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The mechanism of the propagation step in free-radical copolymerisation

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Abstract

The propagation mechanism of free-radical copolymerisation is critically reviewed and it is concluded that the 'explicit' or complete penultimate model should be regarded as the base model for the majority of copolymerisation reactions. This conclusion is based on the weight of evidence from the cumulative findings of a diverse range of studies, viz. the determination of average propagation rate coefficients in co and terpolymerisation systems, moderated copolymerisation studies, solvent effects studies, ESR studies of model-radicals, and both experimental and theoretical studies of gamma-substituent effects in small-radical addition reactions. The consequences of this finding for the understanding of copolymerisation are wide-ranging. In particular, it implies that the widely published terminal-model reactivity ratios should only be regarded as adjustable parameters that do not adequately reflect the elemental processes in the copolymerisation mechanism. In addition, the studies reviewed in this paper indicate that a number of factors, including polar interactions, radical stabilisation effects, direct interactions, and entropic effects all are responsible for the penultimate unit effect in free-radical copolymerisation.

Keywords: Copolymerisation; Radical; Penultimate; Sequence distribution; Reactivity ratio; Kinetics

Contents

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1. Introduction

Copolymerisation models are used to predict the overall propagation rate coefficients of a copolymerisation, and the composition and sequence distribution of the resulting copolymer, as a function of the feed ratio of the comonomers and a small set of characteristic constants. In order to derive these models it is necessary to make simplifying assumptions as to the factors influencing the rate of the propagation step, and the types of side-reactions that may occur. If the models are to be meaningful then they should reflect the physical chemistry of the copolymerisation reaction.

One of the simplest models is the *terminal (or Mayo–Lewis) model*, in which it is assumed that side-reactions are not significant, and that the reactivity of the propagation reaction is governed only by the nature of the monomer and the terminal unit of the polymer radical. For many years it was thought that this model could describe the majority of copolymerisation systems and it was thus considered the basis of copolymerisation kinetics. Those systems, which did not obey the terminal model, were thus regarded as exceptions, with the failure of the model being attributed to the particular chemical properties of these monomers, which rendered them susceptible to additional system-specific influences. For these ‘exceptional’ systems, alternative models were proposed. These took into account the influence of additional units of the polymer radical and/or the interference of side reactions (such as complex formation, monomer partitioning and depropagation).

Although the terminal model was widely accepted as the basis of copolymerisation kinetics, critical testing of this model was, until relatively recently, rarely undertaken. Instead the model was merely fitted to the available copolymer composition data by selecting appropriate values for its characteristic parameters (known as reactivity ratios). When, in 1985, Fukuda et al. [1] used these characteristic parameters to predict the terminal model propagation rate for the system styrene with methyl methacrylate, they found that the predicted and their measured values were completely different. Subsequent studies have since demonstrated the almost general failure of the terminal model to describe simultaneously the composition and propagation rate in free-radical copolymerisation. To replace the terminal model as the basis of copolymerisation kinetics, workers have adopted some of the alternative models which had been originally reserved for exceptional systems—suggesting that these models may in fact have more general significance than previously assumed. The most popular of these models is the *implicit penultimate model*, in which it is assumed that both the terminal and penultimate units of the polymer radical affect its reactivity, but only the terminal unit affects its selectivity. While this model can successfully describe the available experimental data, other models can also be fitted to the same data. Some of these alternative models include the *explicit penultimate model*, in which it is assumed that both the terminal and penultimate units of the radical may affect both the reactivity and selectivity of the radical, and the *bootstrap model*, in which it is assumed that some form of monomer partitioning occurs. A large number of these alternative models can be successfully fitted to the same experimental data and hence attempts to discriminate between the alternative models on this basis have been largely unsuccessful.

A more promising approach to model discrimination is to examine the physical validity of the assumptions inherent in the alternative models. In a recent review of solvent effects in free-radical copolymerisation, [2] we applied this approach and showed that, while they were likely to be important in certain exceptional systems, copolymerisation models based on solvent-effects were unlikely to provide a physically realistic description of the chemistry of the propagation step in ordinary copolymerisation systems (such as the bulk copolymerisation of styrene with methyl methacrylate). In this review we apply a similar methodological approach and examine the literature for evidence concerning the physical validity of the alternative penultimate models with a view to establishing which (if either) of these models can replace the terminal model as the basis of copolymerisation kinetics. Before proceeding to this study of the penultimate unit effect in free-radical copolymerisation, we first outline in general terms the types of assumptions that are inherent in copolymerisation models, and summarise the evidence against the terminal model.

2. Propagation kinetics and copolymerisation models

In order to model the overall propagation rate of a copolymerisation, and the composition and sequence distribution of the resulting copolymer, it is necessary to kinetically model each of the individual propagation steps. Given the complex nature of polymerisation chain reactions, this would appear to entail numerous kinetic expressions and hence, not only would the development of an overall model be very complicated, but the resulting model would also contain numerous characteristic parameters (corresponding to the numerous kinetic constants) and would thus be of little practical value. To address this problem it is necessary to reduce the number of reactions that need to be characterised. This is achieved by making simplifying assumptions as to the fundamental influences on radical reactivity, which thereby enable the large set of chemically different reactions to be grouped into a small number of sets of kinetically different reactions. Three types of such simplifying assumptions that are made in deriving a copolymerisation model are as follows:

1. *Long chain assumption.* Provided the chain length of the propagating radical is greater than around three units in length, the rate of the propagation step can usually be assumed to be chain-length independent [3]. It is thus possible to treat the reactions of long radicals that differ only in their chain

length as being kinetically equivalent. However, in any free-radical polymerisation the initiation and other small-radical addition steps will nevertheless occur. In order that the contribution of these kinetically different steps may be ignored, the "long chain assumption" is frequently made. That is, it is assumed that the average chain length of polymer radicals is long enough for the contributions of the short chain reactions to be negligible. Based on this same assumption, it can also be assumed that the effect of selective termination or transfer reactions on the relative radical concentrations is negligible. Finally, for linear polymers, the long chain assumption directly implies the quasi-steady-state assumption [4]. This assumption, which states that the relative radical concentrations are constant, is used explicitly in some of the methods for deriving copolymerisation models.

