Kinetic Model for Free-Radical Addition–Fragmentation Associated with Initiation and Primary Radical Termination

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ABSTRACT: A kinetic model has been proposed for a free-radical polymerization in the presence of an added initiator and an addition–fragmentation agent. The present one is considered as a special case where the addition–fragmentation agent acts also as an initiator. The model takes into account the chain termination process by way of primary radicals and excludes the mutual termination of primary radicals. The general model has been applied to the case of methyl methacrylate (MMA) polymerization in the presence of a peroxyketal, viz., ethyl 2-[((1-*n*-butoxyethyl)peroxy)ethyl]propenoate (EBEPEP) as the addition–fragmentation agent. An expression for the molar mass of the formed polymer has also been derived considering the various initiation and termination processes as an improvement over the conventional Mayo equation. The kinetics were performed at various temperatures to prove the validity of the equation, and the different kinetics factors relevant to initiation, addition–fragmentation, and primary radical termination were evaluated. The addition–fragmentation agent in this case manifested retardation until 70 °C beyond which the polymerization rate increased with increase in concentration of addition–fragmentation agent caused by the thermal decomposition of the peroxy group on EBEPEP.

Introduction

Free-radical addition–fragmentation is becoming recognized as an effective means for chain transfer control as it permits exclusion of conventional sulfur-based chain transfer agents. In addition to chain regulation, it also permits design of mono- and difunctional polymers and is being looked into as an alternate method to derive macromonomers in a single-step reaction.[1] Several compounds have been reported to function as chain regulators by way of radical addition and fragmentation, and in nearly all cases, the polymerization in the presence of such compounds has been found to cause retardation.[2–5] The reported chain transfer constants based on the conventional Mayo equation[6] are incorrect as they do not take into account the accompanying retardation. We have recently proposed a general kinetic model to discuss such situations considering the addition–fragmentation as a binary copolymerization.[1] Such a model takes into account all phenomena including chain termination involving addition–fragmentation processes, primary radical termination of growing radicals, and mutual termination of the primary radicals (the latter usually encountered in cases of soft expelled radicals). In this paper we describe a special case where the addition–fragmentation agent can also act as an initiator and the expelled radicals are so reactive that their mutual recombination can in all probability be excluded. An equation for predicting precisely the molar mass is also proposed. The validity of the model is exemplified for MMA polymerization using a peroxyketal as the addition–fragmentation agent.

Experimental Section

MMA was purified by *vacuum* distillation. Synthesis of EBEPEP has been described elsewhere.[7] Polymerization was performed in sealed ampules using weighed amounts of monomer, initiator, and chain transfer agent in thermostated oil baths at the desired temperatures. The polymer was isolated by precipitation into heptane. Conversions were determined gravimetrically and were kept below 10% for kinetic studies. Molar mass was determined by size exclusion chromatography (Waters WISP710 automatic injector, Shimadzu pump connected to 4 PL-Gel columns coupled with a Waters R401 refractometer).

Results and Discussion

Rate of Polymerization. The various phenomena operative in a free-radical polymerization process in the presence of an addition–fragmentation (AF) agent are shown in Scheme 1.

The chain transfer in the presence of EBEPEP can be represented as shown in Scheme 2 (cf. ref 7a for more details about experimental determinations of polymer functionalization). In such a case, the relative rate of polymerization is given as (see Appendix)

$$\left[\frac{R_p}{R_{p0}}\right]^2 = \frac{1 + A\frac{[AF]}{[M]}}{1 + 2P\frac{[AF]}{[M]}} \tag{1}$$

where

$$\begin{cases} A = 2f'k_{d'}\dfrac{{k_p}^2}{k_t}\dfrac{[M]^3}{R_{p0}} \\ P = \dfrac{k_{tpr}k_{tr}}{k_t k_{i'}} \end{cases}$$

and R_{p0} is the rate of polymerization induced by the added initiator (i.e., AIBN) in the absence of EBEPEP. As the concentrations of both the added initiator and the monomer are constant for all the experiments, the value of R_{p0} has to be considered as a constant in eq 1 (for the same temperature). When conversions are low,

