Moderated copolymerization: 3. Concentration changes in copolymerization with chain transfer: general equations, with special reference to moderated copolymerization

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The technique of moderated copolymerization enables fast reactions of propagating polymer radicals to be studied experimentally by conventional practical procedures. Although problems arising from high conversions are greatly reduced by this technique they are not completely eliminated. This paper presents general relations between monomer and transfer-agent conversions and degrees of polymerization which do not appear to have been reported previously for copolymerization. Their application to moderated copolymerization is described and illustrated by reference to the methyl acrylate/styrene/carbon tetrabromide system.

INTRODUCTION

The technique of moderated copolymerization was introduced to facilitate the study of fast reactions of propagating polymer radicals[1]. Monomer B, of which the radicals $\dot{B}$ are highly reactive towards a reagent S, is copolymerized with an excess of a moderating monomer A, having relatively inactive radicals, in the presence of S. In this way the incidence of $\dot{B}$ radicals in the kinetic chains is greatly reduced and the rate of reaction between S and $\dot{B}$ may be deduced from measurements of degrees of polymerization without recourse to extreme conditions, such as the use of excessively low concentrations of S, which introduce practical problems arising from high conversions[2]. The technique has been used successfully in the study of the transfer reaction of polystyryl radicals with carbon tetrabromide and has revealed the existence of a large penultimate unit effect in chain-transfer in some systems[3].

Although the conversion of S in a moderated copolymerization is normally much less than in a simple homopolymerization of B in the presence of S, significant conversions may be difficult to avoid in some circumstances. Further, since monomer B is present in low concentration, the fractional conversion of B may not always be negligible. It is to be expected that the experimental findings will be particularly sensitive to changes in concentrations of S and B; unless appropriate correction is made for these some effects such as moderate penultimate-unit influences may escape notice.

The present paper is concerned with this matter and describes correction procedures. It also provides general expressions for degrees of polymerization in copolymerization in the presence of a transfer agent when significant conversion of all reactants occurs, which do not seem to have been reported previously.

KINETICS

We employ the conventional kinetic scheme for the copolymerization of two vinyl monomers. This is the same as that written out in equation (7) of ref 1 except that the three possible termination reactions are incorporated:

$$
\begin{aligned}
&\sim\!\sim\dot{A} + \sim\!\sim\dot{A} \xrightarrow{k_{taa}} 2P\\
&\sim\!\sim\dot{A} + \sim\!\sim\dot{B} \xrightarrow{k_{tab}} 2P\\
&\sim\!\sim\dot{B} + \sim\!\sim\dot{B} \xrightarrow{k_{tbb}} 2P
\end{aligned}
\tag{1}
$$

We make the customary assumptions that the mean chain-length is large and that the ratio of the radical concentrations $[\dot{A}]/[\dot{B}]$ is not affected by the presence of the transfer agent S, but is determined solely by the propagation reactions. The latter are considered to be responsible for effectively all the monomer consumption. The total rate of termination may be written as $k_t[\dot{A}]^2$, where k_t is a summary termination rate coefficient which in general will be a function of monomer concentrations and k_{taa}, k_{tab} and k_{tbb}. Then if $\mathscr{I}$ is the rate of initiation we have:

$$\mathscr{I} = k_t[\dot{A}]^2 \tag{2}$$

Chain-transfer to monomers, which would be expected to be unimportant in moderated copolymerizations, is neglected. Application of the stationary state treatment leads to the equations (3a)–(3e)

$$-\frac{d[A]}{dt} = k_{ab}\frac{[\dot{A}]}{[A]}(r_A[A]^2 + [A][B]) \tag{3a}$$

$$-\frac{d[B]}{dt} = k_{ab}[\dot{A}]\frac{[B]}{[A]}([A] + r_B[B]) \tag{3b}$$

$$-\frac{d([A]+[B])}{dt} \equiv \omega =$$

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$$k_{ab}\frac{[\dot{A}]}{[A]}(r_A[A]^2 + 2[A][B] + r_B[B]^2) \tag{3c}$$

$$-\frac{d[S]}{dt} = k_{ab}[\dot{A}]\frac{[S]}{[A]}(r_AC_A[A] + r_BC_B[B])\cdot \tag{3d}$$

$$\frac{d[P]}{dt} = \mathscr{I} + k_{ab}[\dot{A}]\frac{[S]}{[A]}(r_AC_A[A] + r_BC_B[B]) \tag{3e}$$

In equations (3a)–(3e), r_A, r_B are reactivity ratios and C_A, C_B transfer constants for reactions of $\dot{A}$- and $\dot{B}$-type radicals with S, respectively; k_{ab} is the rate coefficient for propagation of $\dot{A}$-radicals with B-monomer.

