Macromolecules 1991, 24, 1641-1647

A Generalized Kinetic Model for Radical-Initiated Template Polymerizations in Dilute Template Systems

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Received December 8, 1989; Revised Manuscript Received May 22, 1990

ABSTRACT: A generalized kinetic model for dilute radical template polymerizations involving preferential monomer adsorption by the template and following classical kinetics is described. By simulation, the influence of preferential monomer adsorption and of various rate constants pertaining to complexation, template propagation, and template termination of growing chain radicals on the rate enhancement induced by a template was examined as a function of template concentration. This model has been applied to some known template polymerization systems. For some of these, template rate constants could be estimated by curve fitting to experimentally determined polymerization rate vs template concentration plots.

1. Introduction

For many years, we have been examining radical polymerization systems in which chain propagation takes place along template macromolecules. As compared to conventional polymerization, such a propagation mode may lead to changes in polymerization kinetics and in structural features of the polymers formed. With regard to kinetics and mechanism, template systems have been classified into two types, which we called type I and type II,[1] according to complete or no preadsorption (stoichiometric complexation) of monomer by (with) the template present in excess (expressed in base moles). Thus, type I leads to propagation of template-bound ("daughter") chain radicals with adsorbed monomer ("zip" reaction), whereas type II to that with free monomer ("pick-up" reaction). Actually, in most template polymerization systems, adsorption of monomer occurs to varying degrees depending on the kind of interaction between the template and the monomer and on the reaction conditions, which may be characterized by a simple adsorption equilibrium constant K_M, which is assumed to be of the Langmuir type. Template polymerization of vinyl monomers is generally performed in a suitable inert solvent with an initiator like azoisobutyronitrile (AIBN). If K_M has some finite value, indicating preferential monomer adsorption by the template, the following consecutive steps may be discerned: (1) initiation of monomer in solution, (2) initial propagation in solution, (3) complexation of (short) chain radicals with template macromolecules owing to cooperative specific interaction, (4) propagation along the template with either preadsorbed monomer or monomer from solution, and (5) termination. To interpret the kinetic results, simple models have been used based on either a pure type I ($K_M = \infty$) mechanism or a pure type II ($K_M \simeq 0$) mechanism. Recently, Smid[3] proposed a generalized model incorporating a finite K_M, which was applied successfully to the template polymerization of methacrylic acid along poly(2-vinylpyridine).[2-4]

The purpose of this paper is to show how by computer simulation the different kinetic parameters would affect the template polymerization at constant initial monomer concentration and to analyze the outcome. Furthermore, examples will be given to demonstrate the application of this generalized model to some template polymerization systems extracted from the literature.

2. Kinetic Model

When a template system is considered, two loci where polymerization reactions take place should be distinguished, viz. on the template macromolecules ("the template") and in the surrounding medium ("the solution"). Moreover, there are reactions at the interface of both loci. The generalized kinetic model may then be represented by the following scheme representing the sequence of reaction steps as already mentioned in the Introduction.

A. reaction steps in solution

(1) initiator decomposition

$$I \xrightarrow{k_d} 2R^\bullet$$

(2) initiation

$$R^\bullet + M_f \xrightarrow{k_i} P^\bullet_{B,1}$$

(3) blank propagation

$$P^\bullet_{B,n} + M_f \xrightarrow{k_{p,B}} P^\bullet_{B,n+1}$$

(4) blank termination

$$P^\bullet_{B,n} + P^\bullet_{B,m} \xrightarrow{k_{t,BB}} P_B$$

B. complexations

(1) monomer adsorption

$$M_f + T \overset{K_M}{\rightleftarrows} M_T$$

(2) radical complexation

$$P^\bullet_{B,n} + T \xrightarrow{k_c} P^\bullet_{T,n}$$

(3) polymer complexation

$$P_B + T \xrightarrow{k_c} P_T$$

C. reaction steps on the template

(1) template propagation

$$P^\bullet_{T,n} + M \xrightarrow{k_{p,T}} P^\bullet_{T,n+1}$$

($M = M_f$ or M_T, depending on the instantaneous situation)

(2) template–template termination

$$P^{\bullet}_{T,n} + P^{\bullet}_{T,m} \xrightarrow{k_{t,TT}} P_T$$

(3) cross-termination

$$P^{\bullet}_{B,n} + P^{\bullet}_{T,m} \xrightarrow{k_{t,BT}} P_B \quad (\text{or } P_T)$$

For the sake of brevity, propagation and termination proceeding in the solution and on the template are given the predicates "blank" (i.e., nontemplate) and "template", respectively. M_f signifies the monomer in the solution, whereas M_T is the monomer adsorbed on the template. The following remarks should be made: (1) The complexation of living and dead polymers with template macromolecules is, strictly speaking, an equilibrium process. However, its equilibrium constant will rise rapidly with chain length because of the cooperativity of interacting forces, all the more if there is preferential adsorption of monomer. The back-reaction (decomplexation) is therefore neglected. Of course, k_c will still depend on the chain length n of the complexing radicals (or preterminated chains) in the sense that k_c would decrease with larger n due to diffusion. In order not to complicate matters, it is assumed that k_c represents an average constant quantity and that a proportionate fraction of chains with different n's is complexed. (2) The template propagation along each chain in fact consists of a combination of the addition of either adsorbed monomer ("zip" propagation: $P^{\bullet}_{T,n} + M_T$ with rate constant $k_{p,I}$) or free monomer ("pick-up" propagation: $P^{\bullet}_{T,n} + M_f$ with rate constant $k_{p,II}$) depending on the situation at hand. (3) Reactions at the template–solution interface not only involve the complexation but also termination between template-bound and free polymer radicals (cross-termination). It should be reminded that all kinds of termination reactions are actually diffusion controlled. For the sake of simplicity, its effect will be disregarded. (4) Chain-transfer reactions to monomer or solvent as well as to template are assumed to be absent.