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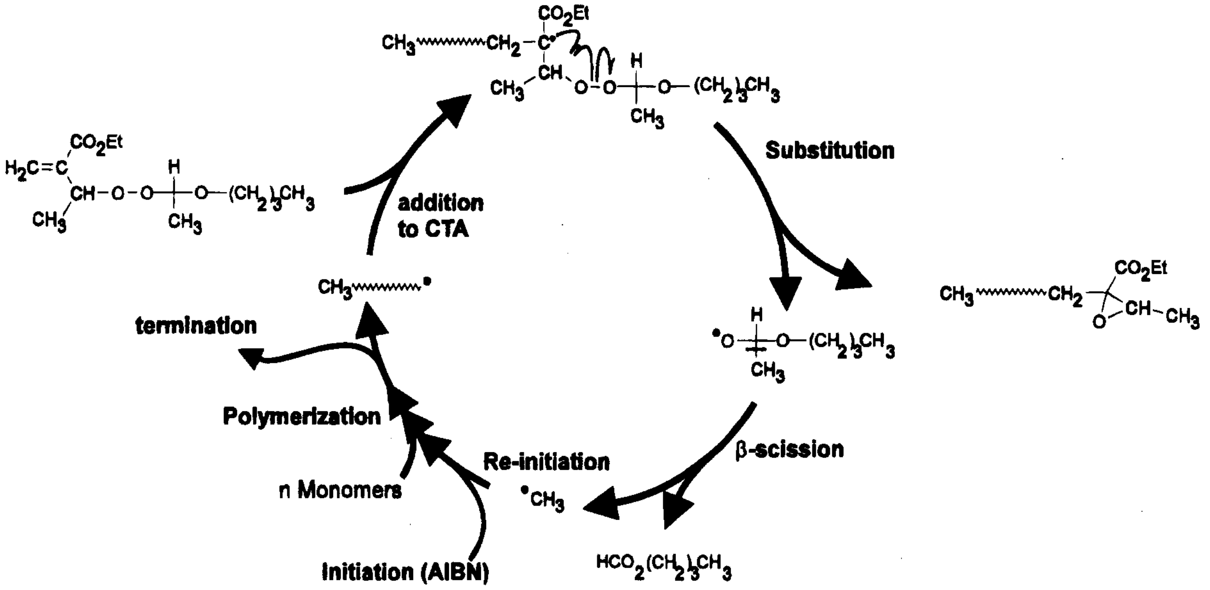
Scheme 1. Reactions Involved in Free-Radical Polymerizations in the Presence of EBEPEP

Initiator	$\xrightarrow{k_d}$	R•	Thermolysis of Initiator(s)
R• + M	$\xrightarrow{k_i}$	RM•	Initiation
RM•(or FM•) + nM	$\xrightarrow{k_p}$	P•	Propagation
P• + AF	$\xrightarrow{k_{tr}}$	PA + F•	Transfer to AF agent (addition-fragmentation)
F• + M	$\xrightarrow{k_{i'}}$	FM•	Re-Initiation
F• + P•	$\xrightarrow{k_{tpr}}$	FP	Termination by primary radicals
P• + P•	$\xrightarrow{k_t}$	P-P	Termination (depending upon the termination process)

Scheme 2. Radical Addition–Fragmentation Process in the Presence of EBEPEP



[M] is practically constant and equal to $[M]_0$, and the parameter A can be considered as a constant.

Equation 1 describes the variation of R_p with the concentration of addition–fragmentation agent. The validity of this equation was checked by determining the relative polymerization rate at varying concentrations of the addition–fragmentation agent (at very low conversion to assume $[M] \approx [M]_0$). The results are given in Table 1.