We now consider two cases. In (i) monomer concentrations, $\mathscr{I}$ and ω remain effectively constant during copolymerization, although appreciable conversion of S may occur. This situation will be expected to arise frequently when transfer constant C_B has moderate values (e.g. about 50, as in the moderated copolymerization of styrene and methyl methacrylate in the presence of carbon tetrabromide[1]). In case (ii) all concentrations change as the reaction proceeds. This is evidently the most general case.

Case (i)

Elimination of $[\dot{A}]$ between equations (3c) and (3d) leads to the relation:

$$-\frac{d[S]}{dt} = [S]\sigma\omega \tag{4}$$

where

$$\sigma = \frac{r_AC_A[A] + r_BC_B[B]}{r_A[A]^2 + 2[A][B] + r_B[B]^2} \tag{5}$$

Since [A], [B], ω are assumed constant, equation (4) may be integrated directly to give:

$$[S] = [S]_0\exp(-\sigma\omega t) \tag{6}$$

in which $[S]_0$ is the initial concentration of transfer agent. Elimination of $[\dot{A}]$ between equations (3c) and (3e) and insertion of [S] from equation (6) into the resulting equation yields:

$$\frac{d[P]}{dt} = \mathscr{I} + [S]_0\sigma\omega\exp(-\sigma\omega t)$$

which on integration gives equation (7):

$$[P] = \mathscr{I}t + [S]_0[1 - \exp(-\sigma\omega t)] \tag{7}$$

since [P] = 0 when $t = 0$.

By dividing equation (7) by the monomer consumption $\Delta(A + B) = \omega t$, we obtain an equation of the Mayo form:

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_n^0} + \frac{[S]_0}{\Delta(A+B)}\left\{1 - \exp[-\sigma\Delta(A+B)]\right\} \tag{8}$$

We note that as $\Delta(A + B) \to 0$, equation (8) approaches the conventional relation:

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_n^0} + \sigma[S]_0 \tag{9}$$

An equation similar in form to equation (8) has been derived by Harker, Thomson and Walters[4] for homopolymerization in the presence of a transfer agent which undergoes significant conversion during polymerization.

Equation (8) is the required relation for deducing σ from the experimental data; in this equation all quantities are known or measurable except σ, which may therefore be evaluated. The transfer constant C_B is then calculated from equation (5).

Case (ii)

The functional dependence of k_t on the monomer concentrations is not generally known, hence the radical concentrations $[\dot{A}]$, $[\dot{B}]$ cannot be simply calculated as a function of reaction time. It is therefore desirable to avoid the use of the latter as an independent variable. Elimination of t between equations (3a) and (3b) leads to the copolymerization equation, which, as noted by Mayo and Lewis[5], may be integrated directly. If we write:

$$[B] = u[A] \tag{10}$$

in the copolymerization equation and so eliminate [B] we find that:

$$\frac{(r_A + u)du}{u(r_Bu - u - r_A + 1)} = \frac{d[A]}{[A]} \tag{11}$$

which may be integrated to give the equation:

$$-\frac{r_A}{r_A - 1}\ln\frac{u}{u_0} + \frac{r_Ar_B - 1}{(r_A - 1)(r_B - 1)}\ln\frac{u(r_B - 1) - r_A + 1}{u_0(r_B - 1) - r_A + 1} = \ln\frac{[A]}{[A]_0} \tag{12}$$

in which u_0 is the initial value of u (i.e. $[B]_0/[A]_0$) when $[A] = [A]_0$. This result was reported by Mayo and Lewis[5]. Determination of the conversion of A (ΔA) allows u to be calculated from equation (12). Experimentally it is simplest to measure the total conversion $\Delta(A + B)$, rather than ΔA, at the end of reaction, although in moderated copolymerizations the two quantities will normally not be very different. Since $\Delta(A + B) = [A]_0 - [A] + [B]_0 - [B]$, we see that:

$$\ln\frac{[A]}{[A]_0} = \ln\left\{1 + u_0 - \frac{\Delta(A+B)}{[A]_0}\right\} - \ln(1 + u) \tag{13}$$

hence equation (12) may be written in the form:

$$-\frac{r_A}{r_A - 1}\ln\frac{u}{u_0} + \frac{r_Ar_B - 1}{(r_A - 1)(r_B - 1)}\ln\frac{u(r_B - 1) - r_A + 1}{u_0(r_B - 1) - r_A + 1} + \ln(1 + u) = \ln\left\{1 + u_0 - \frac{\Delta(A+B)}{[A]_0}\right\} \tag{14}$$

Equation (14) permits calculation of u from $\Delta(A + B)$; numerical or graphical methods may readily be applied for this purpose and an example of the latter is presented below. Note that in accordance with our basic assumptions u is independent of [S].