2. *Unimportance of Remote Substituent Effects.* Although the rate of the propagation reaction depends on the composition and sequence distribution of the radical, in practice the effect on radical reactivity of all but those substituents near to the active chain end can be considered to be negligible. Thus, by assuming that substituent effects beyond some remote position on the polymer radical are insignificant, it is possible to treat the reactions of radicals differing only in their remote substituents as being kinetically equivalent. If, for instance, it is assumed that only the terminal unit of the polymer radical can affect its reactivity, then in any free-radical copolymerisation it is only necessary to consider two types of radical—corresponding to the two types of terminal unit. Alternatively, if it is assumed that both the terminal and penultimate units of the polymer radical can affect its reactivity, then four types of radicals need to be considered—corresponding to the possible combinations of the two types of terminal and penultimate units. And so forth.
3. *Side-Reactions.* A number of side-reactions may also affect the rates of propagation of the different types of monomers and radicals. In deriving a copolymerisation model, these reactions must be taken into account. Some of the types of side-reactions that may affect the copolymerisation kinetics, include: depropagation, monomer partitioning, and various forms of complex formation. Rather than include all of these side-reactions (and thus end up with an absurdly complex model containing countless characteristic parameters), simplifying assumptions as to the importance or unimportance of these various types of side-reaction are made. If, for instance, spectroscopic data indicate that complex formation does not occur, side-reactions involving complexes can be ignored. Alternatively, if thermodynamic data indicate that the comonomers are ideally mixed, monomer partitioning may be ignored, and so forth. Some models, such as the terminal model, ignore all of these side-reactions, while other models may take into account several different side reactions.

The alternative copolymerisation models all make the long chain assumption (1), but differ in the particular assumptions they make with respect to (2) and (3). Some of the main alternative copolymerisation models, and their corresponding inherent assumptions, are shown in Fig. 1. Having made these assumptions, it is possible to derive expressions for the overall propagation rate constant in a free-radical copolymerisation, and the composition and sequence distribution of the resulting copolymer, as a function of the monomer concentrations (frequently expressed as molar feed fractions) and some characteristic constants (i.e. the rate coefficients or, where relevant, equilibrium constants of the individual reactions).

The focus of this review is on defining the fundamental mechanism of the propagation step in free-radical copolymerisation, in the absence of additional system-specific influences. To this end, we will not be discussing copolymerisation models that incorporate side reactions such as solvent effects (which we have reviewed elsewhere [2]) and depropagation. As we have argued elsewhere [2,5], such effects are

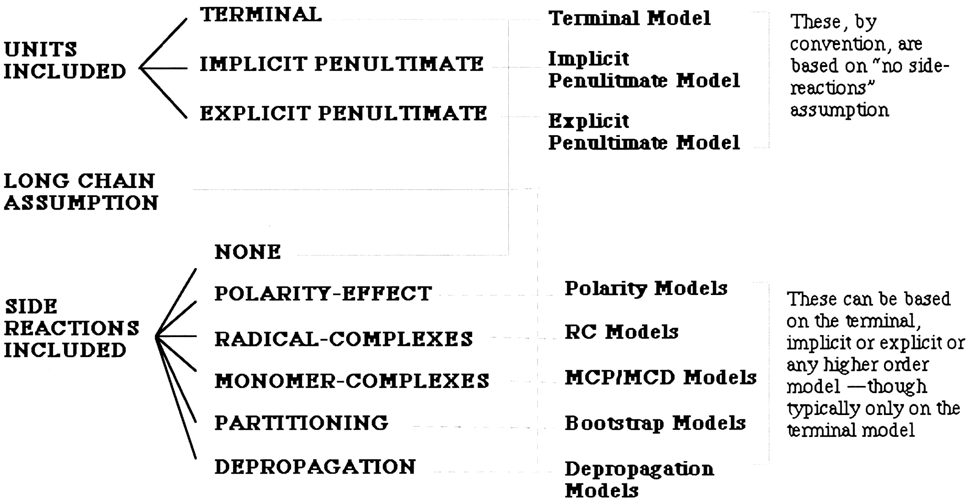

Fig. 1. The main copolymerisation models and their assumptions.

(at least under normal operating conditions) limited to relatively few monomers and are unlikely to be responsible for the general failure of the terminal model in ordinary copolymerisation systems. Instead, for the remainder of this review we will concentrate on the evidence concerning the terminal and various penultimate models, with the aim of establishing a basic model which reflects the elemental processes taking place in the majority of copolymerisation systems.

3. Terminal model

3.1. Description of the model

In the terminal model it is assumed that the terminal unit of a propagating polymer radical is the only factor influencing its reactivity, and that side-reactions are not significant. As a result, there are only four types of propagation reaction in the free-radical copolymerisation of any two given monomers (M_1 and M_2):

$$RM_i + M_j \xrightarrow{k_{ij}} RM_iM_j \qquad i,j = 1 \text{ or } 2$$

From this assumption, Jenkel [6], Mayo and Lewis [7] and Alfrey and Goldfinger [8] all independently derived an expression for the copolymer composition (F_1/F_2) as a function of the monomer feed fractions (f_1 and f_2) and the reactivity ratios (r_1 and r_2) of the monomers:

$$\frac{\mathrm{F}_1}{\mathrm{F}_2} = \frac{f_1}{f_2}\frac{r_1f_1 + f_2}{r_2f_2 + f_1} \qquad \text{where } r_i = \frac{k_{\mathrm{ii}}}{k_{\mathrm{ij}}} \qquad i \neq j \text{ and } i,j = 1 \text{ or } 2 \tag{1}$$

Alfrey and Goldfinger [8] also derived expressions for the sequence distribution and the number average degree of polymerisation expected for a copolymerisation obeying the terminal model. They later extended the terminal model to describe polymerisations involving three or more monomers [9,10].

Fukuda et al. [1] derived the following expression for the copolymerisation propagation rate constant $\langle k_p \rangle$ under the terminal model:

$$\langle k_p \rangle = \frac{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}{[r_1 f_1 / k_{11}] + [r_2 f_2 / k_{22}]} \tag{2}$$

This equation follows from the kinetic analysis of copolymerisation by Melville et al. [11] and Walling [12], who arrived at an expression for the overall rate of copolymerisation, assuming a terminal model for both propagation and termination.

3.2. Experimental evidence

The terminal model was widely accepted for a number of years because it could successfully describe the copolymer composition for most systems tested. While systems deviating from the terminal model were known to exist, and higher-order models (incorporating penultimate unit effects and/or side reactions) were proposed, such systems were regarded as exceptional and the terminal model was nevertheless regarded as the basis of copolymerisation kinetics. The widespread acceptance of the terminal model for describing the composition of copolymerisation systems is evident in the large sets of terminal model monomer reactivity ratios that have been published [13], and in the attention that has been given to developing and theoretically justifying empirical schemes for predicting these terminal model parameters (such as the Q-e [14] and Patterns schemes [15]). Numerous papers have also been written on the optimal experimental design and data analysis for determining reactivity ratios, assuming the veracity of the terminal model [16,17]. To this day, the terminal model is still widely used for describing copolymer composition, and terminal model reactivity ratios are routinely reported for most new systems studied.