The relative polymerization rates are shown in Figure 1 at different temperatures. The data have been treated by eq 1 to resolve the constants A and P given in Table 2. The data conform well to the equation. It can be seen that retardatin is significant till 70 °C, beyond which an inversion in the $(R_p/R_{p0})^2$–[AF]/[M] curve is observed due to the chain initiation by the peroxide initiator groups located on EBEPEP. At 70 °C, the retardation effect is just nullified by the initiation by the same molecule, so the values of A and P are equal and indeterminate.

Degree of Polymerization. The degree of polymerization is given as (see Appendix)

$$\frac{1}{\mathrm{Dp_n}} = C_{tr}\frac{[AF]}{[M]} + \frac{1}{\mathrm{Dp_{n0}}}\frac{R_p}{R_{p0}}\left(1 + \frac{P}{1-\alpha/2}\frac{[AF]}{[M]}\right) \qquad (2)$$

where α stands for the fraction of growing chains which undergo termination by recombination[8] and P is the same constant as in eq 1, R_{p0} and $\mathrm{Dp_{n0}}$ being the rate of polymerization and the degree of polymerization, respectively, *in the absence of the addition–fragmentation agent.*

Equation 2 predicts the molecular weights of the formed polymers in the presence of the added chain transfer agent having a chain transfer constant C_{tr}. The "correction" factor $K = (R_p/R_{p0})[1 + [P/(1-\alpha/2)]([AF]/[M])$ takes into account *both the initiation by EBEPEP and the termination by primary radicals* originating from it. K can be calculated (cf. Table 2) using the values of P obtained from eq 1. Finally, the degree of polymerization of the formed polymers can be compared to the classical Mayo equation:

$$\frac{1}{\mathrm{Dp_n}} - \frac{1}{\mathrm{Dp_{n0}}} = C_{tr}\frac{[AF]}{[M]} \qquad \text{Mayo's equation}$$

$$\frac{1}{\mathrm{Dp_n}} - \frac{K}{\mathrm{Dp_{n0}}} = C_{tr}\frac{[AF]}{[M]} \qquad \text{modified equation} \qquad (3)$$

We can observe that, in the absence of initiation ($R_p = R_{p0}$) and termination by primary radicals ($P = 0$) due to chain transfer agent, $K = 1$ and the eq 2 becomes identical to the Mayo equation.

C_{tr} is obtained by plotting $1/\mathrm{Dp_n} - K/\mathrm{Dp_{n0}}$ *versus* [AT]/[M] or taking the mean value of $C_{tr,i} = (1/\mathrm{Dp_{n,i}} - K_i/\mathrm{Dp_{n0}})/([AF]/[M])_i$ as was done in this study (the latter method is statistically better as it gives the same weighting to all the experiments). A plot (for a temperature of 80 °C) is shown in Figure 2 using eq 2 and

Table 1. Polymerization of MMA in the Presence of EBEPEP: Relative Rate of Polymerization, Degree of Polymerization, and "Correction" Factor (Eq 2)

