Penultimate Unit Effects in Free Radical Copolymerization

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Summary: The penultimate unit effects (PUEs) on the propagation, termination, and reversible addition-fragmentation chain transfer (RAFT) processes in free radical copolymerization are discussed on the basis of recent publications. The propriety of the implicit and explicit PUE models in propagation and chain transfer processes is commented. The penultimate termination model with the geometric-mean approximation and the related rate equation are highlighted.

Introduction

In the rotating-sector (RS) study reported in 1985,[1)] we showed that the terminal model fails to describe the rate constant of propagation $(\bar{k}_p)$ of styrene (ST: monomer 1) / methyl methacrylate (MMA: monomer 2) copolymerization in the bulk, even though the same model conforms to the composition curve of this system. (We attach a bar "$^-$" over the variables related to copolymerization to stress that they are, or can be, a function of composition and other variables.) The dilution of this system with a solvent (toluene) gave essentially the same result,[2)] meaning that the failure of the terminal model should be ascribed to a penultimate unit effect (PUE) (or a higher-order effect), not to an environmental effect, e.g., a solvent effect. Since then, a number of copolymerization systems including ST/MMA[3,4)] have been studied by pulsed laser polymerization (PLP), RS or ESR, establishing that the PUE in $\bar{k}_p$ is a general rule rather than an exception.[5-8)]

Before this recent progress concerning the propagation step, the termination process of copolymerization had not been well understood, either. This was because no paper except one[9)] had experimentally dealt with absolute values of termination rate constant $(\bar{k}_t)$ in copolymerization. Discussion on termination had

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been exclusively based on experimental data for the copolymerization rate index $\bar{\omega} = \bar{k}_p / \bar{k}_t^{1/2}$ with $\bar{k}_p$ being assumed to be given by the terminal model. The Walling equation[10)] is among the representative rate equations formulated along this line: it includes a single adjustable parameter ϕ given by

$$\phi = k_{t1\cdot 2}/(k_{t1\cdot 1}k_{t2\cdot 2})^{1/2} \quad (1)$$

where $k_{ti\cdot j}$ is the termination rate constant between polymer radicals i and j, i.e., polymer radicals with a terminal unit i and j, respectively ($i, j = 1$ or 2). Values of ϕ deduced by this analysis strongly depend on composition in many cases. Instead of the terminal termination model adopted in the Walling equation, Russo and Munari[11,12)] proposed to adopt the penultimate termination model, and using an approximation, they derived a rate equation that includes the two adjustable parameters δ_1 and δ_2 which will be discussed in detail later on. This Russo-Munari equation is known to fit the experimental $\bar{\omega}$ vs. f_1 curves of most systems extremely well. Needless to say, however, values of δ_1 and δ_2 as well as ϕ deduced by these analyses are of little physical significance, for those rate equations are based on the generally incorrect terminal propagation model.

In this work, we will give a brief overview of recent studies on the PUEs in the propagation and termination processes of copolymerization. We will focus on three specific topics. First, we wish to make comments on the origins of PUE on the propagation step. Second, we will discuss the possible PUE on the termination process and the related rate-of-copolymerization equation. The third, more contemporary topic concerns the possible PUE on a RAFT (reversible addition-fragmentation chain transfer) process.

Penultimate Unit Effect (PUE) in Propagation

The penultimate model is characterized by the eight propagation rate constants k_{ijm}, where i, j, and m denote the penultimate unit, the terminal unit, and the monomer, respectively ($i, j, m = 1$ or 2). The four monomer reactivity ratios are defined by $r_{11} = k_{111}/k_{112}$, $r_{21} = k_{211}/k_{212}$, $r_{22} = k_{222}/k_{221}$, and $r_{12} = k_{122}/k_{121}$, and the two radical reactivity ratios are defined by

$$s_1 = k_{211}/k_{111}, \quad s_2 = k_{122}/k_{222} \quad (2)$$

The general (unrestricted) penultimate model, therefore, includes all the six reactivity ratios and the two homo-propagation rate constants k_{111} and k_{222}.

