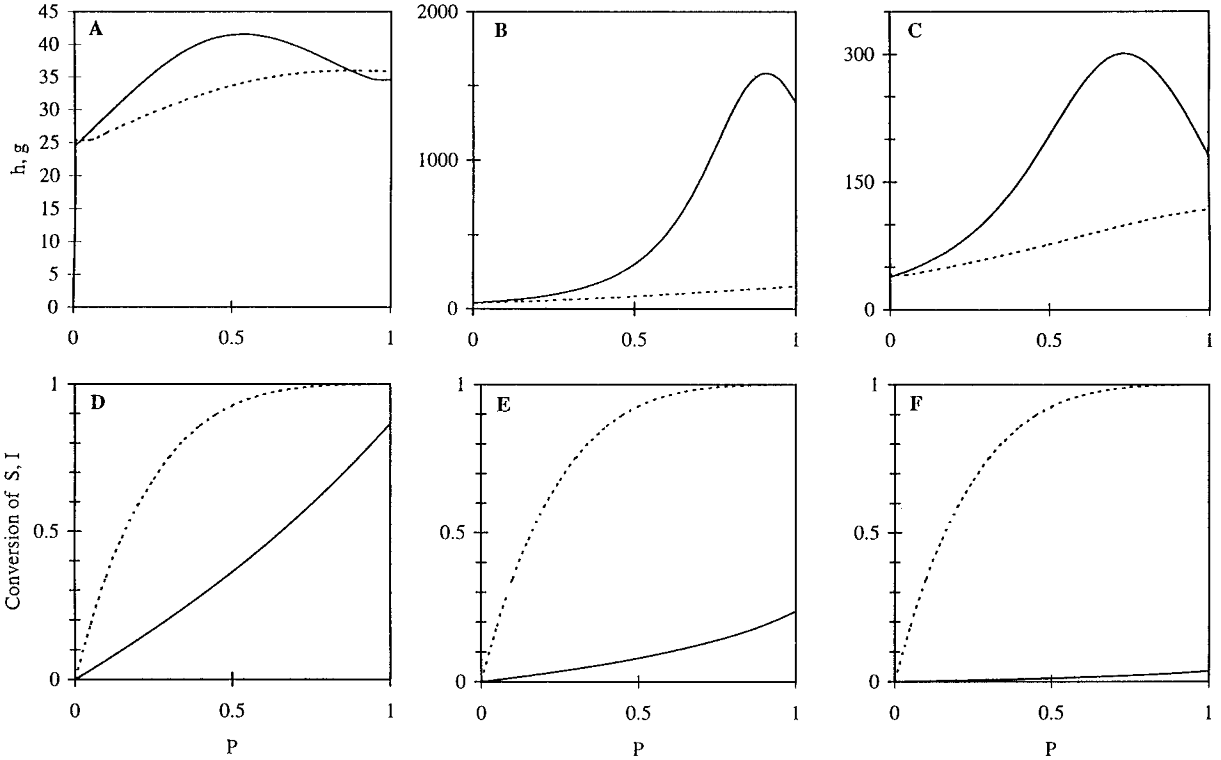

Figure 8. Effect of conversion up to 80% ($P = 1$) on instantaneous (full line) and cumulative (dashed line) number average degrees of polymerization for high (A), low (B), and medium (C) rates of initiation and on the conversion of initiator (full line) and chain transfer agent (dashed line) for high (D), low (E), and medium (F) initiation rates. Chain transfer constants $c = 5$ and termination by combination in all cases.

