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Transfer and Propagation Reactions in Free-Radical Copolymerization

Thomas P. Davis, Johan P. A. Heuts, Christopher Barner-Kowollik,
Simon Harrisson, David A. Morrison, Lachlan H. Yee,
Heidi M. Kapfenstein-Doak, Michelle L. Coote

Center for Advanced Macromolecular Design, School of Chemical
Engineering and Industrial Chemistry, University of New South Wales,
Sydney, Australia

Summary: The contribution of entropic factors to the penultimate unit effect in free-radical copolymerizations is discussed and exemplified. In addition, significant penultimate unit effects on radical selectivity in transfer reactions are demonstrated and are shown to have a significant polar component. Further, ring-opening copolymerization studies are presented and describe surprising results that seem to originate from strong solvent effects in copolymerization. These results could not have been predicted with current knowledge, prior to the experiment. The present contribution demonstrates in detail that radical reactions are highly complex and there are significant dangers and drawbacks in employing simplified kinetic models when in search of fundamental understanding.

Introduction

It is now generally accepted that most copolymerizations do not behave according to the terminal model and the cause of this is a significant contribution from γ-substituents – or the penultimate unit effect (PUE).[1,2] There has been some reluctance to acknowledge the development of copolymerization theory since the 1940s with many groups retaining over-confidence in the validity of the model fitting and the subsequent meaning of the derived reactivity ratios. The reactivity ratios remain important parameters, like many other dimensionless parameters in Chemical Engineering, as they

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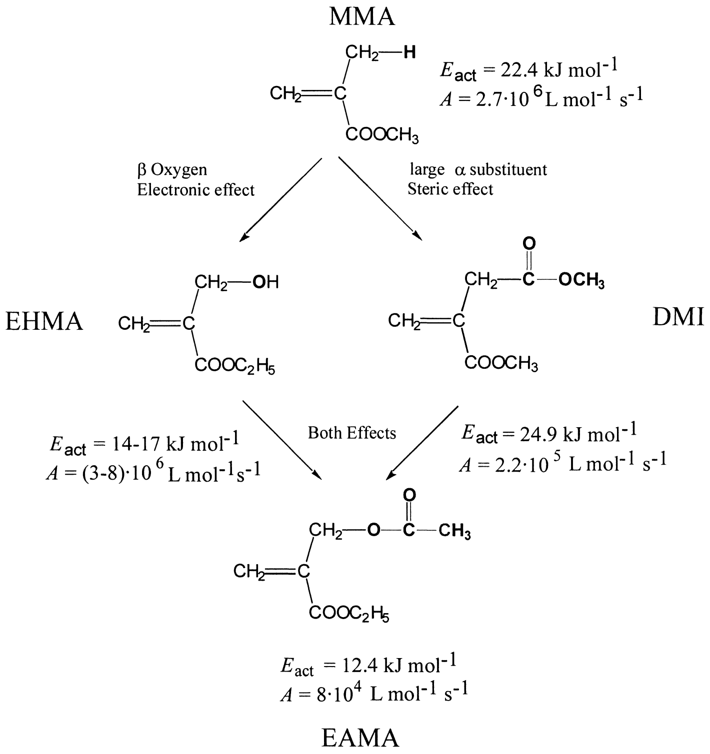
allow us to 'iron out' all the complex and non-ideal facets of radical chemistry (these facets are pervasive) and allow the widespread application of copolymerization in industrial practice. However, if a true physical understanding of the complexity of copolymerization is to be gained then the precise chemistry and physics of the factors governing radical reactivity need to be probed. This fundamental requirement for understanding goes beyond the realm of polymer science to other important areas involving radical reactivity. We have tackled this area using both theoretical and experimental approaches in the recognition that any one approach alone (e.g. model fitting to average propagation rate coefficients) is likely to lead to an incomplete picture and possible misinterpretation.