In former times, copolymerization models were tested only against experimental data on composition and/or sequence distributions, which are a function of the monomer reactivity ratios alone. Only a few systems seemed to require the penultimate model to accurately reproduce the composition and/or sequence distribution data, while most systems could be well described by the terminal model, meaning that $r_{11} = r_{21}$ ($= r_1$) and $r_{22} = r_{12}$ ($= r_2$) within experimental error. On the other hand, the recent RS, PLP, and ESR studies on $\bar{k}_p$ revealed that the penultimate unit effect (PEU) is a rule, i.e., s_1 and/or s_2 significantly differ from unity in most systems (see above). These results gave rise to the terms implicit and explicit PUEs. Namely, implicit PUE affects the radical reactivity ratios (e.g., $s_1 \neq 1$) but not the monomer reactivity ratios (e.g., $r_{11} = r_{21} = r_1$), while explicit PUE appears on the monomer reactivity ratios as well as on the radical reactivity ratios. Experimental results indicate that implicit PUE is most general, while explicit PUE is rater exceptional.

There has been controversy regarding the origin(s) of PUE. In the radical stabilization model proposed by Fukuda et al.,[13)] the stabilization energy of the radical is assumed to be affected by the penultimate unit, and a fixed portion of this energy is assumed to be carried over to the energy barrier (Evans-Polanyi's rule). This model predicts an implicit PUE, namely $r_{21} = r_{11} = r_1$, etc., and gives the following relation, when all other effects are neglected:

$$s_1 s_2 = r_1 r_2 \qquad (3)$$

The radical stabilized by a foreign unit at the penultimate position would be slow to react (small s), whereas the cross-propagation leading to a stabilized radical would be fast (small r). This is a qualitative interpretation for the correlation of s and r.

Equation 3 has been tested against experimental values of s_1 and s_2 deduced from $\bar{k}_p$ data. Figure 1 shows the plot of log $(s_1 s_2)^{-1}$ vs. log $(r_1 r_2)^{-1}$. Numerical data are essentially the same as those given in a previous review,[6)] excepting that some recent data[14-16,20)] were added. Even though the data points are widely scattered, there appears to be a positive correlation between the two products of the

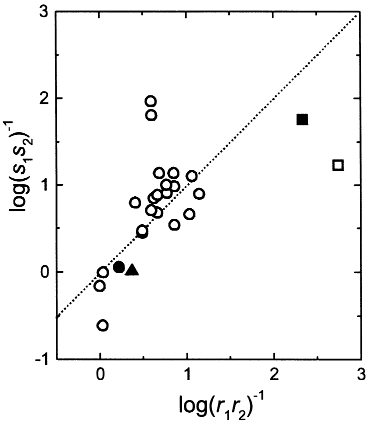


Figure 1. Plot of log $(s_1s_2)^{-1}$ vs. log $(r_1r_2)^{-1}$: (●)*p*CS/ST,[16] (▲)*p*CS/*p*MOS,[16] (□) *p*BOS/DBF,[14] (■)ST/DEF.[20] For other data, see ref. 6.

parameters.

Davis and his co-workers recently made detailed PLP studies to explore the origin of PLP. For a ST/MMA bulk system, they attempted to measure the temperature dependence of s_1 and s_2.[17,18] Even though it was not possible to determine whether or not the individual s_1 and s_2 were temperature dependent, it was found that the extent of deviation from the terminal model (as measured by fitting a single parameter to the data, i.e., $s_1 = s_2 = s$) was temperature dependent, and thus the PUE in this system had a significant enthalpic contribution. On the other hand, these authors examined the copolymerizations of *p*-chlorostyrene with styrene (*p*CS/ST) and *p*CS with *p*-methoxystyrene (*p*CS/*p*MOS) and noted that these systems do not exactly follow Eq. 3 (see the filled circle and triangle, respectively, in Figure 1). Then they claimed that the results obtained for these sterically similar monomers are counter-examples to the radical stabilization model, and the PUE for these systems is likely to originate from polar interactions. Moreover, regarding the log $(r_1r_2)^{-1}$ vs. log $(s_1s_2)^{-1}$ plot such as shown in Figure 1, they commented that "most of the data is simply scattered around a central point and the correlation is thus quite poor."[7)]