polymerization conditions	10^3[EBEPEP][a] (mol/L)	R_p/R_{p0}[b]	K[c] (eq 2)	Dp_n[b]
temp = 50 °C	*0.00*	*1.00*	*1.00*	*7740*
t = 90 min	*2.39*	*0.99*	*1.01*	*6540*
[MMA] = 9.01 mol/L	*4.79*	*0.98*	*1.03*	*5510*
[AIBN] = 2.92×10^{-3} mol/L	*9.57*	*0.97*	*1.06*	*4270*
	23.9	*0.96*	*1.19*	*2610*
	47.9	0.93	1.37	1300
	76.6	0.90	1.59	1050
	115	0.88	1.89	674
	144	0.87	2.12	530
temp = 60 °C	*0.00*	*1.00*	*1.00*	*6140*
t = 30 min	*2.37*	*0.99*	*1.02*	*5450*
[MMA] = 8.9 mol/L	*4.73*	*0.98*	*1.05*	*4660*
[AIBN] = 2.88×10^{-3} mol/L	*9.47*	*0.96*	*1.09*	*4040*
	23.7	*0.94*	*1.27*	*2630*
	47.3	0.88	1.49	1490
	75.8	0.86	1.81	1050
	114	0.84	2.24	768
	142	0.83	2.55	580
temp = 70 °C	*0.00*	*1.00*	*n.d.*	*4550*
t = 20 min	*2.33*	*0.99*	*n.d.*	*4140*
[MMA] = 8.78 mol/L	*4.67*	*1.00*	*n.d.*	*3830*
[AIBN] = 1.42×10^{-3} mol/L	*9.33*	*1.01*	*n.d.*	*3160*
	23.3	*0.99*	*n.d.*	*2050*
	46.7	1.00	n.d.	1030
	74.6	1.01	n.d.	783
	112	1.00	n.d.	526
	140	0.99	n.d.	433
temp = 80 °C	*0.00*	*1.00*	*1.00*	*3240*
t = 15 min	*2.30*	*1.00*	*1.03*	*3000*
[MMA] = 8.66 mol/L	*4.60*	*1.01*	*1.08*	*2790*
[AIBN] = 1.40×10^{-3} mol/L	*9.20*	*1.03*	*1.17*	*2350*
	23.0	*1.06*	*1.42*	*1550*
	46.0	1.08	1.81	983
	73.6	1.10	2.29	721
	110	1.11	2.90	546
	138	1.12	3.39	440

[a] [EBEPEP] < 24×10^{-3} mol/L (in italic). [b] By SEC analysis. [c] n.d. = not determined.

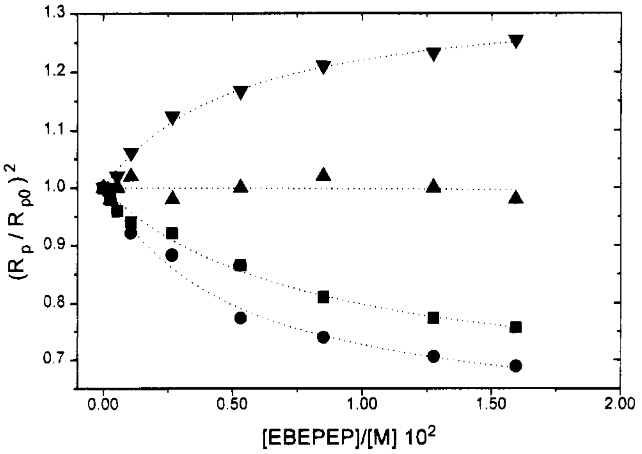


Figure 1. Dependency of relative rates of polymerization (expressed as its square) on the concentration of the addition–fragmentation agent: (■) 50 °C; (●) 60 °C; (▲) 70 °C; (▼) 80 °C.

the Mayo equation. Both the Mayo equation and eq 2 are fitted to the experimental data to give a linear relationship, but only eq 2 gives the correct values for C_{tr}. The mean values obtained at various temperatures are given in Table 3.

Table 2. Values of Parameters A and P (Eq 1) at Different Temperatures for the Polymerization of MMA in the Presence of EBEPEP (Least Squares Fit)

temp (°C)	A[a]	P[a]
50	79 ± 20	62 ± 14
60	108 ± 20	93 ± 14
70	n.d.	n.d.
80	263 ± 34	99 ± 14

[a] n.d. = not determined ($A \approx 2P$).