Based on the above scheme and assuming termination of blank radicals, $P^{\bullet}_B$, by combination only and steady state of $[R^{\bullet}]$, i.e., $d[R^{\bullet}]/dt = 0$, the complete set of equations can be given by

$$R_i = 2fk_d[I] \qquad (1)$$

(or ΦI_a in the case of photoinitiation with Φ = quantum yield and I_a = intensity of absorbed light)

$$d[P^{\bullet}_B]/dt = R_i - 2k_{t,BB}[P^{\bullet}_B]^2 - k_{t,BT}[P^{\bullet}_B][P^{\bullet}_T] - k_c[P^{\bullet}_B][T] \qquad (2)$$

$$d[P^{\bullet}_T]/dt = k_c[P^{\bullet}_B][T] - k_{t,BT}[P^{\bullet}_B][P^{\bullet}_T] - 2k_{t,TT}[P^{\bullet}_T]^2 \qquad (3)$$

$$-d[M]/dt = R_p = R_{p,B} + R_{p,T} = (k_{p,B}[P^{\bullet}_B] + \bar{k}_{p,T}[P^{\bullet}_T])[M_f] \qquad (4)$$

$$d[P_B]/dt = k_{t,BB}[P^{\bullet}_B]^2 - k_c[P_B][T] \qquad (5)$$

$$-d[T]/dt = 2\nu_B k_c[P_B][T] + \nu_B k_c[P^{\bullet}_B][T] + \bar{k}_{p,T}[P^{\bullet}_T][M_f] \qquad (6)$$

The kinetic chain length of the blank radicals is

$$\nu_B = k_{p,B}[M_f]\tau_B \qquad (7)$$

with τ_B being the average lifetime of the blank radicals

$$\tau_B = [P^{\bullet}_B]/R_i \qquad (8)$$

The composite rate constant $\bar{k}_{p,T}$, which is dependent on the free monomer concentration, is given by

$$\bar{k}_{p,T} = \frac{k_{p,I}k_{p,II}(1 + K_M[M_f])}{K_M k_{p,II}[M_f]^2 + k_{p,I}} \qquad (9)$$

where

$$[M_f] = \frac{-Q + (Q^2 + 4K_M[M])^{1/2}}{2K_M} \qquad (10)$$

with $Q = K_M([T] - [M]) + 1$ and [M] being the sum of free and adsorbed monomer concentrations.

It is assumed that $k_{p,I}$ is independent of the array length of monomer on the template sites. Moreover, it is assumed that all constants are independent of template concentration, except of course $\bar{k}_{p,T}$ since $[M_f]$ changes with [T].

If K_M is very large and $[M]_0 > [T]_0$, then $K_M[M_f] \gg 1$, $K_M k_{p,II}[M_f]^2 \gg k_{p,I}$, and (9) simplifies to $\bar{k}_{p,T} \simeq k_{p,I}/[M_f]$. On introduction into (4), we get the rate for a type I polymerization system, $R_p = k_{p,B}[P^{\bullet}_B][M_f] + k_{p,I}[P^{\bullet}_T]$ with $[M_f]_0 = [M]_0 - [T]_0$. When $[T]_0 = [M]_0$, $[M_f]_0$ reduces to zero and R_p becomes $R_{p,I} = k_{p,I}[P^{\bullet}_T]$. If K_M is very small, then $K_M[M_f] \ll 1$, $K_M k_{p,II}[M_f]^2 \ll k_{p,I}$, and (9) reduces to $\bar{k}_{p,T} = k_{p,II}$. Furthermore, $[M_f] = [M]$ so that (4) becomes $R_p = (k_{p,B}[P^{\bullet}_B] + k_{p,II}[P^{\bullet}_T])[M]$, which typifies the rate for a type II polymerization system. This is correct as long as the scheme pertains to dilute template solutions, i.e., when [T] is below the critical overlap concentration, $[T]^*$.[1,5] For $[T] \geq [T]^*$, all blank chain radicals may complex with template macromolecules and the above set of equations has to be modified accordingly; e.g., (2) becomes $d[P^{\bullet}_B]/dt = R_i - k_c[P^{\bullet}_B][T]$, and (5) should be deleted. Moreover, it is possible that under such semidilute conditions propagating daughter chains after reaching one end of a template coil can hop to another, thereby further lowering $R_{t,TT}$ and $k_{t,TT}$[1] and increasing substantially the average molecular weight of the daughter polymer. Of course, such a complication may arise in type I systems as well. It is precisely because of this that all type I (like) systems have been studied under dilute conditions so far.

3. Computer Simulations

A method used frequently to study a template effect is to plot the initial rate $R_{p,0}$ as a function of template concentration $[T]_0$ (in base mol·dm^{-3}) at constant monomer concentration, $[M]_0$, or as a function of $[T]_0/[M]_0$.[1,5]

A convenient way to obtain $R_{p,0}$ is to determine the maximum heat evolution, $(dQ/dt)_{max}$, by microcalorimetry.[6] It is generally assumed that dQ/dt is proportional to $-d[M]/dt$. Further, it may be shown that $(-d[M]/dt)_{max}$, corresponding to $(dQ/dt)_{max}$, approximates the stationary rate where $d[P^{\bullet}]/dt = 0$, i.e., $-(d[M]/dt)_{max} \simeq R_{p,0}$.[6] Hence, by establishing $(dQ/dt)_{max}$ in an isothermal thermogram, one gets $R_{p,0}$ easily. The linear relationship between $-d[M]/dt$ and dQ/dt enables one to simulate thermograms by using the above set of kinetic equations (1)–(10) after introducing the proper kinetic parameters or constants. Since the differential equations are coupled, the full set of equations can only be solved numerically, e.g., by a Runge–Kutta–Merson method.[7] From such computed $R_{p,0}$'s at different $[T]_0$'s, theoretical $R_{p,0}$ vs $[T]_0/[M]_0$ curves are constructed.