The next step is the calculation of $[S]/[S]_0$. Elimination of t from equations (3a) and (3d) leads to the result:

$$\frac{d[S]}{d[A]} = \frac{[S]}{[A]}\,\frac{r_AC_A + r_BC_Bu}{r_A + u} \tag{15}$$

which, with the aid of equation (11) may be converted into the relation:

$$\frac{d[S]}{du} = \frac{r_AC_A + r_BC_Bu}{u(r_Bu - u - r_A + 1)}\,[S] \tag{16}$$

Integration of equation (16) leads to equation (17):

$$-\frac{r_AC_A}{r_A - 1}\ln\frac{u}{u_0} + \left(\frac{r_AC_A}{r_A - 1} + \frac{r_BC_B}{r_B - 1}\right)\times$$
$$\ln\left[\frac{(r_B - 1)u - r_A + 1}{(r_B - 1)u_0 - r_A + 1}\right] = \ln\frac{[S]}{[S]_0} \tag{17}$$

Equations (12) and (17), which apply generally to copolymerization with chain-transfer, are the analogues of the equation:

$$\ln\frac{[S]}{[S]_0} = C_s \ln\frac{[M]}{[M]_0} \tag{18}$$

which holds for homopolymerization^6, since, in principle, elimination of u between equation (12) or (14) and equation (17) provides a relation between monomer and transfer-agent conversions. Relation (17) does not seem to have been previously reported.

From equations (3d) and (3e) we see that:

$$\frac{d[S]}{dt} + \frac{d[P]}{dt} = \mathscr{I} \tag{19}$$

so that

$$[S]_0 - [S] = [P] - \int\mathscr{I}dt \tag{20}$$

It is clear from equation (2) that $\int\mathscr{I}dt$ is the number of polymer molecules formed by bimolecular radical termination (disproportionation). According to our basic assumptions this is not affected by the presence of the transfer agent, so that $(\int\mathscr{I}dt)/\Delta(A + B) = 1/\bar{P}_n^0$. Division of equation (20) by $\Delta(A + B)$ and rearrangement therefore gives the relation:

$$\frac{[S]}{[S]_0} = 1 - \frac{\Delta(A + B)}{[S]_0}\left(\frac{1}{\bar{P}_n} - \frac{1}{\bar{P}_n^0}\right) \tag{21}$$

so that, with the aid of equation (17), we have:

$$\ln\left\{1 - \frac{\Delta(A + B)}{[S]_0}\left(\frac{1}{\bar{P}_n} - \frac{1}{\bar{P}_n^0}\right)\right\}$$
$$= -\frac{r_AC_A}{r_A - 1}\ln\frac{u}{u_0} + \left(\frac{r_AC_A}{r_A - 1} + \frac{r_BC_B}{r_B - 1}\right)\times$$
$$\ln\left[\frac{(r_B - 1)u - r_A + 1}{(r_B - 1)u_0 - r_A + 1}\right] \tag{22}$$

This is the required general equation; since u is known from equation (14), equation (22) permits evaluation of C_B from measurements of $\bar{P}_n$ if r_A, r_B and C_A are known. An illustration of the procedure for the methyl acrylate/styrene/carbon tetrabromide system is presented later.

So far we have assumed that chain-transfer to monomers plays a negligible role. If such transfer is significant, equation (20) must include an additional term to represent the concentration of polymer molecules arising from transfer to monomers. However, equation (21) will still hold, with a different value of $\bar{P}_n^0$, provided the original assumption that radical concentrations are independent of [S] remains valid. Similarly, equation (22) will also hold, with $\bar{P}_n^0$ dependent on u_0. The procedure we have described for determining C_B will therefore be valid, even if transfer to monomers is significant.

In general, for given u_0, $\bar{P}_n^0$ is a function of conversion, so that, strictly, $\bar{P}_n^0$ should be measured (or estimated) for the conversion holding in each experiment with transfer agent present. Normally, however, the precise value of $\bar{P}_n^0$ is not very important, (indeed it may be too high to measure accurately) so that this refinement is hardly necessary.

Although termination by disproportionation has been assumed, the basic equations (14) and (22) are not affected by the intervention of combination.