However, as Hill et al. [18] and Fukuda et al. [1] later revealed, the ability of the terminal model to describe copolymer composition is not a sufficient test of its validity—a problem first suggested by Berger and Kuntz in 1964 [19]. This is because the characteristic parameters of the terminal model (i.e. the monomer reactivity ratios) are typically measured by fitting the terminal model to the composition data. The values of monomer reactivity ratios obtained in this way are those which enable the terminal model to provide the best fit to the data. Hence, it is hardly surprising that the terminal model can adequately describe data to which it has already been fitted. In order to critically test the terminal model, the parameters obtained from fitting the terminal model to the composition data must be used to make a prediction that can then be tested against independently measured experimental data (such as the sequence distribution or overall propagation rate coefficients for the same copolymerisation). Until relatively recently, measurements of the propagation rate and sequence distribution were difficult, and the terminal model was thus rarely subjected to such critical testing. Furthermore, one of the few such tests of the terminal model [20] was performed, by chance, on two copolymerisations (methyl methacrylate with dodecyl methacrylate and with butyl methacrylate) which are exceptional in that the terminal model can adequately describe their kinetic behaviour.

In recent years, however, improvements to experimental techniques for measuring sequence distribution and propagation rate coefficients—notably the development of ^{13}C NMR and pulsed laser polymerisation [21], respectively—have facilitated critical testing of the terminal model and such critical tests have revealed its widespread failure to describe the propagation kinetics of most systems tested. This experimental evidence against the terminal model is as follows.

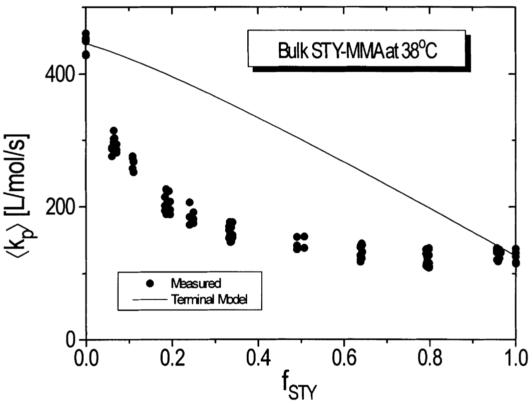

Fig. 2. The propagation rate coefficients and corresponding terminal model predictions for the bulk copolymerisation of styrene with methyl methacrylate at 38°C [24,25].

In 1985, Fukuda et al. [1] demonstrated that, although it could be fitted to the composition data, the terminal model failed to predict the propagation rate coefficients for the free-radical copolymerisation of styrene with methyl methacrylate. What was particularly important about this work was that the failure of the terminal model was demonstrated in a system for, which, based on the composition data alone, the terminal model had previously been believed to be valid. Subsequent measurements of the propagation rate in free-radical copolymerisation have since verified Fukuda's results for the styrene with methyl methacrylate system [22,23], and kinetic studies of other copolymerisations have revealed similar behaviour in almost all cases. To illustrate the extent of failure of the terminal model, Fig. 2 shows the measured propagation rate coefficients for the bulk copolymerisation of styrene with methyl methacrylate system at 38°C [24,25] together with the corresponding terminal model predictions. As this figure shows, the discrepancies between the predicted and measured values in this typical system are very large. Some of the systems that have been so far tested in this way are listed in Table 1. As this table shows, the terminal model fails to predict the propagation rate coefficients of all the copolymerisations tested except for the monomer pairs *p*-methoxystyrene/styrene, methyl methacrylate/dodecyl methacrylate, methyl methacrylate/butyl methacrylate, methyl methacrylate/perdeuterated methyl methacrylate, and *p*-chlorostyrene/*p*-methoxystyrene systems.

Studies of the sequence distribution in free-radical copolymerisation have been less conclusive. In 1982, Hill et al. [18] measured the composition and sequence distribution for the copolymerisation of styrene with acrylonitrile and found that, while its composition could be adequately described by the terminal model, the predicted and measured sequence distribution differed significantly. The failure of the terminal model to predict the propagation rate coefficients of this system was later demonstrated by Ma et al. [26] However, in the case of the styrene with methyl methacrylate system, Maxwell et al. [27] concluded that the terminal model could predict the sequence distribution data, on the basis of reactivity ratios measured from composition data. Given that the failure of the terminal model to predict the propagation rate coefficients for this system had been clearly demonstrated, the success of this model in predicting the sequence distribution would appear to have important implications for copolymerisation kinetics. However, closer inspection of this work reveals that the fit of the terminal model to the sequence distribution data for the styrene with methyl methacrylate system had not in fact been critically

Table 1
Systems tested for terminal model $\langle k_p \rangle$ (based on reactivity ratios obtained from a terminal model fit to the composition data)

Comonomers[a]	Temp.°C	R_1r_2[b]	Terminal model predicts $\langle k_p \rangle$	Reference
MMA/BMA	30	1.00	Yes	Ito and O'Driscoll [20]
MMA/DMA	30	1.00	Yes	Ito and O'Driscoll [20]
STY/MMA	40	0.24	No	Fukuda et al. [1]
PCS/MA	40	0.17	No	Ma et al. [64]
STY/MMA	40	0.24	No	Davis et al. [23]
STY/MMA	25, 40	0.24	No	Olaj et al. [22]
MMA/MMA-d	25	1.00	Yes	Olaj et al. [69]
STY/EMA	25,55	0.22	No	Davis et al. [108]
STY/BMA	25,55	0.32	No	Davis et al. [108]
STY/DMA	25	0.26	No	Davis et al. [108]
PMOS/STY	25	0.95	Yes	Piton et al. [68]
PMOS/MMA	25	0.092	No	Piton et al. [68]
STY/MA	25,50	0.14	No	Davis et al. [63]
STY/BA	25, 50	0.17	No	Davis et al. [63]
MMA/VAc	40	0.39	No	Ma et al. [109]
STY/EA	40	0.13	No	Ma et al. [65]
STY/AN	40	0.018	No	Ma et al. [26]
MMA/AN	40	0.25	No	Ma et al. [26]
STY/DEF	40	0.004	No	Ma et al. [26]
STY/MAH	25,35,50	0[c]	No	Sanayei et al. [110]
PBS/DBF	60	0.0018	No	Sato et al. [111]
CHMIm/DBI	50	0.071	No	Sato et al. [112]
PBS/DBM	60	0	No	Sato et al. [113]
MMA/BA	20,60	0.20	No	Hutchinson et al. [114]
STY/MMA	17.9–57.2	0.24	No	Coote et al. [24,25]
PCS/STY	40	0.60	No	Coote and Davis [73]
PCS/PMOS	40	0.43	Yes	Coote and Davis [73]

[a] Abbreviations: STY = styrene; MMA = methyl methacrylate; MMA-d = perdeuterated(methyl methacrylate); EMA = ethyl methacrylate; BMA = butyl methacrylate; DMA = dodecyl methacrylate; PCS = p-chlorostyrene; PBS = p-tertbutoxystyrene; PMOS = p-methoxystyrene; MA = methyl acrylate; EA = ethyl acrylate; BA = butyl acrylate; DEF = diethyl fumurate; DBF = dibutyl fumurate; DBM = dibutyl maleate; CHMIm = cyclohexyl maleimide; DBI = dibutyl itaconate; MAH = maleic anhydride; AN = acrylonitrile; MAN = methacrylonitrile; VAc = vinyl acetate.