As has been stressed in previous work,[5,6)] Eq. 3 should be regarded as a crude approximation at best: for it totally neglects the frequency factor, and it is based on the Evans-Polanyi rule, a semi-empirical rule. Moreover, the intrinsic difficulty of accurately determining s_1 and s_2 [5,7)] can also cause scattering of date points. The importance of steric contributions to PUE has been stressed by Heuts et al.[19)] The copolymerizations of *p*-butoxystyrene with dibutyl fumarate (*p*BOS/DBF)[14)] and of styrene with diethyl fumarate (ST/DEF),[20)] shown by the open and filled squares, respectively, in Figure 1, are presumed to be typical systems in which the entropic, rather than enthalpic, contributions to PUE are primarily important (for the ST/DEF system, see also below). All these factors can badly smear the possible correlation predicted by Eq. 3, rendering the discussion on individual systems little meaningful, and requiring a large number of samples to see whether or not the predicted correlation exists. Indeed most of the data in Figure 1 may appear to be simply scattered around a central point, as Coote and Davis[7)] commented, but the question to be asked is as to why the central point lies near the line predicted by Eq. 3. In this context, existing counter-evidence to the radical stabilization model is not strong enough to invalidate it.

Recent ab initio molecular orbital calculations on the addition of γ-substituted small radicals to simple alkenes indicate that polar effects as well as enthalpic and entropic contributions are important as origins of PUE.[21,22)] Moreover, these results suggest that strong effects on radical reactivity are always likely to be accompanied by selectivity variations, and polar or specific interactions in radical interactions are also likely to be commonplace. It follows that the PUE resulting in a large stabilization effect is likely to influence selectivity too, namely, it is more likely explicit than implicit.[7)] On the other hand, there is a large body of ab initio calculations carried out on the rate constant ratio $r_{1,\mathrm{calcd}} = k_{R1}/k_{R2}$,[22-24)] where R is a small radical as a model for monomer 1, e.g., benzyl radical for ST[23)] and methoxycarbonyl-2-propyl radical for MMA,[24)] and 1 and 2 denote different monomers. The fact that these calculations generally well reproduce the experimental values of the monomer reactivity ratio $r_1 = k_{11}/k_{12}$ suggests that PUE is essentially implicit, or explicit PUE is generally small, if any present, and that the experimental values of r_1 have in fact a physical meaning. This is so because the r_1 values observed for copolymerizations are well approximated by those of the model reactions with small radicals *without a penultimate unit.*

Penultimate Unit Effect (PUE) on Termination

Recent experimental studies, in particular, those by Buback and his co-workers[25-27] have firmly established that the bimolecular termination of polymer radicals in the dilute regime is determined by segmental diffusion. More specifically, they remark that the termination in this regime is "controlled by the diffusivity of a small number of segments at the free site. The size of k_t is determined by steric shielding and by intra-coil viscosity".[26] However, the picture of "steric shielding" is not fully clear. In this regard, the ST/DEF copolymerization[20] is particularly interesting, since the k_t of DEF is nearly four orders of magnitude smaller than that of ST, and therefore the

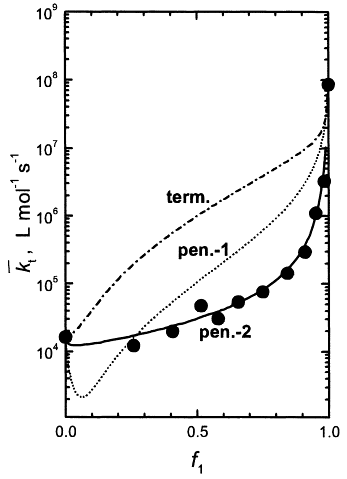


Figure 2. Plot of lot $\bar{k}_t$ vs. f_1 for ST/DEF bulk copolymerization at 40 °C.[20] The curves are the best-fit results by the terminal termination model (term.) and the penultimate termination models with the algebraic (pen.-1) and geometric (pen.-2) mean approximation.

copolymerization of these two monomers would give information about the velocity at which polymer radicals with extremely different diffusivities undergo termination. This can provide a new clue to better understand the nature of termination reactions.