In order to find trends as a function of the magnitude of some parameters, a reference set of experimentally estimated kinetic constants is taken from the template

Table I
Reference Set of Rate Constants

k_d, s^{-1}	3.3×10^{-7}	K_M, dm^3·mol^{-1}	3
k_p, dm^3·mol^{-1}·s^{-1}	70	$k_{p,I}$, s^{-1}	800
k_t, dm^3·mol^{-1}·s^{-1}	5×10^6	$k_{p,II}$, dm^3·mol^{-1}·s^{-1}	50
f	0.7	$k_{t,BT}$, dm^3·mol^{-1}·s^{-1}	2400
k_c, dm^3·base mol^{-1}· s^{-1}	0.026	$K_{t,TT}$, dm^3·mol^{-1}·s^{-1}	1000

polymerization of methacrylic acid along poly(2-vinylpyridine)[3] (see Table I). In view of the complications with semidilute solutions discussed in the previous paragraph, the results of the following simulations are only valid for polymerization solutions below [T]*. Also, in the succeeding examples of application of the model, only systems are selected whereby the template concentrations are below [T]*.

4. Results and Discussion

Influence of K_M. Figure 1 shows how the magnitude of K_M affects the initial rate $R_{p,0}$ on varying $[T]_0$, keeping the other parameters constant (see Table I). At low K_M values, say $K_M < 1$ dm^3·mol^{-1}, preferential monomer adsorption is (practically) absent and template polymerization should proceed by a mechanism of type II only. The rate will increase monotonously with $[T]_0$ until all the instantaneously formed radicals in solution, $P^{\bullet}_B$, are able to complex with template macromolecules, the rate reaching a constant level. As soon as there is some preferential monomer adsorption, part of the monomer will be withdrawn from the solution resulting in a decrease of free monomer, M_f, which is the source for the pick-up rate, $R_{p,II}$. The decrease of $[M_f]$ becomes gradually more serious with increasing $[T]_0$ so that the zip rate, $R_{p,I}$, competes more effectively with $R_{p,II}$ until beyond some $[T]_0$ the adsorbed monomer is "diluted" by excess template, leading to shortening of the monomer sequences along the template macromolecules and thus a decrease in $R_{p,0}$. It should be remarked at this stage that all considerations are based on the assumption that adsorbed monomer molecules are incapable of moving along the template (site binding). As long as K_M is still small but larger than one, the maximum in the rate, $R_{p,max}$, is (very) weak (see Figure 1, curve 2). This maximum below $[T]_0/[M]_0 = 1$ shifts from high $[T]_0$ to lower $[T]_0$, when K_M increases. At large values of $K_M > 100$ dm^3·mol^{-1} when $R_{p,I}$ dominates, $R_{p,max}$ shifts back to higher $[T]_0$ and approaches the expected location at $[T]_0/[M]_0 = 1$ when K_M attains values approximating infinity. One may use the direction of the shift in $R_{p,max}$ with K_M as a means to distinguish roughly between type I (like) ($K_M > 100$ dm^3·mol^{-1}) and type II (like) ($K_M < 100$ dm^3·mol^{-1}) mechanisms according to the dominating influence of either zip rate or pick-up rate, but such a distinction is highly subject to the magnitude of the other constants, e.g., of $k_{p,I}$ and k_c, to say nothing of the concentrations of monomer and initiator. The border between type I and II may drop to lower K_M if $k_{p,I}$ or k_c is greater. In practice, it is generally difficult to establish a system to belong either to type I or type II unless rate constants are known. However, a good indication can be obtained already by measuring K_M independently by using, e.g., spectroscopic methods or equilibrium dialysis.

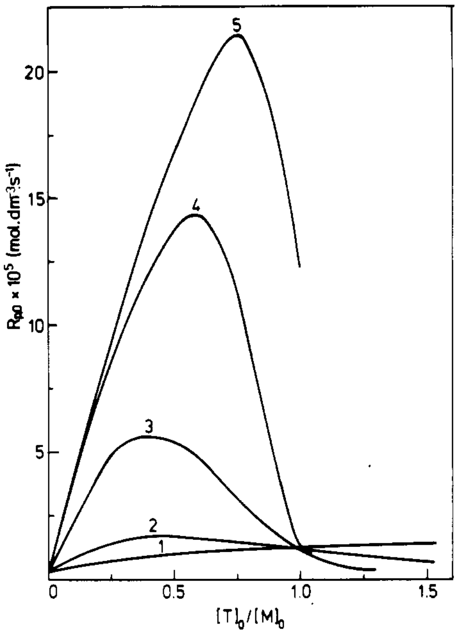

Figure 1. Theoretical curves of initial rate, $R_{p,0}$ vs template (T) to monomer (M) ratio, $[T]_0/[M]_0$, at constant $[M]_0 = 0.4$ mol·dm^{-3} for a template polymerization system having different K_M values: (1) 0.01, (2) 10, (3) 10^2, (4) 10^3, (5) 10^4 dm^3·mol^{-1}. For the other rate constants, see Table I.

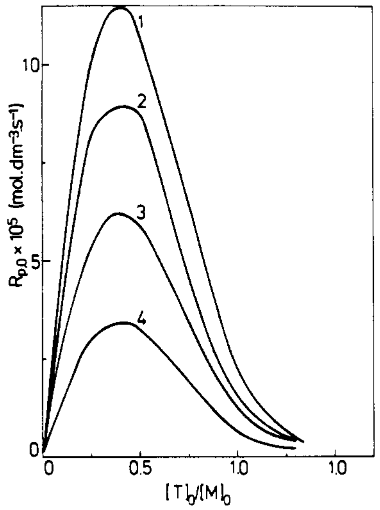

Figure 2. Theoretical curves of initial rate, $R_{p,0}$, vs template to monomer ratio, $[T]_0/[M]_0$, at constant $[M]_0 = 0.4$ mol·dm^{-3} for a template polymerization system with $K_M = 100$ dm^3·mol^{-1} and different k_c values: (1) 0.10, (2) 0.05, (3) 0.03, (4) 0.01 dm^3·mol^{-1}·s^{-1}. For the other rate constants, see Table I.