[b] From the best fit of the terminal model to the composition data.

[c] Since MAH cannot homopropagate.

tested. While, in principle, the terminal model can be critically tested by comparing the measured triad or pentad fractions with those predicted using the reactivity ratios obtained from composition data, in practice, the direct measurement of these triad/pentad fractions is not possible. Instead, additional information—such as the peak assignments and the coisotacticity factor (σ)—is required in order to convert the peak fractions measured from NMR spectra into the triad/pentad fractions predicted by the model. Unfortunately the independent measurement of σ is often difficult, if not impossible, and thus it is frequently estimated by fitting the triad/pentad fraction data that are converted from measured peak fractions (via the peak assignments and σ value) to the predictions of a model—typically the terminal model. In the work of Maxwell et al. [27] the σ value they used [28] had been obtained in this way, and thus their 'measured' data set (having been already implicitly fitted to the terminal model via the σ value) was not suitable for model discrimination purposes, and thus their work is not a critical test of the terminal model. It is noteworthy that, in the study of styrene with acrylonitrile by Hill et al. [18], the measured peak fractions were converted to triad/pentad fractions without recourse to a fitted σ value (thus enabling critical testing of the terminal model) and, as noted above, the terminal model was shown to be deficient under this critical testing.

Other tests of the terminal model, based on a comparison of predicted and 'measured' sequence distribution data, have also had mixed results. For instance, the terminal model was found to be inadequate in studies of α-methylstyrene with methacrylonitrile [29] and with acrylonitrile [29], citraconic anhydride with *p*-chlorostyrene [30], methyl methacrylate with acrylonitrile [31], styrene with methacrylonitrile [32], acrylonitrile with vinyl acetate [33], and styrene with maleic anhydride [34]. In contrast, it was found to be adequate in studies of methacrylonitrile with *p*-methylstyrene [35], 2-(*N*,*N*-dimethyl)aminoethyl methacrylate with acrylonitrile [36], vinyl acetate with ethyl acrylate [37], with butyl acrylate [37], and with ethyl methacrylate [38], and methyl methacrylate with methyl acrylate [39]. However, given the above problem with independently measuring the sequence distribution of copolymers, the results of these studies should be treated with caution as it is likely that the terminal model was not in fact critically tested. In summary, despite a large number of publications purporting to measure sequence distribution, there is still a dearth of reliable *model-independent* data. Until this situation is rectified discrimination among the alternative models on the basis of their ability to describe such data will not be possible—a conclusion that was reached by Berger and Kuntz [19] as early as 1964.

> "What we suggest is that until data are available on the distribution of monomer units in copolymers, the final selection of terminal or penultimate copolymerisation models for most comonomer systems cannot be made."

3.3. Assessment of the terminal model

Based on the above studies, it is now generally accepted that the terminal model cannot adequately describe the copolymerisation kinetics of common copolymerisation systems. While it can be fitted to the composition data of most copolymerisation systems, when the reactivity ratios obtained are used to make terminal model predictions of the propagation rate or sequence distribution, there are large discrepancies between the predicted and independently measured values. In the case of the propagation rate coefficients, this failure of the terminal model has been almost universal in the systems that have been so far tested. In the case of sequence distribution data, the terminal model has had mixed success. However, as noted above, in a number of systems for which the terminal model has been successful in 'predicting' the sequence distribution data, this success may have been aided by treating the coisotacticity factor as an adjustable parameter. It should in any case be noted that, based on the same assumptions about the propagation reaction, the terminal model predicts a number of different properties for any given copolymerisation, including its composition, its sequence distribution and its overall propagation rate coefficients. The failure of the terminal model to describe simultaneously the overall propagation rate coefficients and composition of most systems tested is thus sufficient evidence for the invalidity of its inherent assumptions in these systems. It is thus clear that a new basis model for free-radical copolymerisation kinetics is required.

4. Explicit and implicit penultimate models

4.1. Description

An obvious extension of the terminal model is the penultimate model in which, as its name suggests, it is assumed that both the terminal and penultimate unit effects of a polymer radical can affect its reactivity toward a given radical. Two types of penultimate models have been proposed: the implicit and the explicit.

In the *explicit penultimate model*, it is simply assumed that both the terminal and penultimate units of a polymer radical may affect the rate of the propagation reaction. As in the terminal model, side-reactions are considered to be insignificant. The explicit penultimate model was first suggested by Merz et al. in 1946 [40], who derived equations for predicting the composition and sequence distribution under this model. A full description of the model—including an expression for $\langle k_\mathrm{p} \rangle$—has since been provided by Fukuda et al. [41], and it is their notation that is used in what follows.

In the presence of a penultimate unit effect, there are eight different types of propagation reactions to characterise:

$$RM_iM_j + M_k \xrightarrow{k_{ijk}} RM_iM_jM_k i,j,k = 1 \qquad \text{or} \ \ 2$$

From their eight different propagation rate constants, four different monomer reactivity ratios (r_i and r'_i) and two radical reactivity ratios (s_i) can be defined as follows:

$$r_i = \frac{k_{iii}}{k_{iij}} \ \ r_i{}' = \frac{k_{jii}}{k_{jij}} \ \ s_i = \frac{k_{jii}}{k_{iii}} \qquad \text{where} \ \ i \neq \ j \text{ and } i,j = 1 \text{ or } 2$$

These are used to calculate the adjusted parameters, $\bar{r}_i$ and $\bar{k}_{ii}$:

$$\bar{r}_i = r_i{}'\left(\frac{f_i r_i + f_j}{f_i r_i{}' + f_j}\right) \qquad \text{where} \ \ i,j = 1 \text{ or } 2 \text{ and } i \neq j \tag{3}$$

$$\bar{k}_{ii} = k_{iii}\left(\frac{r_i f_i + f_j}{r_i f_i + f_j/s_i}\right) \qquad \text{where} \ \ i,j = 1 \text{ or } 2 \text{ and } i \neq j \tag{4}$$

These are used in place of r_i and k_{ii}, in the terminal model expressions for composition (Eq. (1)) and $\langle k_\mathrm{p} \rangle$ (Eq. (2)).