The $\bar{k}_t$ vs. f_1 data for this system is given in Figure 2. Upon the premise that the segmental diffusivity that controls the radical-radical reaction is determined by one or more monomer units at the active chain end, the simplest would be the terminal termination model in which only the terminal unit is assumed to play the main role. This model includes the single unknown quantity, i.e., the termination rate constant $k_{t1\cdot 2}$ or ϕ (Eq.1). As Figure 2 shows, this model badly overestimates the $\bar{k}_t$ data even for $k_{t1\cdot 2} = 0$ (the lowest physically possible limit). This means that we have to take at least the penultimate unit into account.

The penultimate termination model includes 16 termination rate constants $k_{tij\cdot kl}$, where $k_{tij\cdot kl}$ refers to the termination between radicals *ij* and *kl* (*i*, *j*, *k*, and *l* = 1 or 2).[11)] Two different types of simplifications may be possible: let us consider the limiting case in which the reaction between radicals A and A is fast, while the reaction between radicals B and B is zero in velocity. If the reason for the zero B-B reaction is due to extremely slow diffusion of B, an A-B reaction will occur still at a high rate, since A will diffuse to B fast. This corresponds to the algebraic-mean approximation, i.e., $k_{tA\cdot B} = (k_{tA\cdot A} + k_{tB\cdot B})/2$. On the other hand, if the reason for the zero B-B reaction is due to the radical B being shielded or unable to take a suitable conformation to react, then there will be no A-B reaction, even if A moves fast. This picture suggests us to introduce the "shielding coefficient" *q*, in terms of which we give $k_{tA\cdot B}$ as the product of the two coefficients, $q_A q_B$. This is equivalent to assuming the geometric-mean approximation,[11)] i.e., $k_{tA\cdot B} = (k_{tA\cdot A} k_{tB\cdot B})^{1/2}$. Both approximations lead to $\bar{k}_t$ equations which commonly include the two parameters δ_1 and δ_2:

$$\delta_1 = (k_{t21\cdot 21} / k_{t11\cdot 11})^{1/2} \qquad (4)$$

for δ_2, exchange 1 and 2 in Eq. 4.

As Figure 2 shows, the algebraic-mean model completely fails to reproduce the experimental data for any (positive) values δ_1 and δ_2. On the other hand, the geometric-mean model can very well reproduce the data for $\delta_1 = 0.067$ and $\delta_2 = 0.81$.

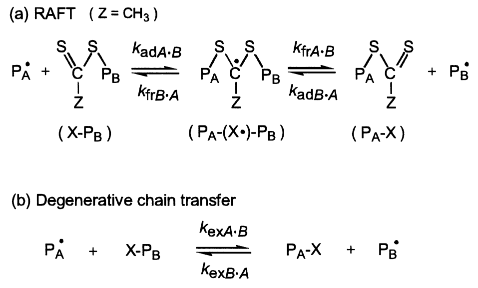
Incidentally, the s_1 and s_2 values deduced from the $\bar{k}_\mathrm{p}$ data for this system were: s_1 = 0.055 and s_2 = 0.32. The exceptionally small values of δ_1 and s_1 were explained in terms of a strong shielding effect of the penultimate DEF unit on the terminal ST radical in both propagation and termination.20)

Presumably terminal segments longer than two monomer units will be responsible for the absolute values of termination rate constant. However, our interest in a copolymerization system focuses on relative differences from the relevant homopolymerization systems, and for this reason, chain-length dependent properties are automatically canceled out to a large extent in ratios such as δ_1 and δ_2. In this regard, what is essential in copolymerizations (and copolymers28)) is the existence of A-B or B-A alternating units in the chain, whose properties cannot be simply deduced from the properties of A-A and B-B units. The penultimate termination as well as propagation models do focus on the chemical and physicochemical properties of the alternating units, and this may be the reason for the remarkable success of these models despite their simplicity compared to higher-order models.