In our theoretical work we were restricted to small radical addition reactions.[3] The studies we undertook clearly demonstrated that penultimate unit effects are endemic in radical addition and transfer reactions. In summary, evidence has been accrued within our laboratory that the penultimate unit effect (PUE) is a general ‘umbrella’ term for complex interactions involving the terminal and penultimate units (and ante-penultimate units – diminishing in importance further from the reaction center) and the incoming monomer. They encompass radical stabilization energies, polar interactions and entropic factors. However, formulating an appropriate working model for copolymerization remains problematic as the statistical uncertainty associated with model fitting experimental data to such a complex reaction scheme leads to meaningless parameter estimates. The simplicity of approximate models such as the terminal or implicit penultimate unit models make their adoption attractive. However, their use can lead to substantial errors in the interpretation of transfer or termination data, derived assuming the validity of these models. It is therefore important to recognize that kinetic values obtained for termination or transfer, assuming a model for propagation, are not absolute measurements but model-dependent ones.

Entropic Contributions to the Penultimate Unit Effect

The kinetic mechanisms governing the propagation step in copolymerizations have long been debated. The most widely used model is the so-called 'penultimate unit effect model' (PUE), which was introduced by Fukuda and co-workers in 1985.[2,4,5] These authors demonstrated on the example of the free radical copolymerization of styrene and methyl methacrylate (MMA) the failure of the terminal model to predict both copolymer composition and rate data simultaneously. Subsequently, the failure of the terminal model was observed to be widespread and it has been accepted since that the penultimate unit is very important in influencing the rate of propagation. Although the existence of the penultimate unit effect is no longer questioned, there is an ongoing debate about the underlying physical chemistry. A recent review summarized all the available experimental and theoretical evidence, resulting in the conclusion that a number of different factors such as polar interactions, radical stabilization and entropic effects have to be taken into account.[6] The experimental evidence at hand largely suggests that the penultimate effect manifests itself as a reduction of the average propagation rate coefficient. This observation is consistent with Fukuda's early postulate that the penultimate unit acts to stabilize the propagating radical. Only a few cases are reported where this stabilization is not observed, mainly in copolymerizations where the monomers have similar substituents.[7,8] The above evidence suggests that the overall observed penultimate unit effect in any copolymerization originates from a combination of different contributions.

The work carried out in our group on polymerizations of sterically hindered monomers, such as dimethyl itaconate (DMI), leads to the postulate that the penultimate unit effect may be caused by strong entropic contributions in hindered systems, i.e. that the origins of steric hindrance in homopropagation may involve both terminal and penultimate units (so called 1,3-interactions).



Scheme 1. Illustrating the effect of different contributions (i.e. steric and electronic) to the activation parameters using different monomers.

In general, however, it should always be kept in mind that the term 'penultimate unit effect' is a term comprising complex interactions involving terminal and penultimate units and the incoming monomer. We have therefore adopted a strategy of investigating the kinetic behavior of homo- and copolymerizations that allows a reasonable separation of these diverse effects. Such a separation of individual contributions using different monomers is illustrated in Scheme 1. While electronic effects should be reflected in the activation energy, E_a, steric effects are associated with the pre-exponential factor, A.

When going from methyl methacrylate (MMA) to dimethyl itaconate (DMI), a substantial decrease in the pre-exponential factor of about one order of magnitude is observed (r.h.s. of Scheme 1). This decrease is due to the sterically more demanding nature of the propagating DMI radical. When going from MMA to ethyl α-hydroxymethyl acrylate (EHMA), the pre-exponential factor remains unchanged, but the activation energy is reduced due to the electronic effect of the additional β-oxygen atom (l.h.s. of Scheme 1). Both effects may be combined in one monomer (ethyl α-acetoxymethyl acrylate, bottom of Scheme 1) with a resulting decrease in the activation energy and the pre-exponential factor.

If electronic and steric contributions can be readily separated in homopolymerizations, the same may be done in copolymerizations in specific cases. By judicious combination of monomers, it may therefore be possible to observe a penultimate unit effect that can be regarded as a 'relief' of the actual penultimate unit effect present in homopolymerizations. This 'relief' caused by a different penultimate unit has been speculated upon previously for the hypothetical case of penultimate effect solely consisting of entropic contributions in a copolymerization of two monomers of considerably different size. In the following we will demonstrate, using two examples, that the factor causing the discrepancy (i.e. underestimation) between a terminal model prediction and the experimental data is a penultimate effect which largely originates in the pre-exponential factors of the co-propagation reactions. Both cases combine a reactive and a relatively unreactive (i.e. sterically hindered) monomer. The first system is the copolymerization of styrene and dimethyl itaconate (DMI),[9] whereas the other system consists of dodecyl acrylate and dodecyl methacrylate.[10] The (average) propagation rate coefficients for both systems – which were studied under very different experimental conditions – can be found in Figures 1 and 2.