Influence of k_c (and $k_{t,TT}$). The influence of k_c on $R_{p,0}$ as a function of $[T]_0$ (or $[T]_0/[M]_0$) is demonstrated in Figure 2. Increasing k_c signifies elevation of $[P^{\bullet}_T]$ and hence elevation of $R_{p,0}$ in such a manner that $R_{p,0}$ vs $[T]_0$ curves retain their gross shape. If there is a $R_{p,max}$, then a higher k_c leads to curves in which the location of $R_{p,max}$ with respect to $[T]_0$ does not shift but only increases in "height". In Figure 2, a value for K_M of 100 has been selected in order to follow the changes more clearly. The same tendency may be anticipated if k_t decreases; i.e., the $R_{p,max}$ will become more pronounced with lower values for $k_{t,TT}$ (and $k_{t,BT}$).

Influence of $k_{p,I}$ and $k_{p,II}$. Raising the value of $k_{p,I}$ nearly 3-fold from 800 to 2000 has very little influence on $R_{p,0}$. In contrast, relatively small changes in $k_{p,II}$ between 35 and 70 mol·dm^{-3}·s^{-1} have a marked influence on $R_{p,0}$ as shown in Figure 3. This is understandable considering the low K_M of 3. At high values of K_M, it can be expected that the influence of $k_{p,I}$ and $k_{p,II}$ on $R_{p,0}$ will be reversed.

Influence of $[M]_0$ at Constant $[T]_0$. An alternative way to examine a template system is to vary $[M]_0$ while keeping $[T]_0$ constant. Figure 4 shows the influence of the variation of the monomer concentration as a function of K_M at constant $[T]_0 = 0.4$ mol·dm^{-3} and $[I]_0 = 0.1$ mol·dm^{-3}. The assumption was made that the propagation and termination rate constants did not vary over the entire monomer concentration range.

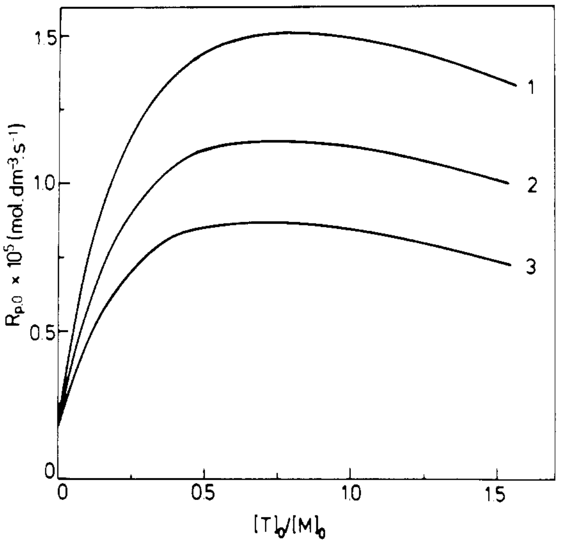

Figure 3. Theoretical curves of initial rate, $R_{p,0}$, vs template to monomer ratio, $[T]_0/[M]_0$, at constant $[M]_0 = 0.4\ \mathrm{mol{\cdot}dm^{-3}}$ for a template polymerization system having different $k_{p,II}$ values: (1) 70, (2) 50, (3) 35 $\mathrm{dm^3{\cdot}mol^{-1}{\cdot}s1{-}^1}$. For the other rate constants, see Table I.

At $K_M < 1\ \mathrm{dm^3{\cdot}mol^{-1}}$ (Figure 4, curve 4), the pick-up rate constant, $k_{p,II}$, mainly determines the template polymerization (TP) rate and an increasing $[M]_0$ results in a constant increase of $R_{p,0}$ (mechanism II). Increasing K_M values (Figure 4, curves 3, 2, and 1), i.e., increasing preferential adsorption of monomer, give rise to an (strong) elevation of the TP rate when $[M]_0$ is in excess of $[T]_0$. The "dip" in the curve at low $[M]_0$ values is caused by a deficiency in the free monomer concentration, $[M]_f$, as a consequence of monomer adsorption by the (large) excess of template. It will vanish when K_M approaches infinity. The rate is then at a maximum at $[M]_0 = [T]_0$ (pure mechanism I).

Influence of $[I]_0$. The influence of $[I]_0$ is very important in that it determines the fraction of chain radicals that complex with template macromolecules. Chain radicals formed in solution, $P^{\bullet}_B$, can either be complexed by the template (see the reaction scheme, step B2) or be prematurely terminated (step A4) and complexed as a dead polymer chain (step B3). The latter does not of course contribute to the template reaction rate and should be avoided. This can be done by decreasing the $[P^{\bullet}_B]$ or, in other words, by decreasing $[I]_0$. This can also be clarified in terms of the fraction of radicals that get complexed

$$f(P^{\bullet}_T) = \frac{R_c}{R_c + R_{t,BB} + R_{t,BT}} \simeq \frac{R_c}{R_c + R_{t,BB}} = \frac{k_c[T]}{k_c[T] + k_{t,BB}[P^{\bullet}_B]}$$

Lowering $[I]_0$ has the additional advantage that the termination of template-associated chain radicals, $P^{\bullet}_T$, is postponed and much more so than in the case of blank (conventional) polymerization since $k_{t,TT}$ is much smaller than $k_{t,BB}$. Since at lower $[I]_0$ values $[P^{\bullet}_B]$ as well as $[P^{\bullet}_T]$ is depressed, both nontemplate and template rates, $R_{p,B}$ and $R_{p,T}$, slow down, though (much) less with the latter in view of the above considerations. The same is true with respect to a comparison between the blank rate, R_B (in the absence of a template), and $R_{p,T}$.

This is manifested as a higher rate enhancement by the template, expressed in terms of the relative rate, which is defined as R_{rel} = (rate in the presence of template)/(rate in the absence of template) = $R_p/R_B = (R_{p,B} + R_{p,T})/R_B$, which at high [T] approximates $R_{p,T}/R_B$. This is confirmed by computational results, compiled in Table II.