The *implicit penultimate model* was first suggested by Fukuda et al. [1] in 1985, in order to describe their observation that the terminal model could be fitted to the composition data for the copolymerisation of styrene with methyl methacrylate, though it could not simultaneously describe the propagation rate coefficients. In this model, the following restriction is placed on the explicit penultimate model.

$$r_i\left(= \frac{k_{iii}}{k_{iij}}\right) = r_i{}'\left(= \frac{k_{jii}}{k_{jij}}\right) = \frac{k_{ii}}{k_{ij}} \qquad \text{where} \ \ i \neq j \text{ and } i,j = 1 \text{ or } 2 \tag{5}$$

The penultimate unit effect is thus assumed to be absent from the monomer reactivity ratios, which are equivalent to their terminal model forms, and only to exist in the radical reactivity ratios (i.e. through values of $s_i \neq 1$). This amounts to assuming that the magnitude of the penultimate unit effect on reactivity is independent of the type of monomer with which it is reacting (since the equality $k_{jiii}/k_{iii} = k_{jij}/k_{iij}$ follows directly from the assumption that $r_i = r_i'$). In other words, it assumed that there is a penultimate unit effect on reactivity but not selectivity.

Based on the above assumption (i.e. Eq. (5)), Eq. (3) collapses into:

$$\bar{r}_i = r_i{}'\left(= \frac{k_{jii}}{k_{jij}}\right) = r_i\left(= \frac{k_{iii}}{k_{iij}}\right) = \frac{k_{ii}}{k_{ij}} \qquad \text{where } i \neq j \text{ and } i,j = 1 \text{ or } 2$$

Thus the adjusted monomer reactivity ratios of the penultimate model are replaced simply by their corresponding terminal model values. However, since the penultimate unit effect can remain in the radical reactivity ratios (i.e. through values of $s_i \neq 1$), Eq. (4) does not collapse to its equivalent terminal model form (i.e. $\bar{k}_{ii} \neq k_{iii}$). Since the composition and triad/pentad fraction equations contain only $\bar{r}_i$ terms, they collapse to the corresponding terminal model equations. However, since it contains both $\bar{r}_i$ and $\bar{k}_{ii}$ terms, the propagation rate equation, though simpler than that of the explicit penultimate model, continues to differ from that of the terminal model. There is thus an implicit penultimate unit effect—that is, a penultimate unit effect on the propagation rate but not the composition or sequence distribution.

4.2. Theoretical basis: are penultimate unit effects implicit or explicit?

There are thus two versions of the penultimate model: the implicit and the explicit. In the implicit penultimate model, the composition and sequence distribution equations collapse into those of the terminal model and thus the continued use of these equations, in systems for which the terminal model propagation rate equation fails, can be justified. In the explicit penultimate model, the composition, sequence distribution and propagation rate equations all differ from the terminal model, and thus the continued use of the terminal model composition and sequence distribution equations, in systems for which the terminal model propagation rate equation fails, cannot be justified. It is therefore important to determine not only whether or not penultimate unit effects exist, but also whether they are implicit or explicit—that is, whether or not they are independent of the coreactant.

Whether a penultimate unit effect will be implicit or explicit will depend on its origin. An important means of discriminating between the alternative penultimate models is thus to examine the origin of the penultimate unit effect. To date, three main accounts of its origin have been proposed, each making different predictions with regard to the implicit or explicit nature of the penultimate unit effect. These accounts are as follows.

1. *Polar model.* Giese et al. [42], based on a study of the effect of polar β and γ substituents on the selectivity of alkyl radicals in addition reactions with alkenes, proposed a polar origin for the penultimate unit effect. They suggested that substituents at the penultimate position could undergo “a through space repulsive interaction” with polar substituents on the alkenes. Under the curve-crossing model [43], polar effects are viewed as the relative stabilisation of the transition structure by charge-transfer configurations, which occurs when the transition structure can form a charge-transfer configuration that is relatively low in energy. Thus a polar penultimate unit effect may be viewed as the relative stabilisation of a charge-transfer configuration of the transition structure by substituents at the penultimate position of the polymer radical. Whether an electron-withdrawing substituent at the penultimate position will stabilise or destabilise the charge-transfer configuration will clearly depend upon whether the substituents on the monomer are themselves electron

withdrawing or electron-donating. Polar penultimate unit effects are therefore dependent upon the nature of the coreactant and are thus strongly explicit. This is argued more formally by Heuts et al. [44] who, based on simple electrostatic considerations, showed that polar penultimate unit effects will be larger in monomer reactivity ratios (which appear in both the composition and propagation rate equations) than in radical reactivity ratios (which only appear in the propagation rate equation). Thus, any polar penultimate unit effect in the propagation rate must simultaneously appear in the composition and sequence distribution.

2. *Radical stabilisation model.* Fukuda et al. [41] proposed, as a theoretical justification of the implicit penultimate model, the radical stabilisation model. They suggested that the penultimate unit could affect the stability of the propagating radical, and thus the reaction enthalpy. Assuming that the Evans–Polanyi rule [45,46] was valid (i.e. that the barrier is proportional to the enthalpy), this penultimate unit effect would thus appear as an implicit penultimate unit effect in the reaction barrier. A formal derivation of this result may be found in the original paper of Fukuda et al. [41] and is summarised in Appendix A. It should be noted that the Evans–Polanyi rule would generally be expected to hold in radical addition reactions, provided that there are no significant polar interactions [47,48] (or other direct interactions such as steric interactions) in the transition structure. Fukuda et al. [41] also showed that, if it could be additionally assumed that there were no penultimate unit effects in the frequency factors, then the products of the monomer and radical reactivity ratios would be equal (i.e. $r_1 r_2 = s_1 s_2$). For a derivation of this result, the reader is referred to the original paper of Fukuda et al. [41] A number of workers have since speculated on the possible means by which the penultimate unit could affect radical stability, and the suggested mechanisms include some form of direct interaction between the radical's α and γ substituents [49], or some form of a penultimate unit effect on the spin distribution of the propagating radical [50].
3. *Entropic model.* Heuts et al. [44], based on a comparison of the frequency factors for ethyl and propyl addition to ethylene (i.e. β-substituent effects), proposed that penultimate unit effects in the frequency factor may be significant. They argued that it would be possible for the penultimate unit to hinder certain internal motions in the transition structure, which were important contributions to the frequency factor, and that penultimate unit effects on these different internal motions would be multiplicative. Via a series of simple steric considerations, they also showed that a penultimate unit effect in the frequency factor would be expected to result in larger penultimate unit effects in the radical reactivity ratios than in the monomer reactivity ratios. Thus, they argued that it is possible for an entropic penultimate unit effect to be implicit or explicit, depending on its magnitude; an implicit effect occurring if penultimate unit effects are large enough to appear in the radical reactivity ratios (and thus the propagation rate) but still small enough to be insignificant in the monomer reactivity ratios (and thus the composition and sequence distribution).