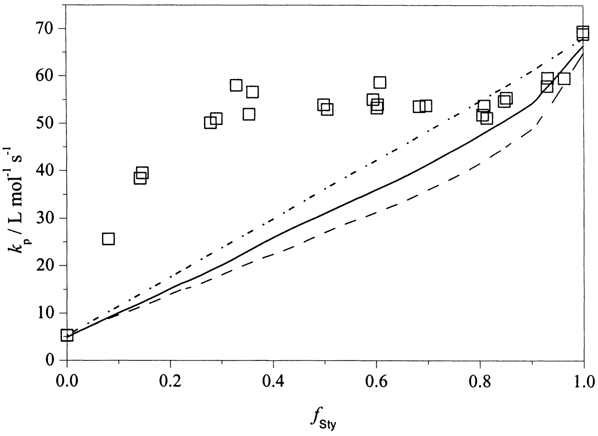


Figure 1. Propagation rate coefficients, k_p, in the free radical copolymerization of styrene and dimethyl itaconate (DMI) at 20 °C using a polystyrene calibration. The plot shows the terminal model prediction (solid line) and the extent of variation in the terminal model prediction when the extremes of 95% confidence in r_1 and r_2 are taken into account (dashed line). r_{sty} and r_{DMI} are close to 0.14 and 0.19, respectively.

The styrene/DMI system has been thoroughly described in a previous publication and it had been pointed out that the increase in k_p over the terminal model prediction (see Figure 1) is most likely associated with the fact that DMI propagates faster with a styrene penultimate unit than if it has another DMI penultimate unit.[9] The enthalpic penultimate unit effect is generally manifest as a radical stabilization effect that slows the average propagation rate. It is therefore very likely that the increase in k_p (see Figure 1) over the terminal model prediction is primarily caused by entropic factors. It had thus been proposed that the homopropagation kinetics of DMI are dominated by interactions between the terminal and penultimate groups resulting in a substantially reduced pre-exponential factor.

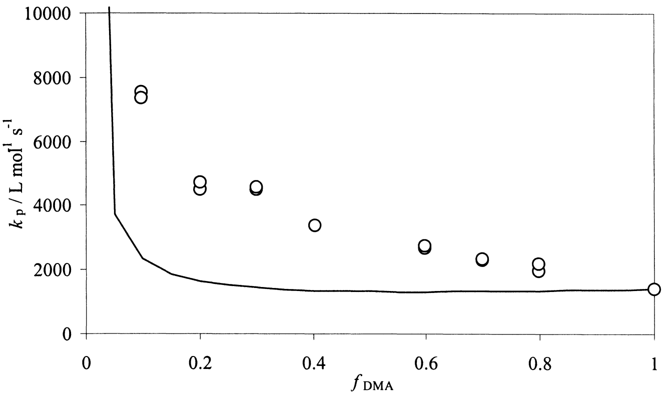


Figure 2. Propagation rate coefficients, k_p, in the free radical copolymerization of dodecyl acrylate (DA) and dodecyl methacrylate (DMA) at 40 °C and 1000 bar. The data are from ref.[10] The line gives the terminal model prediction using r_{DA}=0.29 and r_{DMA}=2.55.

The same effects may be operational in the second example case, i.e. the free radical copolymerization of dodecyl acrylate (DA) and dodecyl methacrylate (DMA). The pre-exponential factor observed in DMA polymerizations ($2.51 \cdot 10^6$ L mol^{-1} s^{-1})[11] is substantially lower than the one obtained from DA polymerizations ($1.09 \cdot 10^7$ L mol^{-1} s^{-1})[12]. Inspection of Figure 2 clearly shows that underestimation of the experimental data by the terminal model prediction is quite evident in this system as well.

It may thus be inferred that any copolymerization which involves significant 1,3-interactions will have significant entropic contributions to the penultimate unit effect. It is very likely that results obtained for acrylate/methacrylate systems (see above) can be explained by a similar hypothesis. An explanation for the underestimation of copolymerization propagation rate coefficients via the terminal model, which incorporates entropic considerations, has more credibility than an enthalpic based approach for monomers bearing similar substituents (i.e. both ester groups) where the scope for the occurrence of enthalpic stabilization is minimal. This conclusion also has consequences for a wide range of common copolymerization reactions including styrene/MMA where an entropic contribution would also be expected. This means that the observed deviation from the terminal model in this system is in fact derived from penultimate unit effects with both an enthalpic (slows k_p) and entropic (increases k_p) origin and what we observe experimentally is an average effect.