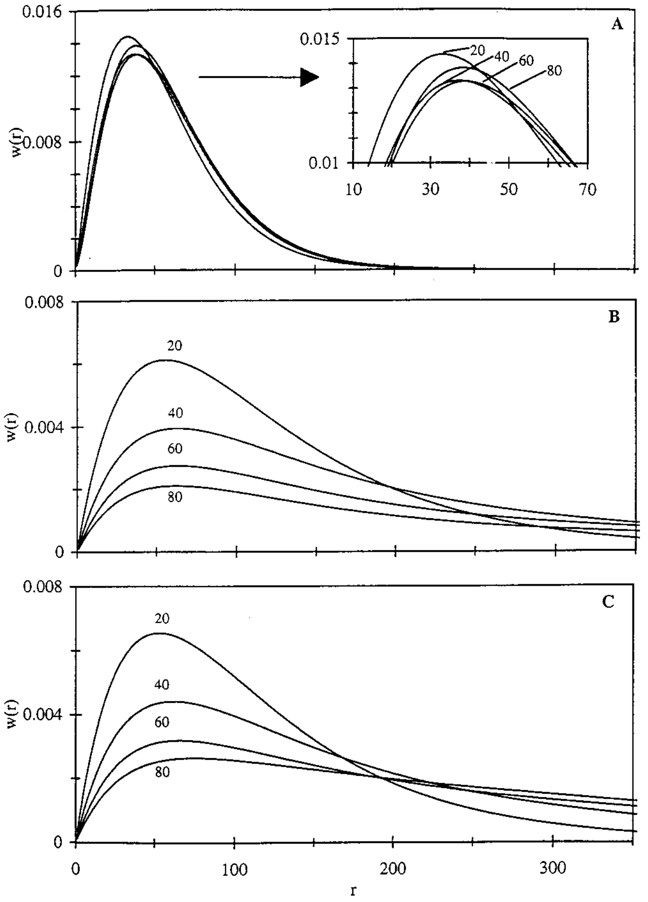

Figure 9. MWDs of polymers produced at 20, 40, 60 and 80% conversion with chain transfer constant $c = 5$ at high (A), low (B), and medium (C) rates of initiation. Termination by combination.

would be desirable to terminate such reactions at a lower conversion for optimum yields, e.g., at about $P = 0.4$, or 32% conversion.

Significantly less broadening of the MWD occurs if a larger concentration of initiator is used, as in case C_3. Here the PDI only reaches 2.6 at 80% conversion compared with 6.8 for the reaction with a low concentration of initiator, but the average fraction of target molecules is quite low, $\bar{\chi} = 0.60$ (see Table 2).

Computational Methods

All the calculations were carried out in a matter of seconds on a standard PC (Compaq, Prolinea 4/33) using commercially available software for the numerical integration of the ordinary differential eq sets (VISSIM, Visual Solutions) and MW and MWD calculations (EXCEL, Microsoft), both of which were run under the supervisory control of WINDOWS 95 (Microsoft).

Conclusions

It has been shown that the influence of conversion on MWs, MWDs, and the efficiency of production of targeted end-group-functionalized polymers by the addition−fragmentation chain transfer method can be readily simulated by solving the sets of ordinary differential equations that represent the appropriate reaction and by manipulation of the data thus obtained. Selective simulations have shown that, when the initiation rate is moderate, the efficiency with which it is possible to produce target functionalized polymers at high conversions in a batch process is best achieved when chain transfer agents with transfer constants less than 1 are used. When the transfer constant has the ideal value of 1, the MWD is virtually unaffected with conversion but the efficiency of target polymer produc-

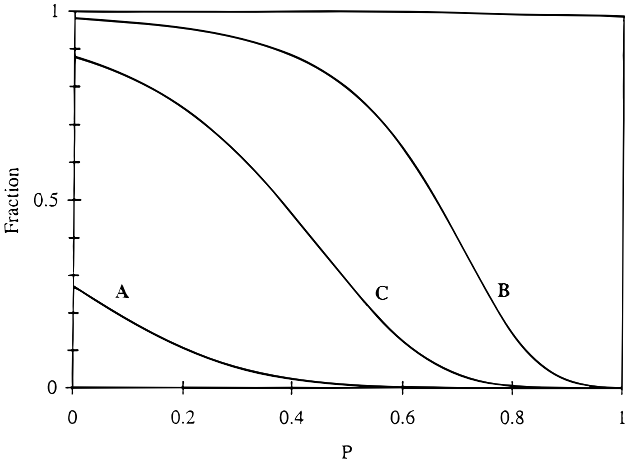

Figure 10. Instantaneous efficiencies of production of target polymer molecules as a function of conversion up to 80% ($P = 1$) with chain transfer constant $c = 5$ at high (A), low (B), and medium (C) rates of initiation. Termination by combination.

tion can decrease to values below 0.8 at very high conversion. Fast initiation rates result in very low yields of the target functionalized polymers. Slow initiation, coupled with dominant chain transfer reactions lead to the very efficient production of target functionalized polymers over a wide range of conversion. However, this desirable outcome is accompanied by very significant broadening of the MWD of the product, which might be less than desirable, particularly if the materials are to be incorporated into linear segmented block copolymers where the properties of the copolymers are dependent on phase separation to achieve the desired properties.

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