There are thus a number of possible causes of penultimate unit effects, some or all of which may be important in common copolymerisation systems. Depending on the relative importance of these different causes, penultimate unit effects may be implicit or explicit. It is important to note that, for the implicit penultimate model to be valid, explicit penultimate unit effects must be absent from both the barrier and frequency factor of the propagation reaction. Thus, the presence of (explicit) polar penultimate unit effects in the propagation reaction would be sufficient to undermine the implicit penultimate model, regardless of whether or not implicit radical stabilisation effects or implicit entropic effects were also significant in these reactions. Given that the implicit or explicit nature of the penultimate unit effect depends on its origin, studying the origin of the penultimate unit effect provides a possible means of discriminating between the implicit and explicit penultimate models. Thus, in the following review of experimental evidence for and against the different penultimate models, particular attention will be paid to those experiments that shed light on the origin of the penultimate unit effect.

4.3. Experimental evidence

An obvious means of testing the applicability of the implicit and explicit penultimate models is to examine their ability to describe the composition, sequence distribution and propagation rate coefficients of various copolymerisation systems. However such studies have, in most cases, been unable to discriminate between the alternative higher-order models. The main reasons for this failure are as follows.

The first problem is that the various copolymerisation models contain a number of different reactivity ratios which are not independently measured but are instead treated as adjustable parameters in the model fitting procedure. By selecting appropriate values of these adjustable parameters, any number of different models can be made to fit the same experimental data. It is particularly difficult to discriminate between the implicit and explicit penultimate models (and indeed a number of other higher-order models) because these models have more adjustable parameters than is actually required (given the functional form of the model and the experimental data) to describe simultaneously the composition and propagation rate coefficients of common copolymerisation systems. This is not to say that these parameters are necessarily superfluous in a physical sense—merely that they cannot be properly estimated by fitting the models to composition and propagation rate data and should instead be measured directly.

In consequence of this, it is generally observed that a number of different models can provide adequate simultaneous fits to the composition and propagation rate coefficients of common copolymerisation systems. For instance, Maxwell et al. [27] showed that, provided they had more than three adjustable parameters, a number of different copolymerisation models could describe the composition and propagation rate coefficients for the bulk copolymerisation of styrene with methyl methacrylate. A large number of studies have shown that the implicit penultimate model can provide an adequate simultaneous fit to the composition and propagation rate coefficients of most copolymerisation systems tested [51]. However, although the fit of the explicit penultimate model to these systems is rarely examined, this model could also be made to provide an adequate simultaneous fit to the same data, since it has a similar functional form to the implicit penultimate model and even more adjustable parameters. For instance, in the case of styrene with methyl methacrylate copolymerisation (a system usually fitted with the implicit penultimate model), the fit of the explicit penultimate model to composition and propagation rate data for this system has also been demonstrated [52].

The second problem is that, as noted above (Section 3.2), the sequence distribution of a polymer is not measured directly but is instead converted from the measured peak fractions of an NMR spectrum, via the peak assignments and, where relevant, information on the tacticity of the copolymer (usually contained in the coisotacticity parameter, σ). It is difficult to measure this σ value independently and it is thus sometimes estimated by fitting 'measured' (i.e. converted from peak fraction data via the peak assignments and σ value) triad/pentad fraction data to the predictions of a particular model. The 'measured' triad/pentad fraction data set that is obtained in this way is not suitable for model discrimination as it has already been fitted to the predictions of a particular model.

Attempts to discriminate between the implicit and explicit versions of the alternative models by examining the ability of the terminal model to describe simultaneously the composition and sequence distribution data, are often invalidated by the above problem. This is unfortunate since, when the sequence distribution data can be independently measured, these studies can enable much more sensitive model discrimination than studies that use composition and propagation rate data. The reasons for this are as follows:

- the composition and sequence distribution equations of the higher-order models have fewer adjustable parameters than their corresponding propagation rate equations;
- unlike the propagation rate equation, the equations contain the same sets of adjustable parameters, thus enabling one data set to be predicted using parameters measured from the other;
- there are a number of different triad/pentad fractions that can be predicted and measured for any given sample, thus providing a much more thorough test of the model.

Indeed, as noted above (Section 3.2), a number of studies have shown that the terminal model fails to predict the sequence distribution of a copolymerisation, based on reactivity ratios measured from the composition data. This provides strong evidence against the use of implicit models in these systems. These systems were listed in Section 3.2 and typically involve acrylonitrile, methacrylonitrile, or anhydride monomers. In contrast, in other systems it has been found that the terminal model can provide an adequate simultaneous fit to the data of both systems which would tend to support the use of implicit models for these systems. However, in these studies, the success of the terminal model (and thus the implicit penultimate model) may have been aided by the use of a fitted coisotacticity factor. For example, as noted above, a fitted coisotacticity factor was used in the study of the styrene with methyl methacrylate system [27], and thus it is not possible to discriminate between the implicit and explicit models for this system on the basis of this data.

Given the above problems with these simple model-fitting studies, alternative means of discriminating between the models are required, and these will be discussed in the remainder of this section.

4.3.1. Terpolymerisation studies

The study of terpolymerisation propagation kinetics may offer a method of discriminating between the implicit and explicit penultimate unit models. This is because, under the terminal and implicit penultimate models, the composition, microstructure and propagation rate coefficients of a free-radical terpolymerisation are entirely predictable using parameters measured from data for the constituent copolymerisations [53,54]. In contrast, some of the explicit penultimate model parameters contain contributions from all three components and thus, under this model, the terpolymerisation behaviour cannot be independently predicted from the copolymerisation data. It may therefore be possible to provide a critical test of the terminal and implicit penultimate models by measuring the propagation rate coefficients of the three-component system, and comparing this measured data set with that predicted—without recourse to additional adjustable parameters—using parameters estimated entirely from the constituent copolymerisations.

Coote and Davis applied this model discrimination strategy to two systems: the terpolymerisation of styrene, methyl methacrylate and *p*-methoxystyrene (STY–MMA–PMOS) [55], and the terpolymerisation of styrene, methyl methacrylate and methyl acrylate (STY–MMA–MA) [56]. The model testing for this latter system was based on propagation rate coefficients that were published by Schoonbrood et al. [57] Unfortunately, like their copolymerisation counterparts, these model discrimination studies were largely inconclusive. In the case of the STY–MMA–PMOS system, it was found that the implicit penultimate model (though not of course the terminal model) could successfully predict the terpolymerisation propagation rate coefficients using parameters that were estimated in independent studies of the constituent co and homopolymerisation systems. However, while this appeared to provide strong evidence for the implicit penultimate model—both in the ter- and the constituent copolymerisation systems—it was argued that, since one of the constituent copolymerisation systems (STY/PMOS) obeyed the terminal model, the system did not provide a critical test of the implicit penultimate model.