Halogen Atom Chain Transfer in Copolymerizations of Styrene and Methyl Methacrylate

While most recent work[2,3,4,5,13,14,15,16] on PUEs has focused on the propagation step, Bamford and coworkers[17,18,19,20,21] in the '70s and '80s investigated chain transfer in copolymer systems using a technique they termed "moderated copolymerization". They proposed a PUE in the chain transfer step of styrene-terminated radicals to CBr_4 in methyl methacrylate (MMA) / styrene (STY) copolymerizations. This result, it was claimed[21] indicated that the PUE had steric origins, and thus both the radical chain end type and the incoming monomer contributed to the effect. Work by Coote and coworkers[3,13-16] has recently shown that polar effects may play an important role in the PUE. If true, this would also suggest that the incoming monomer participates in determining the extent of the PUE.

At the time the experiments were carried out it was assumed that the terminal model was an adequate representation of $\langle k_p \rangle$ in copolymerization. Since the work of Bamford et al.,[17-21] there has been a paradigm shift in our understanding of copolymerization kinetics. It is now evident that PUEs play a major role in copolymerization propagation reactions and that both entropic and enthalpic factors are important in determining the magnitude of these effects. It is highly likely that there is a PUE on chain transfer, and it is possible (for the first time) to separate this from the effect on the propagation reaction, since accurate $\langle k_p \rangle$ data are readily available from the pulsed laser polymerization technique.[22]

The effect of a chain transfer agent on the molecular weight of a polymer is quantitatively determined by the Mayo equation (eq.1),[23,24] which expresses the reciprocal of the number-average degree of polymerization (DP_n) as a function of the rates of chain propagation and termination:

$$\frac{1}{DP_n} = \frac{1}{DP_n^0} + C_S \frac{[S]}{[M]} \tag{1}$$

In this equation, DP_n^0 is the molecular weight of the polymer in the absence of added chain transfer agent, [M] the monomer concentration, and [S] the concentration of chain transfer agent. C_S represents the ratio of the chain transfer and propagation rate coefficients (k_{tr}/k_p). Hence C_S may be determined from a plot of DP_n^{-1} vs [S]/[M], known as a Mayo plot.

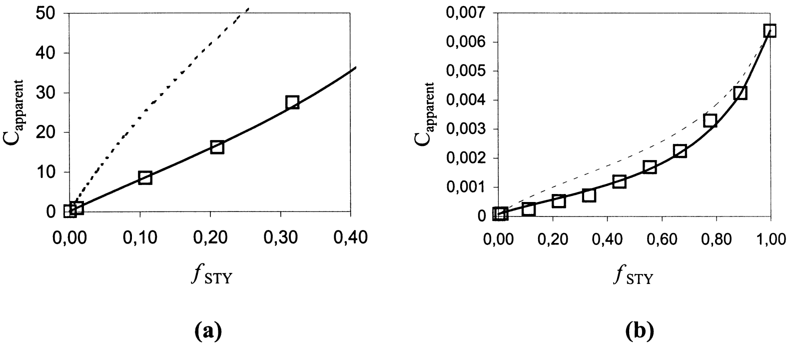
The Mayo equation can be extended to the case of copolymerization in a similar manner. If terminal kinetics are assumed (i.e. penultimate and antepenultimate units have no effect on the kinetics of either propagation or transfer), an apparent chain transfer constant, $\langle C_S \rangle$ may be determined from a plot of DP_n^{-1} vs $[S]/[M_1+M_2]$, given by equation 2:

$$\langle C_S \rangle = \frac{r_1 C_S^1 f_A + r_2 C_S^2 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}} \tag{2}$$

An identical equation is obtained if an implicit penultimate unit effect is assumed, as in such a case the stabilization afforded by the penultimate unit is independent of the co-reagent. This means that the penultimate unit effect will be identical on both propagation and transfer reactions.