Special cases and approximations

Although equations (14) and (22) are applicable if $r_A = 1$ or $r_B = 1$, they cannot be used if both reactivity ratios are equal to unity, in which case u remains constant. However, in these circumstances it may be shown without difficulty that:

$$\ln\frac{[S]}{[S]_0} = \left(\frac{C_A[A]_0 + C_B[B]_0}{[A]_0 + [B]_0}\right)\ln\frac{[A] + [B]}{[A]_0 + [B]_0} \tag{23}$$

This relation is similar in form to equation (18) and indicates that the copolymerization resembles the polymerization of a single monomer with effective transfer constant equal to the weighted value in parentheses in equation (23). The relation analogous to equation (22), obtained by combining equations (21) and (23), is:

$$\ln\left\{1 - \frac{\Delta(A + B)}{[S]_0}\left(\frac{1}{\bar{P}_n} - \frac{1}{\bar{P}_n^0}\right)\right\}$$
$$= \frac{C_A[A]_0 + C_B[B]_0}{[A]_0 + [B]_0}\ln\frac{[A] + [B]}{[A]_0 + [B]_0} \tag{24}$$

If $(u_0 - u)/u_0 \ll 1$, equations (14) and (22) assume relatively simple forms, regardless of the extent of conversion. In these circumstances, we obtain by expanding the logarithms in equation (14) (after subtraction of $\ln(1 + u_0)$ from each side) and neglecting powers of $(u_0 - u)/u_0$ higher than the first:

$$\left[\frac{u_0 + r_A}{u_0(r_B - 1) - r_A + 1} + \frac{u_0}{1 + u_0}\right]\left(\frac{u}{u_0} - 1\right)$$
$$= \ln\left\{1 - \frac{\Delta(A + B)}{[A]_0 + [B]_0}\right\} \tag{25}$$

Similar treatment of equation (22) yields equation (26):

$$\frac{r_\mathrm{A}C_\mathrm{A}+r_\mathrm{B}C_\mathrm{B}u_0}{u_0(r_\mathrm{B}-1)-r_\mathrm{A}+1}\left(\frac{u}{u_0}-1\right)=$$

$$\ln\left\{1-\frac{\Delta(\mathrm{A}+\mathrm{B})}{[\mathrm{S}]_0}\times\left(\frac{1}{\bar{\bar{P}}_n}-\frac{1}{\bar{\bar{P}}{}_n^0}\right)\right\} \tag{26}$$

and by eliminating u from equations (25) and (26) we finally obtain the relation (27):

$$C_\mathrm{B}=\frac{1}{r_\mathrm{B}[\mathrm{B}]_0}\Bigg[\Bigg(\frac{(r_\mathrm{A}[\mathrm{A}]_0^2+2[\mathrm{A}]_0[\mathrm{B}]_0+r_\mathrm{B}[\mathrm{B}]_0^2}{([\mathrm{A}]_0+[\mathrm{B}]_0)\ \ln\left\{1-\dfrac{\Delta(\mathrm{A}+\mathrm{B})}{[\mathrm{A}]_0+[\mathrm{B}]_0}\right\}}\times$$

$$\ln\left\{1\,\frac{\Delta(\mathrm{A}+\mathrm{B})}{[\mathrm{S}]_0}\left(\frac{1}{\bar{\bar{P}}_n}-\frac{1}{\bar{\bar{P}}{}_n^0}\right)\right\}\Bigg)\Bigg)-r_\mathrm{A}C_\mathrm{A}[\mathrm{A}]_0\Bigg] \tag{27}$$

The validity of equation (27) depends on changes in u being small, as already mentioned. If, in addition, the extent of conversion is sufficiently small, equation (27) reduces to equation (28):

$$C_\mathrm{B}=\frac{1}{r_\mathrm{B}[\mathrm{B}]_0}\left\{\frac{1}{[\mathrm{S}]_0}\left(\frac{1}{\bar{\bar{P}}_n}-\frac{1}{\bar{\bar{P}}{}_n^0}\right)\right.$$

$$\left.(r_\mathrm{A}[\mathrm{A}]_0^2+2[\mathrm{A}]_0[\mathrm{B}]_0+r_\mathrm{B}[\mathrm{B}]_0^2)-r_\mathrm{A}C_\mathrm{A}[\mathrm{A}]_0\right\} \tag{28}$$

This equation may readily be deduced directly on the assumption of infinitesimal concentration changes; it was used in ref 1.