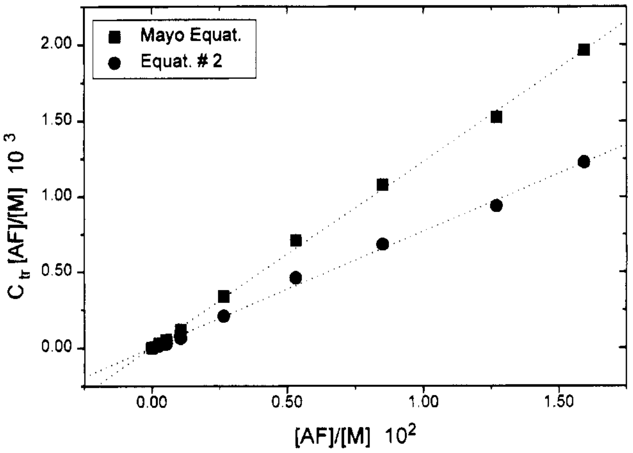


Figure 2. Comparison between Mayo's equation and eq 2 for the polymerization of MMA in the presence of EBEPEP at 80 °C: (■) Mayo's equation; (●) eq 2.

Table 3. Transfer Constants in the Free-Radical Polymerization of MMA in the Presence of EBEPEP Calculated from Mayo's Equation and Eq 2 (Mean Values)

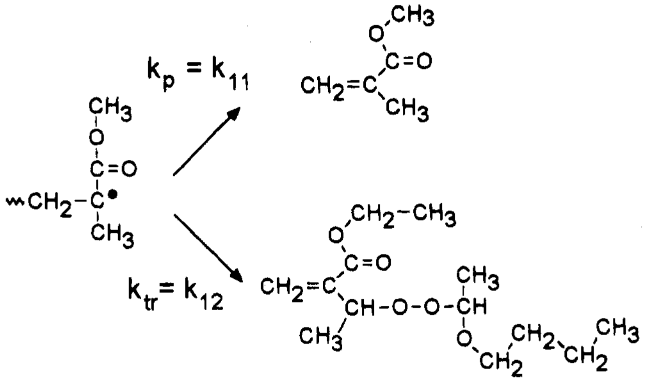
temp (°C)	Mayo	eq 2[a]
50	0.102 ± 0.009	0.094 ± 0.008
60	0.088 ± 0.008	0.074 ± 0.008
70	0.107 ± 0.023	n.d.
80	0.116 ± 0.014	0.069 ± 0.013

[a] n.d. = not determind ($A \approx 2P$).

These results are not very different from those reported in a previous paper,[7a] the different coming from the fact that, in the present studies, the concentration of EBEPEP is higher than in the previous study (≈140 × 10^{-3} mol/L in this study, ≈23 × 10^{-3} mol/L in the previous work). Thus, in the present case, the Mayo equation is no longer applicable because of the increased effect of the initiation resulting from thermolysis of EBEPEP and retardation accompanying the transfer. We can also observe that the correction factor K is increasing with rising EBEPEP concentration. Finally, the values obtained from Mayo's equation are not coherent: they decrease from 50 to 60 °C and increase from 60 to 80 °C. On the other hand, the corrected values obtained from eq 2 show a regular decrease from 50 to 80 °C. We can assume that values calculated from Mayo's equation for temperatures of 70 and 80 °C are highly perturbed by the secondary reactions of EBEPEP.

Thus, the corrected C_{tr} values show a tendency to decrease with a rise in temperature. This behavior is not classical: in the case of thio derivative transfer agents, the C_{tr} values increase with a rise in temperature if their values are less than unity. In fact (cf. Scheme 1), there are two steps involved in the transfer reaction resulting from an addition–fragmentation process: addition of the propagating radical to the double bond and internal fragmentation of the resultant radical. The rate-determining step is the *addition to*

Scheme 3. Possible Reactions of the Growing Radical



the double bond because the second step is known to be about 100 times faster.[9] Thus, the value of C_{tr} is dependent on the competition between this addition reaction and the homopolymerization of MMA as shown in Scheme 3.