The MMA-STY-CX_4 (X = Cl, Br) systems are ideal subjects for these experiments, as there are abundant data on the reactivity ratios and $\langle k_p \rangle$ values of MMA-STY, the ”fruit-fly” of copolymerizations. STY-terminated radicals are far more reactive than MMA-terminated radicals towards both carbon tetrahalides, which means that in almost all cases, reactions of MMA-terminated radicals with CX_4 have a negligible effect on the kinetics. This causes a substantial reduction in the number of parameters necessary to model the system, and allows the determination of penultimate unit effects on STY-terminated radicals without interference from effects by radicals with MMA endgroups. In addition, any polar effects on the PUE on transfer should be easier to observe, due to the strong electron-withdrawing character of the CX_3 moiety (X = Cl, Br).

Apparent chain transfer constants to CBr_4 and CCl_4 were determined across a range of monomer feed ratios (f_{STY} = 0-0.33 for CBr_4, 0-1 for CCl_4) at 40, 50 and 60 °C.[25] Figure 3 shows typical results for each chain transfer agent. In each case, the terminal/implicit penultimate model of chain transfer (eq. 2) fails to describe the chain transfer constants observed, which are consistently lower than predicted.



(a) **(b)**

Figure 3. Apparent chain transfer constants at 40 °C for (a) MMA-STY-CBr_4 and (b) MMA-STY-CCl_4. The dotted line shows the predictions of the terminal model; the solid line is a fit using the PUE in transfer model developed below.

If it is assumed, however, that the PUE on chain transfer is different to that on propagation, a model for chain transfer can be derived. The apparent chain transfer constant, $\langle C_S \rangle$ is now given by eq. 3.

$$\langle C_S \rangle = \frac{r_1 C_S^1 f_1 \cdot \left(\frac{r_1 f_1 + \frac{f_2}{s_1 \tau_1}}{f_2 + r_1 f_1} \right) + r_2 C_S^2 f_2 \cdot \left(\frac{r_2 f_2 + \frac{f_1}{s_2 \tau_2}}{f_1 + r_2 f_2} \right)}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (3)$$

This equation contains four additional variables, the radical reactivity ratios s_i and the transfer reactivity ratios τ_i (i = 1, 2), describing the PUEs on propagation and chain transfer respectively, and given by eqs 4 and 5.

$$s_i = \frac{k_{jii}}{k_{iii}} \qquad (4)$$

$$\tau_i = \frac{k_{ii,S}}{k_{ji,S}} \quad (i, j = 1, 2; i \neq j) \qquad (5)$$

In eq. 5, $k_{XY,S}$ represents the rate of chain transfer from an XY-type radical to S.

In STY-MMA copolymerizations in the presence of carbon tetrahalides, the chain transfer constant from STY-terminated radicals ($C_{CX_4}^{STY}$) is so much larger than that from MMA-terminated radicals ($C_{CX_4}^{MMA}$) that any PUE on chain transfer from MMA-terminated radicals can safely be neglected (i.e. $\tau_{MMA} . s_{MMA}$ can be set to 1). The only fit parameter is then τ_{STY}, since all other constants can be determined from separate experiments. This model could be fitted to the data with reasonable values of the transfer reactivity ratio (Figure 3).

In the derivation of the model above, an implicit PUE on the kinetics of propagation was assumed (i.e. $r_i = r_i'$). This assumption appears to be empirically valid, as the implicit PUE model adequately describes the composition, sequence distribution and kinetics of the STY-MMA system.[4,5,26] However, the need for a further parameter, τ_{STY} ($\neq 1/s_{STY}$), to achieve a good fit to the data indicates that an implicit PUE cannot describe the chain transfer mechanism occurring in this system. The magnitude of the PUE depends on the co-reagent (monomer or chain transfer agent), and hence the PUE on chain transfer is explicit in nature.

Copolymerizations in DMF

If the PUE is partly due to polar effects, it should be influenced by the use of a polar solvent. In all cases measured, the addition of DMF to the STY-MMA-CCl_4 mixtures produces significantly higher chain transfer constants (Figure 4). In MMA, the presence of DMF produces a five-fold increase in the chain transfer constant, while in STY, a more than two-fold increase is observed.