The combination of the penultimate-model $\bar{k}_\mathrm{p}$ and $\bar{k}_\mathrm{t}$ (with the geometric-mean approximation) gave the rate equation6,20)

$$\frac{\bar{r}_1 f_1^{\,2} + \bar{r}_2 f_2^{\,2} + 2 f_1 f_2}{\bar{\omega}} = \left(\frac{\bar{r}_1 f_1}{\omega_1}\right)\left(\frac{r_{11} f_1 + \lambda_1 f_2}{r_{11} f_1 + f_2}\right) + \left(\frac{\bar{r}_2 f_2}{\omega_2}\right)\left(\frac{r_{22} f_2 + \lambda_2 f_1}{r_{22} f_2 + f_1}\right) \tag{5}$$

where $\bar{\omega} = \bar{k}_\mathrm{p} / \bar{k}_\mathrm{t}^{\,1/2}$, $\omega_i = k_{iii} / k_{\mathrm{t}ii \cdot ii}^{\;\;1/2}$, and $\lambda_i = \delta_i / s_i$ $(i, j$ = 1 or 2). When PUE is implicit, we many put $\bar{r}_i = r_{ii} = r_i$, and then Eq. 5 becomes *formally* identical with the Russo-Munari (RM) equation11) which includes δ_1 and δ_2 instead of λ_1 and λ_2, respectively. Namely, Eq. 5 reduces to the RM equation when all PUEs in propagation are absent. The RM equation and hence Eq. 5 are known to fit the rate-of-copolymerization curves of most systems (including ST/DEF) extremely well.6,11,12,20) This also suggests the validity of the underlying termination and propagation models.



Scheme 1. (a) RAFT process and (b) its simplification (degenerative chain transfer process).

Penultimate Unit Effect (PUE) in a RAFT Process

The RAFT (reversible addition-fragmentation chain transfer) process[29,30] generally includes the addition of a type A radical to the adduct with a type B alkyl (X-P_B) to produce the P_A-(X•)-P_B intermediate radical, and if radical A is released, a RAFT process or an exchange reaction is completed (cf. Scheme 1). Therefore the exchange rate constant is given by

$$k_{\mathrm{ex}A\cdot B} = P_{\mathrm{r}B} k_{\mathrm{ad}A\cdot B} \qquad (6)$$

where $P_{\mathrm{r}B} = k_{\mathrm{fr}A\cdot B}/(k_{\mathrm{fr}A\cdot B} + k_{\mathrm{fr}B\cdot A})$ is the relative probability that radical B is released. For homopolymerization, $P_{\mathrm{r}B} = 1/2$.

Goto et al. kinetically studied the RAFT process in ST and MMA polymerizations[31] and ST/MMA copolymerization.[32] Table 1 gives some preliminary results, where $\overline{C}_{\mathrm{ex}}$ is the exchange (degenerative chain transfer)

Table 1. Values of $\overline{C}_{\mathrm{ex}}$ (or C_{ex}) at 40 °C

	PST•	PMMA•	Copolymer• [d]
PS_0-X[a,b]	220	0.83	75 (82[e])
$PMMA_0$-X[a,c]	420	40	155 (167[e])

[a] X = -SCSCH$_3$. [b] M_n = 1940, M_w/M_n = 1.17. [c] M_n = 5470, M_w/M_n = 1.19.
[d] Random copolymer radical with f_1 = 0.53 (azeotropic composition).
[e] Terminal-model value.