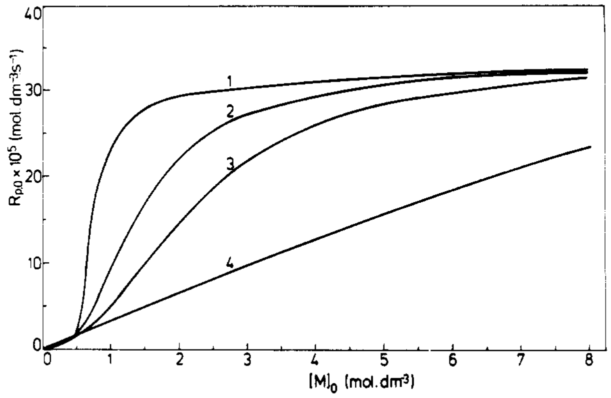

Figure 4. Theoretical curves of initial rate, $R_{p,0}$, vs monomer concentration, $[M]_0$, at constant template concentration, $[T]_0 = 0.4\ \mathrm{mol{\cdot}dm^{-3}}$ for a template polymerization system with different K_M values: (1) 100, (2) 10, (3) 3, (4) 0.1 $\mathrm{dm^3{\cdot}mol^{-1}}$. For other rate constants, see Table I.

Table II
Computed Values of R_B, R_T, and R_{rel} as a Function of $[I]_0$ and $[T]_0/[M]_0$, Utilizing the Set of Rate Constants in Table I

$[I]_0$, $\mathrm{mol{\cdot}dm^{-3}}$	$[T]_0/[M]_0$	10^6R_B, $\mathrm{mol{\cdot}dm^{-3}{\cdot}s^{-1}}$	10^6R_p, $\mathrm{mol{\cdot}dm^{-3}{\cdot}s^{-1}}$	R_{rel}
0.1	0	1.90		
	0.25		9.14	4.8
	0.50		11.10	5.8
	0.75		11.40	6.0
	1.00		11.20	5.9
0.05	0	1.35		
	0.25		7.62	5.6
	0.50		9.25	6.9
	0.75		9.57	7.1
	1.00		9.35	6.9
0.01	0	0.60		
	0.25		4.90	8.2
	0.50		6.10	10.2
	0.75		6.31	10.5
	1.00		6.16	10.3

5. Some Examples

In the literature, there are only a few systems with the proper data available to which the model can be applied. Moreover, in order to avoid arbitrariness, a number of rate parameters, viz. those of the conventional or blank polymerization, are extracted from literature sources and fixed. Some other parametric data are estimated on the basis of previous experience, notably that of $k_{p,II}$, which seems to be generally somewhat lower than $k_{p,B}$ (taken here as 75%) but never higher than $k_{p,B}$ for steric reasons, and that of $k_{t,TT}$, which is generally (much) smaller than $k_{t,BB}$, whereas $k_{t,BT}$ is taken as twice that of $k_{t,TT}$, but both can never be larger than $k_{t,BB}$ for diffusional reasons. The only "true" variables are therefore k_c and $k_{p,I}$. In the cases discussed below, the K_M values are taken from the relevant literature as long as they do not seem to contradict the experimental results on the template polymerization. Because of these constraints, the set of constants may be considered unique, their accuracy depending on the accuracy of the conventional polymerization parameters and the number and accuracy of the available experimental data of the template polymerization system.

Example 1. Results for a system consisting of polymerizations of acrylic acid (AA) and methacrylic acid (MAA) in the presence of poly(4-vinylpyridine) (P4VP) as template in methanol at 60 °C have been reported by

Table III
Rate Constants Used for the Simulation of the Template Polymerization of MAA and AA along P4VP as Template[a]

	MAA polymerization		AA polymerization	
	I	II	I	II
$k_{p,B}$	30×10^3	30×10^3	13×10^3	13×10^3
$k_{t,BB}$	40×10^6	40×10^6	40×10^6	40×10^6
k_d	35×10^{-6}	35×10^{-6}	35×10^{-6}	35×10^{-6}
$k_{p,I}$	5×10^3	5×10^3	20×10^3	50×10^3
$k_{p,II}$	22.5×10^3	22.5×10^3	10×10^3	10×10^3
K_M	100	50	200	100
k_c	1.15	4.25	16.0	27.0
$k_{t,BT}$	6×10^4	40×10^4	1000×10^4	1000×10^4
$k_{t,TT}$	3×10^4	20×10^4	500×10^4	500×10^4
f	0.7	0.7	0.7	0.7

[a] In methanol as solvent at 60 °C.[8] $[MMA]_0 = 0.06$ mol·dm^{-3}; $[AA]_0 = 0.06$ mol·dm^{-3}, and $[AIBN]_0 = 0.0024$ mol·dm^{-3}. For units, see Table I or IV.

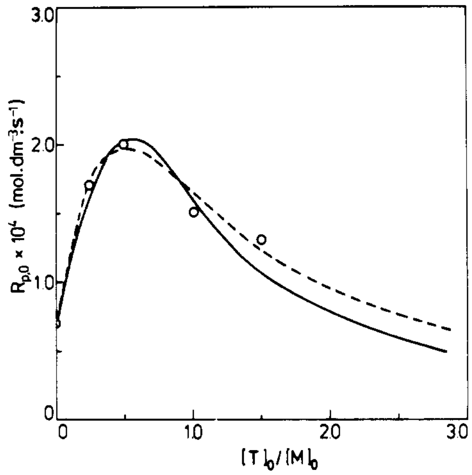

Figure 5. Template polymerization rate of MAA (M) along poly(4-vinylpyridine) (T) as a function of $[T]_0/[M]_0$ at constant $[M]_0 = 0.06$ mol·dm^{-3} in methanol at 60 °C. (○) Data from Fujimori et al.[8] The solid theoretical curve is derived from computed rates using the constants of Table III, column 2, and the dashed one using the constants of column 3.

Fujimori et al.[8] to have $R_{p,max}$ at $[P4VP]_0/[AA]_0 = 0.25$ and $[P4VP]_0/[MAA]_0 = 0.5$, respectively. The K_M values, which the researchers deduced from dialysis experiments, are, however, incredibly low ($K_M < 1$ dm^3·mol^{-1}) and cannot be reconciled with the course of their experimental R_p vs $[T]_0/[M]_0$ plots, which points to a much higher K_M.