In the case of the STY–MMA–MA system, the study of terpolymerisation kinetics should have provided a critical test of the implicit penultimate model since the terminal model was known to fail in all of its constituent copolymerisation systems. However, for this system it was found that the uncertainties in the parameters from the constituent co and homopolymerisation systems prevented successful model discrimination. A number of different estimates of these parameters had been previously published and although, based on their most likely estimates the implicit penultimate model was shown to fail, it was possible to select previously published parameters for this system for which the predictions of the implicit penultimate model (though not the terminal model) were satisfied. Hence, it was not possible to discount the implicit penultimate model on the basis of the terpolymerisation data. It thus appears that, even in terpolymerisation systems, discrimination between the implicit and explicit penultimate models for systems such as bulk STY–MMA is not possible on the basis of co and terpolymerisation data, and alternative strategies are instead required.

4.3.2. Transfer studies

Kinetic studies of transfer reactions have also been used to examine the penultimate unit effect. In two separate studies of transfer-dominated copolymerisations (the moderated copolymerisation of styrene with methyl methacrylate in the presence of 1-butane thiol [58] and the retarded copolymerisation of acrylonitrile with methyl methacrylate in the presence of ferric chloride [59]) it was found that there were no penultimate unit effects in the transfer constants. This was despite the fact that the propagation rate coefficients of these systems, as measured in the absence of chain-transfer agents, were subject to large penultimate unit effects. Based on a detailed kinetic analysis of these results (in which it was assumed that there was a penultimate unit effect in the propagation rate coefficients but not the copolymer composition), Bamford [60] showed that, in order to explain these results, the following equality had to hold:

$$\frac{\lambda_{iiS}}{\lambda_{jiS}} = \frac{k_{iij}}{k_{jij}} = \frac{k_{iii}}{k_{jii}} \qquad \text{where } i,j = 1,2 \ (i \neq j) \tag{6}$$

where λ is the transfer rate constant and S is the transfer agent. Thus, the magnitude of the penultimate unit effect on radical reactivity had to be independent of the coreactant and, indeed, the type of reaction (propagation or transfer) that the radical underwent. In other words there was an implicit penultimate unit effect on both the propagation and transfer reactions.

At the time, Bamford [60] argued that the above equality (Eq. (6)) was unrealistic, and concluded that the assumption of a penultimate unit effect in the propagation reaction was incorrect. The failure of the terminal model propagation rate equation in the non-transfer-dominated system was instead attributed to some error in the measurement of $\langle k_p \rangle$ (to that time, only measured via the technique of rotating sector). However, as noted above, the failure of the terminal model to predict $\langle k_p \rangle$ has since been confirmed using pulsed-laser polymerisation and is now generally accepted. Given this, it would seem that the above equality (Eq. (6)), which supports the implicit penultimate model, should also be accepted. Furthermore, as Fukuda et al. [61] later showed, the equality of penultimate unit effects in propagation and transfer reactions is easily explained in the context of the radical stabilisation model—given that in this model it is held that the penultimate unit effect depends simply on radical stability and not on any additional interactions in the transition structure. Thus it would seem that the above results support not only the implicit penultimate model, but also the radical stabilisation model. However, it should be noted that in the kinetic analysis of the results, the validity of the terminal model composition equation is assumed. Thus, the conclusion that the penultimate unit effect is implicit (and thus not in the composition) may be based on a circular argument. A more detailed kinetic analysis is thus required in order to confirm this result.

In other studies of transfer-dominated systems, penultimate unit effects have been detected in the transfer constant. For instance, in a study of the moderated copolymerisation of styrene with methyl methacrylate in the presence of CBr_4 [62], it was found that there was a penultimate unit effect in the transfer constant for a radical bearing a terminal styrene unit (its two penultimate model chain transfer constants being measured at 337 and 60, for styrene and methyl methacrylate penultimate units respectively). This penultimate unit effect was attributed to a steric interaction between the α-methyl group of the methyl methacrylate unit and the entering Br atom of the CBr_4 molecule. The presence of a penultimate unit effect in the transfer constant indicates that the above equality (Eq. (6)) does not hold [60], and there is thus an explicit penultimate unit effect in the transfer reaction [61].

In summary, studies of chain-transfer dominated copolymerisations indicate that in some instances there is a penultimate unit effect in the transfer constant, and in other instances there is not, and these results suggest that some systems (such as those for which direct steric interactions are important) display an explicit penultimate unit effect, while others display an implicit penultimate unit effect—even in their transfer reactions. Although this latter result supports the implicit penultimate model, and indeed the radical stabilisation model, it may simply be a consequence of the assumption (in the kinetic analysis upon which the result is based [60]) of the validity of the terminal model composition equation. Further work is therefore required to confirm this result.

4.3.3. Values of s_1 and s_2

One means of studying the origin of the penultimate unit effect is to examine the measured values of the radical reactivity ratios for various types of comonomer pairs and determine whether or not the trends in their values are consistent with the alternative theories. To date, these values have been difficult to explain. For instance, Davis et al. [63] detected a strong penultimate unit effect for styrene but not butyl acrylate in the propagation rate coefficients for the copolymerisation of styrene with butyl acrylate. In a similar system, *p*-chlorostyrene with methyl acrylate, there was a strong penultimate unit effect for both monomers [64]. This result cannot be explained from simple polar or steric arguments. However, the sensitivity of the values of the radical reactivity ratios to small errors in the kinetic data may preclude the attachment of any physical significance to their individual values. This problem was highlighted by Ma et al. [65] who showed that, in the styrene (1) with ethyl acrylate (2) system, it was impossible to determine the value of the radical reactivity ratio for ethyl acrylate (s_2) with meaningful accuracy because r_2/k_{222} is smaller than r_1/k_{111} by a factor of about 180, and the fit of the model was thus insensitive to the value of s_2.

Difficulties have also been encountered in reproducing values of s_1 and s_2 for the same system and with similar experimental data. For instance, the radical reactivity ratios that have been measured for the copolymerisation of styrene (1) with methyl methacrylate (2) at 25 and 40°C are as follows:

Fukuda et al. [1] (40°C) : $s_1 = 0.30$ $s_2 = 0.53$
Olaj et al. [22] (40°C) : $s_1 = 0.37$ $s_2 = 0.65$
Olaj et al. [22] (25°C) : $s_1 = 0.30$ $s_2 = 0.80$
Davis et al. [23] (25°C) : $s_1 = 0.466$ $s_2 = 0.175$

Coote et al. [24,25,66] discussed the reasons for this uncertainty in the parameters and concluded that accurate and precise s_1 and s_2 values cannot be extracted from model fitting to $\langle k_p \rangle$ data. Fukuda et al. [67] suggested removing one parameter and letting $s = s_1 = s_2$ be an 'average penultimate unit effect' and showed that, when this single parameter analysis was used, the same result was obtained for each of the above data sets ($s = 0.35 \pm 0.05$) [61]. Davis et al. [63], however, found that for some systems s_1 and s_2 had to be different in order to model the data, and has noted that for some systems the Walling ϕ factor [12] is strongly composition dependent. Thus one adjustable parameter is not expected to be sufficient to model the kinetic data of these systems. In any case, the single-parameter analysis is merely a useful tool for data-fitting, and the 'average s' values obtained have limited physical meaning. Until better experimental techniques can be used to obtain reliable values of the radical reactivity ratios, it is not possible to study the origin of the penultimate unit effect by examining their measured values.