constant given by

$$\bar{C}_{\mathrm{ex}} = \bar{k}_{\mathrm{ex}} / \bar{k}_{\mathrm{p}} \qquad (7)$$

and X is the dithioacetate moiety $-\mathrm{SC(CH_3)} = \mathrm{S}$. Since the addition rate should be nearly independent of the alkyl (polymer) moiety of the adduct, the data in Table 1 indicate that the PMMA radical is released from the PMMA-(X•)-PST intermediate about 100 times faster than the PST radical. Also noteworthy is the fact that the C_{ex} of the PMMA radical is more than one order of magnitude smaller than that of the PS radical. This means that the $\bar{C}_{\mathrm{ex}}$ values observed for the copolymer radical predominantly reflect those of styryl radicals. Namely, in the general penultimate-model expression of $\bar{C}_{\mathrm{ex}}$ 5)

$$\bar{C}_{\mathrm{ex}} = \frac{\bar{r}_1 f_1 \bar{C}_{\mathrm{ex1}} + \bar{r}_2 f_2 \bar{C}_{\mathrm{ex2}}}{\bar{r}_1 f_1^2 + \bar{r}_2 f_2^2 + 2 f_1 f_2} \qquad (8)$$

the $\bar{C}_{\mathrm{ex2}}$ term is relatively so small that it may be approximated by the homopolymerization value C_{ex2}, whether there is PUE in $\bar{C}_{\mathrm{ex2}}$ or not.

Then from the data in Table 1, we have the following results:

$$s_1 = \frac{k_{211}}{k_{111}} \approx \frac{k_{\mathrm{ex21\text{-}11}}}{k_{\mathrm{ex11\text{-}11}}} \approx \frac{k_{\mathrm{ex21\text{-}22}}}{k_{\mathrm{ex11\text{-}22}}} \qquad (9)$$

We should remember that s_1 in this system was evaluated to be 0.30.1) This means that the PUE in this RAFT process is implicit. (This can be more directly seen in Table 1, where the $\bar{C}_{\mathrm{ex}}$ values for the copolymer radical are nearly equal to the values in parenthesis which were calculated with the terminal model.) Another important implication of the approximate relations in Eq. 9 is that PUE affects the addition step but not the fragmentation step. Due to the fast fragmentation of PMMA relative to PST (see above), the ratio $k_{\mathrm{ex21\text{-}22}} / k_{\mathrm{ex11\text{-}22}}$ will be little affected by the fragmentation rate, while the ratio $k_{\mathrm{ex21\text{-}11}} / k_{\mathrm{ex11\text{-}11}}$ will generally be affected by PUE on fragmentation as well as on addition. The approximate equalities in Eq. 9 therefore suggests the absence of significant PUE on fragmentation.

Conclusions

Recent experiments have established that the PUE on $\bar{k}_{\mathrm{p}}$ is a general rule. An important question to be asked now is whether this PUE is implicit or explicit.

Experiments on composition (and sequence distributions) suggest that except for a few systems, such as ST/acrylonitrile,5) it is implicit, or at least, there is no obvious need to discard the terminal model. The addition process in the ST/MMA/ dithioacetate RAFT system is also implicit, namely the terminal model is apparently valid to describe the exchange coefficient $\overline{C}_{\mathrm{ex}} = \overline{k}_{\mathrm{ex}} / \overline{k}_{\mathrm{p}}$ (even though the fragmentation process in the same system seems to be unaffected by PUE). This result for the RAFT system is in line with the fact that the chain transfer reactions of a majority of systems are under the influence of implicit PUE,33-35) excepting the only well-known explicit PUE case with CBr_4 used as a chain transfer agent.34,35)

The implicit PUE in propagation13) and chain transfer35) has been attempted to be justified by the radical stabilization model. On the other hand, the importance of polar and entropic effects have also been stressed. Hence PUE is of multiple origins, but it would not invalidate this simple (radical stabilization) model entirely.

Obviously, the explicit PUE model can give more precise descriptions of copolymerization than the implicit one, since the former includes the latter as a special case. However, at the present time, there seems to be no strong evidence that urges us to use the former as a general model, at the cost of introducing enormous complexity accompanying it. The need for more precise experiments and theory is apparent. Chain transfer experiments may be particularly powerful in providing an unequivocal answer to the implicit vs. explicit controversy.

The penultimate termination model with the geometric-mean approximation and the related rate equation have been justified theoretically and experimentally to a large extent. Despite all the complexities of PUE in propagation and termination, the simplicity of the resulting equations may indeed be noteworthy.

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