Some of the rate constants for the conventional (blank) polymerization of MAA and AA, necessary for the simulations, are known or can be estimated from literature data.[8,9] For blank MAA polymerization, assuming the termination rate constant to be independent of temperature,[9] $k_{t,BB} = 4 \times 10^7$ dm^3·mol^{-1}·s^{-1}, and via a known polymerization rate,[8] $R_B = 7 \times 10^{-5}$ mol·dm^{-3}·s^{-1}, a value for $k_{p,B} = 3 \times 10^4$ dm^3·mol^{-1}·s^{-1} could be calculated. Assuming for the template system $k_{p,II} = 0.75 k_{p,B}$, then $k_{p,II} = 2.25 \times 10^4$ dm^3·mol^{-1}·s^{-1}.

Furthermore, $k_{t,BT}$ is taken as twice the value of $k_{t,TT}$ in accordance with the finding by Smid et al.[2] (see Table I). Since there are only a few experimental points, curve fitting is rather unreliable. Therefore, two sets of tentative rate constants are given in Table III (columns 2 and 3). Simulations lead to the solid and dashed theoretical curves in Figure 5, based on parameters listed in columns 2 and 3 of Table III, respectively. Both curves fit the experimental values (open circles) reasonably well, the dashed one showing a slightly better fit.

In the case of blank AA polymerization,[8] the values for $k_{p,B} = 13 \times 10^3$ dm^3·mol^{-1}·s^{-1} via $k_{t,BB} = 4 \times 10^7$ dm^3·mol^{-1}·s^{-1} and for $R_{p,B} = 3 \times 10^{-5}$ mol·dm^{-3}·s^{-1} could be calculated. Table III, columns 4 and 5, shows two sets of rate constants used for simulations. The outcome is depicted in Figure 6 as the solid and dashed curves, respectively. Both curves fit the rather scattered experimental results.

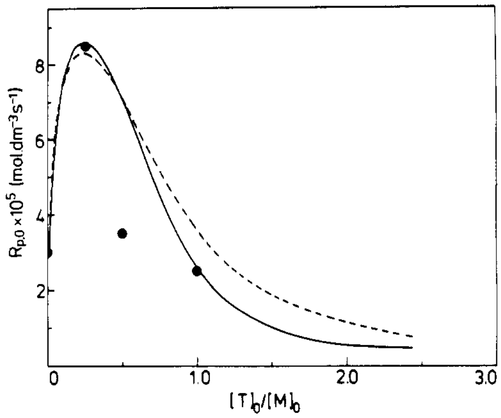

Figure 6. Template polymerization rate of AA (M) along poly(4-vinylpyridine) (T) as a function of $[T]_0/[M]_0$ at constant $[M]_0 = 0.06$ mol·dm^{-3} in methanol at 60 °C. (●) Data from Fujimori et al.[8] The solid theoretical curve is derived from computed rates using the constants of Table III, column 4, and the dashed one using the constants of column 5.

Table IV
Rate Constants Used for the Simulation of the Template Polymerization of AA along PEI[a]

$k_{p,B}$, dm^3·mol^{-1}·s^{-1}	1000	K_M, dm^3·mol^{-1}	200
$k_{t,BB}$, dm^3·mol^{-1}·s^{-1}	20×10^6	k_c, dm^3·base mol^{-1}·s^{-1}	45
R_i, mol·dm^{-3}·s^{-1}	20×10^{-7}	$k_{t,BT}$, dm^3·mol^{-1}·s^{-1}	1500
$k_{p,I}$, s^{-1}	30	$k_{t,TT}$, dm^3·mol^{-1}·s^{-1}	750
$k_{p,II}$, dm^3·mol^{-1}·s^{-1}	750		

[a] In acetone/water (2/1 v/v) as solvent at 25 °C and initiated by UV irradiation using AIBN as initiator.[10] $[AA]_0 = 0.1$ mol·dm^{-3} and $[AIBN]_0 = 0.006$ mol·dm^{-3}.

It should be noted that the K_M's used for constructing the theoretical curves are considerably higher than those found,[8] as expected, and that the larger rate enhancement for AA as compared to MAA may be ascribed not to a more effective suppression of the termination step but rather to a higher monomer adsorption by the template and a larger complexation and zip rate constant.

Example 2. Bamford and Shiiki[10] investigated the polymerization of AA along poly(ethylenimine) (PEI) as template in a mixture of acetone water, 2/1 (v/v), photochemically initiated in the presence of AIBN at 25 °C. This system has a high K_M value[11] of 200 dm^3·mol^{-1}. The blank rate of AA polymerization, $R_B = 2 \times 10^{-5}$ mol·dm^{-3}·s^{-1}, was estimated from Figure 1 in ref 10. The initial monomer and initiator concentrations are 0.1 and 0.006 mol·dm^{-3}, respectively. The rate of initiation, R_i, could be calculated from

$$R_B = k_{p,B}/k_{t,BB}^{1/2} R_i^{1/2} [M]_0 \tag{11}$$

assuming normal kinetics.

For $k_{t,BB}$, a value is assumed to be the same as that of MAA in water at 30 °C, viz. 2×10^7 dm^3·mol^{-1}·s^{-1}. The magnitude of $k_{p,B}$ was estimated at 1000 dm^3·mol^{-1}·s^{-1}, given its polymerization rate is about half that of MAA under comparable reaction circumstances,[8] and $k_{p,B}$(MAA) = 5000 dm^3·mol^{-1}·s^{-1} in water at 30 °C. Then by use of eq 11, $R_i = 2 \times 10^{-6}$ mol·dm^{-3}·s^{-1} ($f = 0.7$). The remaining rate constants were obtained by trial and error, resulting in a set of constants listed in Table IV. This leads to a theoretical curve that fits the experimental data very well (Figure 7).