This reaction scheme is identical to copolymerization of two monomers (denoted 1 and 2), and C_{tr} (as the ratio k_{tr}/k_p) can be seen to be the inverse of the radical reactivity ratio r_1 (by substituting k_{11} and k_{12} by k_p and k_{tr}, respectively). As in copolymerization, the reactivity ratio values increase or decrease with a rise in temperature (resulting in a decrease or increase for C_{tr}, respectively) depending upon the activation energies of the two competitive reactions involved. In the case of EBEPEP, it has to be concluded that the activation energy of homopolymerization is higher than the activation energy of the cross-polymerization. This behavior is identical to the case of copolymerization of methyl methacrylate and methyl α-benzylacrylate[10] (assuming that the bulky α-substituent of the latter monomer is geometrically analogous to that of EBEPEP) where the reactivity ratio increases with a rise in temperature.

Conclusion

The validity of a new kinetic model describing free-radical addition–fragmentation involving initiation and primary radical termination has been exemplified in a typical case of polymerization of MMA in the presence of EBEPEP. The model is capable of predicting precisely the molar masses of the formed polymer. It is suited for cases where retardation is moderate, permitting exclusion of the possibility of mutual termination of the primary radicals. The precise calculation of the chain transfer constant is helpful in correctly predicting the functionalities of the polymer chain ends if the addition–fragmentation results in terminal functionalization.[1]

Appendix

Rate of Polymerization. Let R_i be the rate of initiation (in this case, the initiation is due to both the AIBN and the EBEPEP thermolysis).

Starting from Scheme 1, the steady-state hypothesis can be written for the growing radicals (1) and the addition–gragmentation transfer agent (2) as follows:

$$k_t[P^\bullet]^2 + k_{tr}[P^\bullet][AF] + k_{tptr}[P^\bullet][F^\bullet] = R_i + k_{i'}[F^\bullet][M] \qquad (A1)$$

$$k_{i'}[F^\bullet][M] + k_{tpr}[P^\bullet][F^\bullet] = k_{tr}[P^\bullet][AF] \qquad (A2)$$

Taking the value of $k_{i'}[F^\bullet][M]$ from eq A2, the rate of initiation can be expressed as:

$$R_i = k_t[P^\bullet]^2 + 2k_{tpr}[P^\bullet][F^\bullet] \qquad (A3)$$

The significance of the factor 2 in eq A3 arises from the fact that termination by primary radicals is acting two times in the polymerization process, both ending a growing radical and removing a precursor of a new growing radical.

The concentration of radical fragments can be expressed from eq A2:

$$[F^\bullet] = \frac{k_{tr}[P^\bullet][AF]}{k_{i'}[M] + k_{tpr}[P^\bullet]} \qquad (A4)$$

If termination by primary radicals is of the same magnitude as reinitiation ($k_{tpr} \approx k_{i'}$), the concentration of growing radicals being very low compared with that of monomer, the following hypothesis can be made:

$$k_{tpr}[P^\bullet] \ll k_{i'}[M] \qquad (A5)$$

Equation A4 becomes

$$[F^\bullet] \cong \frac{k_{tr}[P^\bullet][AF]}{k_{i'}[M]} \qquad (A6)$$

Substituting this value of $[F^\bullet]$ into eq A3 gives

$$[P^\bullet]^2 = \frac{R_i}{k_t + 2\dfrac{k_{tpr}k_{tr}}{k_{i'}}\dfrac{[AF]}{[M]}} \qquad (A7)$$

The rate of polymerization R_p is given by

$$R_p = k_p[P^\bullet][M] \qquad (A8)$$

and then taking into account the value of $[P^\bullet]$ expressed in eq A7, it becomes

$$R_p{}^2 = \frac{k_p{}^2}{k_t}[M]^2\frac{R_i}{1 + 2\dfrac{k_{tpr}k_{tr}}{k_tk_{i'}}\dfrac{[AF]}{[M]}} \qquad (A9)$$