Deviations from the terminal model are also increased in DMF solution. The $\langle C_{CCl_4} \rangle$ values of STY-MMA in DMF solution fit an explicit penultimate unit model with a transfer reactivity ratio of 7.2. This is approximately twice that of the chain transfer experiments at 60 °C without DMF ($\tau = 3.3$). This is strong evidence for the involvement of polar effects both in the transfer reaction to CCl_4 and in the penultimate unit effect.

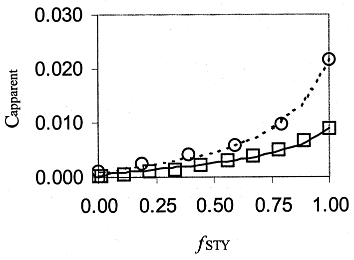


Figure 4. The effect of DMF on chain transfer constants to CCl_4 in MMA-STY copoly-merizations. Squares: no DMF; circles: DMF added. Lines represent the predictions of the PUE in transfer model.

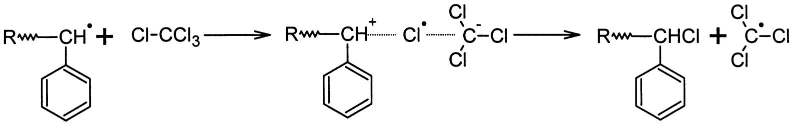
Table 1. Transfer reactivity ratios to CX_4 (X = Cl, Br) in MMA-STY copolymerizations.

T (°C)	τ (CCl_4)	τ (CBr_4)
40	5.2± 0.5	8.3 ± 0.2
50	4.3 ± 0.4	10.1 ± 0.7
60	3.3 ± 0.3	9.4 ± 0.3
60 (in DMF)	7.2 ± 1	—

The Magnitude and Origin of the PUE

Table 1 shows the values of the transfer reactivity ratio, τ_{STY} (equal to the ratio of the rates of transfer from STY-STY-terminated radicals and MMA-STY-terminated radicals to CX_4) for both CCl_4 and CBr_4. This PUE is of a large magnitude, causing changes in the rate of transfer ranging from 3-fold (CCl_4, 60 °C) to as much as 10-fold (CBr_4, 50 °C). It can be seen that τ_{STY} decreases with temperature in the CCl_4 system, although no such trend is seen in the CBr_4 system. At each temperature studied, τ_{STY} is greater in the CBr_4 system than in the CCl_4 system.

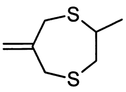
The transfer reactivity ratio for the polymerizations in DMF at 60 °C is much greater than that of the bulk CCl_4 system. The increase of τ_{STY} with the addition of a polar solvent is strong evidence for a polar and therefore explicit origin of the PUE in chain transfer. The most likely explanation for this is that the polar solvent, DMF, helps to stabilize a polar transition state in the chain transfer process, such as the following:[27]



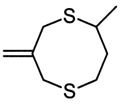
Since the PUE on chain transfer is not equal to the PUE on propagation, radical stabilization cannot be solely responsible. Thus an explicit rather than implicit PUE must be operating in these systems.

Pulsed Laser Copolymerization of Ring-Opening Monomers with MMA

Ring-opening monomers such as 6-methylene-2-methyl-1,4-dithiepane (**1**),[28] 7-methylene-2-methyl-1,5-dithiacyclooctane (**2**)[28] or 2-methylene-1,3-dioxepane (**3**)[29] offer a potential means of distinguishing between the implicit and explicit penultimate unit effects, due to the length of their repeat units. The penultimate unit of a radical with a terminal ring-opening unit should be too far removed from the radical center to have an effect on the radical reactivity. This should lead to a reduction in the number of variables required to model the propagation reaction. Pulsed laser copolymerizations[30] of these monomers with MMA, however, produced results that fit neither terminal nor either form of penultimate unit kinetics.