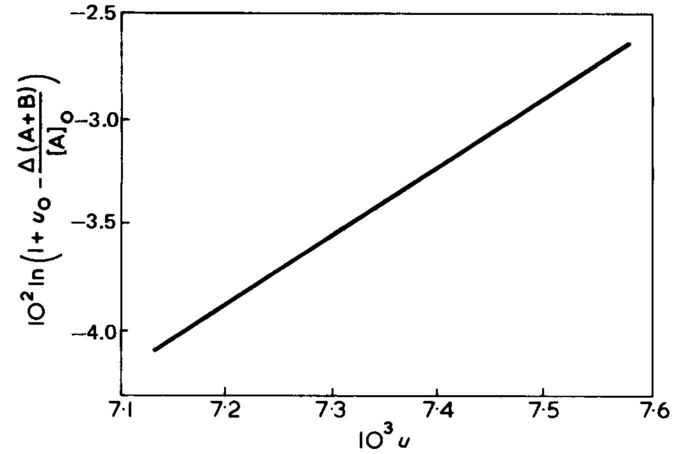

Figure 1 Plot of equation (14) for methyl acrylate/styrene system. $u_0 = 8.792 \times 10^{-3}$; $r_\mathrm{A} = 0.18$; $r_\mathrm{B} = 0.75$

Moderated copolymerization in the methyl acrylate/styrene/carbon tetrabromide system: an example of graphical solution

Solution of equation (14) is easily effected graphically. A plot of the left side of equation (14) *versus* u is constructed, using known values of r_A, r_B, u_0; this represents the variation of $\ln\{1 + u_0 - \Delta(\mathrm{A}+\mathrm{B})/[\mathrm{A}]_0\}$ with u. From the experimental values of $\Delta(\mathrm{A}+\mathrm{B})$ and $[\mathrm{A}]_0$, $\ln\{1 + u_0 - \Delta(\mathrm{A}+\mathrm{B})/[\mathrm{A}]_0\}$ is calculated and the corresponding value of u read off from the graph. Insertion of this into equation (22) then permits calculation of C_B. Only a single graph is required for each set of experiments at constant $[\mathrm{B}]_0/[\mathrm{A}]_0$; this suffices to determine u for all runs in which $[\mathrm{S}]_0$ and the degree of conversion $\Delta(\mathrm{A}+\mathrm{B})$ are varied.

The procedure is illustrated below for the moderated copolymerization of methyl acrylate and styrene in the presence of carbon tetrabromide as transfer agent. The relevant data are:

$r_\mathrm{A} = 0.18$; $r_\mathrm{B} = 0.75$; $C_\mathrm{A} = 0.41$ (ref 7)

$[\mathrm{A}]_0 = 10.35$ mol l^{-1}; $[\mathrm{B}]_0 = 0.091$ mol l^{-1}

$u_0 = 8.792 \times 10^{-3}$

Figure 1 is a plot of the left side of equation (14) against u; it is almost linear since the range in u is narrow. *Table 1* presents the experimental data and the derived values of u from *Figure 1* and C_B from equation (22). In these experi-

Table 1 Moderated copolymerization of methyl acrylate (A) and styrene (B) at 60°C. Concentrations and conversions (mol l^{-1}) at 60°C are given. $[\mathrm{A}]_0 = 10.35$; $[\mathrm{B}]_0 = 0.091$; azobisisobutyronitrile 8.29×10^{-4}

$10^4[\mathrm{CBr}_4]_0$	$\Delta(\mathrm{A}+\mathrm{B})$	$10^4\left(\frac{1}{\bar{\bar{P}}_n}-\frac{1}{\bar{\bar{P}}{}_n^0}\right)$	10^2F*	10^3u	C_B
18.95	0.3806	8.14	−2.838	7.525	141.6
17.05	0.4054	7.16	−3.085	7.443	138.7
15.16	0.4162	5.97	−3.192	7.410	129.1
13.26	0.4263	5.37	−3.293	7.378	134.0
11.37	0.4483	4.79	−3.513	7.310	141.8
9.47	0.4972	4.04	−4.004	7.160	146.9
7.58	0.3897	3.24	−2.929	7.494	141.0
1.895	0.3633	1.03	−2.666	7.578	185.6
				Mean:	144.8

* $F \equiv \ln\left\{1+u_0-\frac{\Delta(\mathrm{A}+\mathrm{B})}{[\mathrm{A}]_0}\right\}$

ments the conversions lay in the following ranges: carbon tetrabromide 16–22%, styrene 16–20%, methyl acrylate 4–5%. These conversions are significant (especially the first two) and allowance must be made for them; however, the correction procedure developed is applicable to much higher conversions, and will hold so long as the basic assumptions in classical copolymerization theory are not invalidated, and the intervention of processes not considered in our treatment (e.g. chain-transfer to polymer) does not become significant.

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