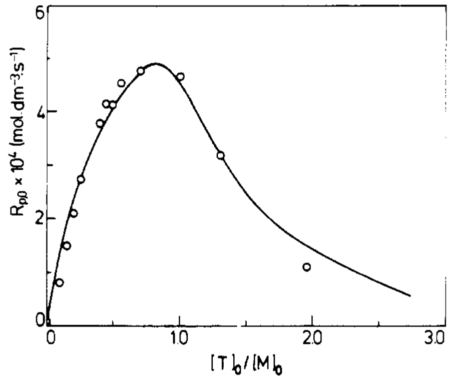

Figure 7. Template polymerization rate of AA (M) along poly(ethylenimine) (T) as a function of $[T]_0/[M]_0$ at constant $[M]_0 = 0.1$ mol·dm^{-3}, in acetone/water (2/1 v/v) at 25 °C. (○) Data from Bamford and Shiiki.[10] The drawn curve is derived from computed rates using the constants of Table IV.

Table V
Rate Constants Used for the Simulation of the Template Polymerization of AA along PVP as Template[a]

	ref 13	ref 12
$k_{p,B}$, dm^3·mol^{-1}·s^{-1}	66×10^3	66×10^3
$k_{t,BB}$, dm^3·mol^{-1}·s^{-1}	18×10^7	18×10^7
k_d, s^{-1}	5×10^{-5}	5×10^{-5}
$k_{p,I}$, s^{-1}	1×10^4	1×10^4
$k_{p,II}$, dm^3·mol^{-1}·s^{-1}	5×10^4	5×10^4
K_M, dm^3·mol^{-1}	65	65
k_c, dm^3·base mol^{-1}·s^{-1}	1.2	1000
$k_{t,BT}$, dm^3·mol^{-1}·s^{-1}	10×10^4	2×10^4
$k_{t,TT}$, dm^3·mol^{-1}·s^{-1}	5×10^4	1×10^4
f	0.7	0.7

[a] In water as solvent at 74 °C with $K_2S_2O_8$ as initiator. $[K_2S_2O_8]_0 = 0.0074$ mol·dm^{-3}; $[AA]_0 = 0.02$, 0.05, and 0.1 (Muramatsu and Shimidzu[13]) and 0.02 mol·dm^{-3} (Ferguson and Shah[12]).

Curve fitting was also realized by Bamford et al.,[10] by means of the semiempirical expression

$$-d[M]/dt = C \exp(-\alpha Z^\beta/kT)[X] \qquad (12)$$

where C is a function of $[P^\bullet{}_T]$, being practically constant, $Z \equiv [T]_0/([M]_0 - [M_f])$, $[X] \equiv [M]_0 - [M_f]$, and α and β are curve-fitting constants. The exponential term allows for the effect of interruption in monomer sequences on the polymerization rate.

From the magnitudes of the constants in Table IV, it may be concluded that the rate enhancements in this case is not so much due to a high K_M, its advantage being counteracted by a rather low $k_{p,I}$, but principally to a very strong decrease of the termination step, which is quite in contrast to the system of the previous example.

Example 3. The polymerization of AA along poly(*N*-vinylpyrrolidone) (PVP) in dilute aqueous solutions using $K_2S_2O_8$ as initiator was examined by Ferguson and Shah[12] as well as by Muramatsu and Shimidzu.[13]

To simulate R_p vs $[T]_0/[M]_0$ curves, the following constants were extracted from the literature:[14,15] $k_{p,B} = 66 \times 10^3$, $k_{t,BB} = 18 \times 10^7$ dm^3·mol^{-1}·s^{-1}, $k_d = 5 \times 10^{-5}$ s^{-1}. A K_M value of 65 dm^3·mol^{-1} was deduced by Muramatsu and Shimidzu[13] by employing their model. Assuming $k_{p,II} = 0.75k_{p,B}$, we obtained $k_{p,II} = 50 \times 10^3$ dm^3·mol^{-1}·s^{-1}. The remaining constants, $k_{p,I}$ and k_c, were obtained by trial and error. A theoretical curve using the set of rate constants listed in Table V, column 3, fits the experimental values of Ferguson et al. (Figure 8) fairly well ($[AA]_0 = 0.02$ mol·dm^{-3}), in spite of the disputable method of applying turbidimetry to follow the reaction and their finding that R_p is proportional to $[AA]^{1.5}$. It should be noted, however, that the found k_c value of 1000 is unusually high as compared to those found so far, casting doubt on the validity to apply the model, which is based on the proportionality of R_p to [AA], to this case.

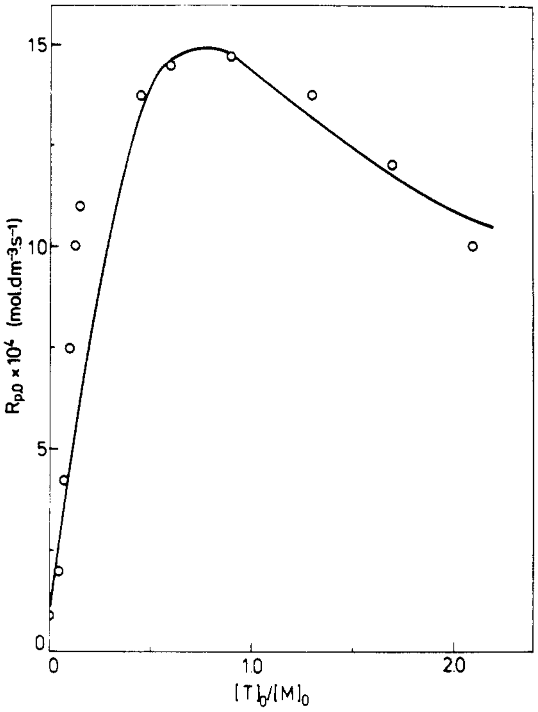

Figure 8. Template polymerization of AA (M) along poly(*N*-vinylpyrrolidone) (T) as a function of $[T]_0/[M]_0$ in water with $K_2S_2O_8$ as initiator at 74 °C. (○) Data from Ferguson and Shah.[12] $[AA]_0 = 0.02$ mol·dm^{-3}. The drawn curve is derived from computed rates using the constants of Table V, column 3.