1



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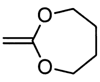
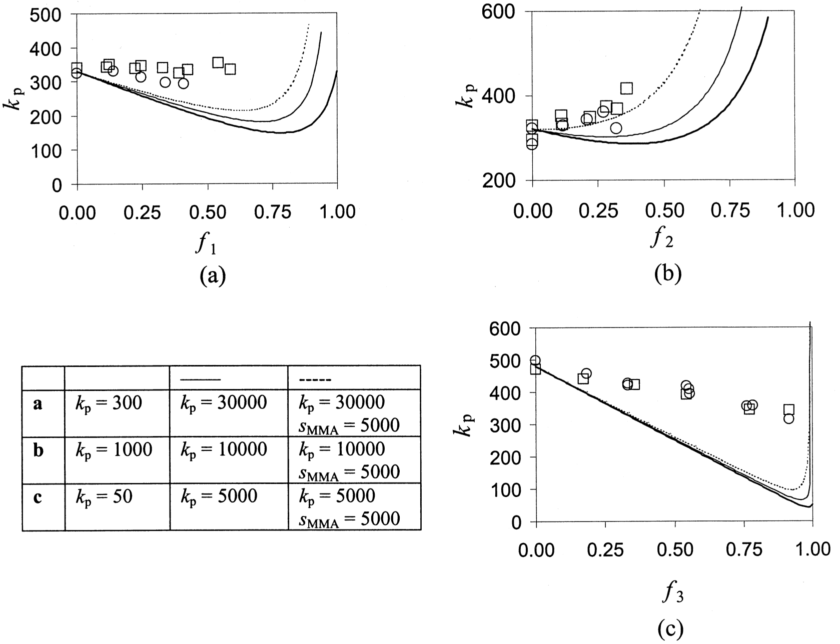


3

Results for the three copolymerizations are shown in Figure 3. It was not possible to obtain k_p data for any of the ring-opening homopolymerizations, due to failure to polymerize under PLP conditions (**1**), or loss of PLP characteristics (**2** and **3**). Monomers **2** and **3** showed a gradual loss of PLP characteristics as the feed ratio of MMA decreased, which prevented the determination of $\langle k_p \rangle$ for f_{MMA} less than 0.4 (**1**) or 0.6 (**2**). This is attributed to high rates of transfer to the ring-opening monomer,[31] causing significant chain stopping and re-initiation during the dark time. For these monomers, k_p of the homopolymerization was estimated from the low-molecular weight points of inflection of the homopolymer molecular weight distributions. The k_p of **3** was estimated from the cross-propagation reaction of ethylene radical with vinyl acetate.[29]

It is apparent from Figure 5, however, that the terminal models cannot be made to fit the experimental data, even when extremely large estimates of the ring-opening monomer k_p

are used. Likewise, setting the MMA radical reactivity ratio as large as 5000 fails to improve the fit for monomers **1** and **3**.



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a	$k_p = 300$	$k_p = 30000$	$k_p = 30000$ $s_{MMA} = 5000$
b	$k_p = 1000$	$k_p = 10000$	$k_p = 10000$ $s_{MMA} = 5000$
c	$k_p = 50$	$k_p = 5000$	$k_p = 5000$ $s_{MMA} = 5000$

Figure 5. k_p data for copolymerizations of (a) **1**, (b) **2** and (c) **3**[29] with MMA. Lines show predictions of terminal (solid) and penultimate unit (dotted) models.

While these parameters produce a reasonable fit to data for monomer **2**, it is difficult to rationalize such a large penultimate unit effect. These results are unlikely to be connected to the ring-opening reaction, as the level of incorporation of **1** and **3** into the copolymer is so low that the amount of ring-opening is negligible compared to the MMA homopropagation reaction. Furthermore, the incorporation of an extra step in the mechanism could only cause a decrease in the observed value of $\langle k_p \rangle$. For similar reasons, the effect of reversible cross-propagation reactions, as observed in copolymerizations of MDTO,[32] can be discounted. The effect must therefore be due to interactions between polyMMA radicals or MMA monomer and the cyclic comonomer, such as comonomer-radical or comonomer-MMA complexes.

Conclusions

The work summarized in this paper builds on two reviews recently published[6,33] on copolymerization theory. The contribution of entropic factors to the penultimate unit effect has been shown, by example, in the STY/DMI copolymerization. Significant penultimate unit effects on radical selectivity in transfer reactions have also been demonstrated and these effects have a significant polar component. It is likely that these effects are manifestations of contributions to all radical addition and transfer reactions. Finally, in the ring-opening copolymerization studies we describe surprising results that seem to originate from strong solvent effects in copolymerization. These results could not have been predicted with current knowledge prior to the experiment. Therefore we must conclude that radical reactions are highly complex and there are significant dangers and drawbacks in employing simplified kinetic models when in search of fundamental understanding.

Acknowledgements

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