The global rate of initiation is the consequence of initiation by both AIBN and EBEPEP:

$$R_i = R_{i,AIBN} + R_{i,EBEPEP} \qquad (A10)$$

Finally, the rate of polymerization is given by

$$R_p{}^2 = \frac{\dfrac{k_p{}^2}{k_t}[M]^2R_{i,AIBN} + \dfrac{k_p{}^2}{k_t}[M]^2R_{i,EBEPEP}}{1 + 2\dfrac{k_{tpr}k_{tr}}{k_tk_{i'}}\dfrac{[AF]}{[M]}} \qquad (A11)$$

The concentration of AIBN is constant for all the experiments (for a given temperature); thus one can write

$$R_{p0}{}^2 = \frac{k_p{}^2}{k_t}[M]^2R_{i,AIBN} \qquad (A12)$$

where R_{p0} is the rate of polymerization initiated by thermolysis of AIBN for all the experiments.

$R_{i,EBEPEP}$ can be expressed as

$$R_{i,EBEPEP} = 2f'k_{d'}[AF] \tag{A13}$$

where f' and $k_{d'}$ stand for the efficiency factor and the rate constant of thermolysis of EBEPEP, respectively. Substituting eqs A12 and A13 into eq A11 gives

$$R_p^{\,2} = \frac{R_{p0}^{\,2} + 2f'k_{d'}\dfrac{k_p^{\,2}}{k_t}[M]^3\dfrac{[AF]}{[M]}}{1 + 2P\dfrac{[AF]}{[M]}} \qquad \text{with } P = \frac{k_{tpr}k_{tr}}{k_t k_{i'}} \tag{A14}$$

Degree of Polymerization. The kinetic chain length is given as

$$\nu = \frac{R_p}{R_t} = \frac{k_p[P^\bullet][M]}{k_{tr}[P^\bullet][AF] + k_{tpr}[P^\bullet][AF^\bullet] + k_t[P^\bullet]^2} \tag{A15}$$

Under steady-state conditions, the rates of interconversion reaction of $F^\bullet$ and $P^\bullet$ have to be the same. Therefore

$$k_{tr}[P^\bullet][AF] = k_{i'}[AF^\bullet][M] \Rightarrow [AF^\bullet] = \frac{k_{tr}[P^\bullet][AF]}{k_{i'}[M]} \tag{A16}$$

$[P^\bullet]$ can be obtained from the equation of the rate of polymerization:

$$[P^\bullet] = \frac{R_p}{k_p[M]} \tag{A17}$$

Substituting eqs A16 and A17 into eq A15 gives

$$Dp_n = \frac{k_p[M]}{k_{tr}[AF] + \dfrac{k_{tpr}k_{tr}}{k_{i'}}\dfrac{R_p}{k_p[M]}\dfrac{[AF]}{[M]} + k_t(1 - \alpha/2)\dfrac{R_p}{k_p[M]}} \tag{A18}$$

where α stands for the fraction of growing chains which undergo termination by recombination. Using the value of P given in eq A14, one can write

$$\frac{1}{Dp_n} = C_{tr}\frac{[AF]}{[M]} + \left(1 + \frac{P}{1 - \alpha/2}\frac{[AF]}{[M]}\right)\frac{k_t(1 - \alpha/2)R_p}{k_p^{\,2}[M]^2} \tag{A19}$$

In the *absence of added transfer agent*, this equation reduces to

$$\frac{1}{Dp_{n0}} = \frac{k_t(1 - \alpha/2)R_{p0}}{k_p^{\,2}[M]^2} \tag{A20}$$

which in fact is the classical expression for homopolymerization in the absence of a transfer reaction. Taking the value of $[k_t(1 - \alpha/2)]/(k_p^2[M]^2)$ from this equation, one can write the final equation

$$\frac{1}{Dp_n} = C_{tr}\frac{[AF]}{[M]} + \frac{1}{Dp_{n0}}\frac{R_p}{R_{p0}}\left(1 + \frac{P}{1 - \alpha/2}\frac{[AF]}{[M]}\right) \tag{A21}$$

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