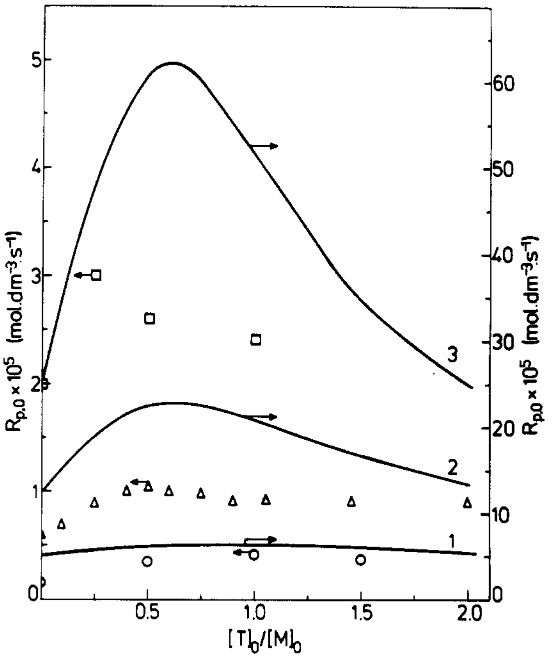

Figure 9. Template polymerization of AA (M) along poly(*N*-vinylpyrrolidone) (T) as a function of $[T]_0/[M]_0$ in water with $K_2S_2O_8$ as initiator at 74 °C. Data from Muramatsu and Shimidzu.[13] $[AA]_0$: (○) 0.02; (△) 0.05, (□) 0.1 mol·dm^{-3}. Drawn theoretical curves are derived from computed rates using the constants of Table V, column 2. $[AA]_0$: (1) 0.02, (2) 0.05, (3) 0.1 mol·dm^{-3}.

In contrast, no curve fitting to the results of Muramatsu and Shimidzu,[13] whereby bromometric titrations were employed to follow the reactions, could be accomplished. Only the profile of the R_p vs $[T]_0/[M]_0$ curve with $[AA]_0 = 0.02$ mol·dm^{-3} could be reasonably approximated (Figure 9, curve 1), using the set of constants in column 2 of Table V. No better results could be obtained if other values for

K_M, $k_{p,I}$, k_c, and $k_{t,TT}$ were selected. This may be due to their finding that R_p appeared to be proportional to $[AA]^{1.9}$! When this same set of rate constants was applied to experiments with $[AA]_0 = 0.05$ and 0.1 mol·dm^{-3} respectively, curves 2 and 3 in Figure 9 were obtained, which deviate considerably from the experimental curves, even in shape. This additional discrepancy may be due to the tacit assumption that such constants, k_c, K_M, and $k_{t,TT}$, are unaffected by pH upon an increase of monomer concentration. Whatever the reason might be, it seems also that in this template polymerization system suppression of the termination rate is mainly responsible for the rate enhancement.

6. Conclusions and Final Remarks

The generalized kinetic model for radical template polymerizations originally developed by Smid et al.[2] and successfully applied to the template polymerization of methacrylic acid along poly(2-vinylpyridine)[2] is also applicable to some extent to other systems described in the literature. By some plausible assumptions and curve fitting to R_p vs $[T]_0/[M]_0$ data, it is possible to estimate template rate constants, provided the rate constants for the blank (nontemplate) polymerization are available. This is demonstrated by some examples. They show that retarded termination is a common feature of template polymerizations. Furthermore, simulations and results from the given examples show that the degree of rate enhancements is highly dependent on the degree of monomer adsorption or complexation by the template (K_M) and the rate constant of complexation of oligomeric radicals formed in solution (k_c). Of course, the great effect of a large K_M can be counteracted by a low zip rate constant, $k_{p,I}$, implying an unfavorable placement of adsorbed monomer molecules with respect to the template-associated polymer radical.

The model may fail when the kinetics deviate from classical kinetics, as shown in the last example where R_p is proportional to $[M]^{1.9}$. Problems may also arise when dealing with template systems whereby aqueous solutions of a polyelectrolyte template are used in view of pH and salt effects.[16-18] With respect to semidilute and concentrated solutions of a template ($[T] > [T]^*$), the model may probably still hold on the provision that the set of equations be adapted to the special circumstance that there are no blank radicals ($P^\bullet_B$) involved in termination steps and that no abnormalities occur, such as a gel effect or jumping of chain radicals from one template coil to another.

Acknowledgment. Discussions with Prof. G. Challa are greatly appreciated.

Glossary

$[I]_0$	initial initiator concentration
$[M]_0$	initial monomer concentration
M_f	free monomer
M_T	monomer adsorbed on template (site)
$[T]_0$	initial template concentration
k_c	complexation rate constant of chain radicals or polymer with template
$k_{p,I}$	zip propagation rate constant
$k_{p,II}$	pick-up propagation rate constant
$k_{p,B}$	blank propagation rate constant
$k_{p,T}$	template propagation rate constant
$k_{t,BB}$	blank termination rate constant
$k_{t,BT}$	termination rate constant for template associated radical with blank radical
$k_{t,T}$	template termination rate constant
$k_{t,TT}$	termination rate constant for two template-associated chain radicals
K_M	equilibrium constant for monomer adsorption by template
$P^\bullet_B$	blank chain radical
$P^\bullet_T$	template-associated chain radical
$f(P^\bullet_T)$	fraction of $P^\bullet_B$ that gets complexed
R_B	(overall) blank rate in the absence of a template
R_c	complexation rate
R_p	overall (propagation) rate in the presence of a template
$R_{p,0}$	initial rate
$R_{p,I}$	zip rate
$R_{p,II}$	pick-up rate
$R_{p,B}$	blank (propagation) rate in the presence of a template
$R_{p,max}$	maximum rate in R_p vs $[T]_0/[M]_0$ plots
$R_{p,T}$	template (propagation) rate
R_{rel}	relative rate = R_p/R_B
$R_{t,BB}$	blank termination rate
$R_{t,BT}$	termination rate for blank radical with template-associated radical
$R_{t,TT}$	termination rate for two template-associated chain radicals

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Registry No. MMA, 79-41-4; AA, 79-10-7; poly(4-vinylpyridine) (homopolymer), 25232-41-1; poly(ethylenimine) (homopolymer), 9002-98-6; poly(*N*-vinylpyrrolidone) (homopolymer), 9003-39-8.