4.3.4. Temperature effects on s_1 and s_2

Despite the above problems, studies of the temperature dependence of the radical reactivity ratios have had some (albeit limited) success in separating the enthalpic and entropic contributions to the penultimate unit effect. In an extensive PLP study of the bulk copolymerisation of styrene with methyl methacrylate, Coote et al. [24,25] attempted to measure the temperature dependence of the radical reactivity ratios of this system. As alluded to above, despite a large experimental design, it was found that the extreme sensitivity of the estimated parameters to small uncertainties in the data prevented the accurate and precise estimation of the individual radical reactivity ratios, and it was thus impossible to determine whether or not the individual parameters were temperature dependent. However, it was found that the extent of deviation from the terminal model (as measured by fitting a single parameter to the data, i.e. $s = s_1 = s_2$) was temperature dependent, and thus the penultimate unit effect in this system had a significant enthalpic component. This can be seen qualitatively in Fig. 3 which shows the scaled propagation rate coefficients for the styrene with methyl methacrylate system at 18 and 57°C [24,25]. Examining this figure it is clear that there is a change in the depth of the propagation rate coefficient curves as the temperature is increased. This result is important as it indicates that the general failure of the terminal model cannot be solely attributed to entropic factors.

4.3.5. The Validity of $r_1r_2 = s_1s_2$

One means of evaluating the radical stabilisation model [41] is to test the validity of one of its predictions—namely that, provided there are no penultimate unit effects in the frequency factors, the equality $r_1r_2 = s_1s_2$ should hold. To test this prediction, Fukuda et al. [51] plotted values of s_1s_2 for various copolymerisations against their r_1r_2 products and concluded that they were correlated. However, upon closer examination of the plotted data (which may be found in the original paper [51]), it is clear that, even plotted as a log–log graph, most of the data is simply scattered around a central point and the

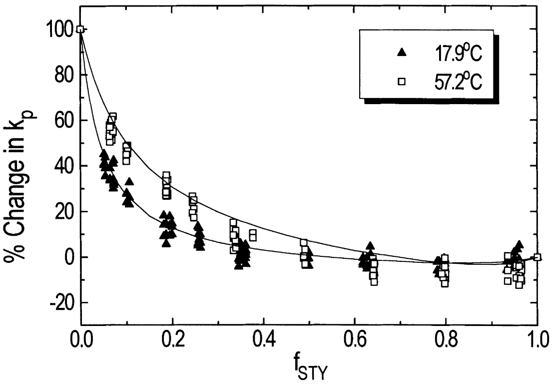

Fig. 3. Scaled propagation rate coefficients for the bulk copolymerisation of styrene with methyl methacrylate at 18 and 57°C [24,25].

correlation is thus quite poor. Furthermore, the uncertainties in the individual monomer and radical reactivities are too large for any firm conclusions to be drawn.

However, while individual values of the radical reactivity ratios are subject to large uncertainties, this equality can be tested with more certainty in systems for which the terminal model is known to hold. Since the absence of a penultimate unit effect would be given by $s_1 = s_2 = 1$, this would be reflected as $s_1 s_2 = 1$ and thus the radical stabilisation model would predict that $r_1 r_2 = 1$. It was therefore suggested that copolymerisations that obeyed the terminal model should be ideal (i.e. should satisfy the condition $r_1 r_2 = 1$) [68]. At first this was indeed believed to be the case, since, of all the systems for which the propagation rate had been directly measured, only four—styrene with *p*-methoxystyrene [68], and methyl methacrylate with perdeuterated methyl methacrylate [69], with dodecyl methacrylate [20] and with butyl methacrylate [20]—appeared to obey terminal model kinetic behaviour, and all of these systems are ideal copolymerisations of sterically similar monomers (see Table 1). Two recent studies, however, have produced results that are incompatible with the relationship $r_1 r_2 = s_1 s_2$, and hence undermine the validity of the radical stabilisation model.

In the first such study, Cuervo-Rodriguez et al. [70], identified a system—the copolymerisation of methyl methacrylate with ethyl α-benzoyloxymethyl acrylate in benzene—in which $r_1 r_2 \neq 1$ but for which the terminal model can adequately describe both the composition and rate of copolymerisation over the entire monomer feed composition range. To test for terminal model kinetics they did not measure $\langle k_p \rangle$ directly but used a rate equation, derived by Fukuda et al. [67], that was based on the penultimate model for propagation and a simple model for $\langle k_t \rangle$. When they fitted this model to experimental values of the overall polymerisation rate, they obtained $s_1 = s_2 = 1$, and therefore $r_1 r_2 \neq s_1 s_2$ (since $s_1 s_2 = 1$ and $r_1 r_2 \neq 1$). However, it should be noted that $\langle k_p \rangle$ has not been measured directly for this system and the assumption of a simple model for termination, although reasonable, may not necessarily be correct. The danger in assuming a model for termination and merely analysing overall rate data was highlighted in studies of the copolymerisation of methyl methacrylate with perdeuterated methyl methacrylate. When Davis and O'Driscoll [71] calculated $\langle k_p \rangle$ for this system, using Wittmer's [72] data for the overall polymerisation rate and assuming a diffusion controlled termination model, they found a strong penultimate unit effect on $\langle k_p \rangle$. Given that this copolymerisation was ideal (i.e. $r_1 r_2 = 1$), this result appeared to undermine the radical stabilisation model. However, when Olaj et al. [69] used

PLP to measure $\langle k_p \rangle$ directly, they found that it *did* obey the terminal model, as predicted by $r_1 r_2 = 1$, and the abnormalities were thus in the termination reaction. Therefore propagation rate data that are calculated from overall polymerisation rate data via an assumption as to the termination model should be treated with caution.

In a more recent study, based on direct measures of the composition and propagation rate coefficients, Coote and Davis [73] demonstrated the failure of the prediction $r_1 r_2 = s_1 s_2$ for the copolymerisation of *p*-chlorostyrene with styrene and *p*-chlorostyrene with *p*-methoxystyrene (at 40°C). For both of these systems it was demonstrated that, even when the uncertainties in the monomer and radical reactivity ratios were taken into account, the products $r_1 r_2$ and $s_1 s_2$ differed significantly, and it was impossible to achieve an adequate simultaneous fit of the implicit penultimate model to the composition and propagation rate coefficients, under the constraint that $r_1 r_2 = s_1 s_2$ (see Fig. 4). It was argued that, since these counter-examples to the radical stabilisation model were obtained in systems of sterically similar monomers, the failure of the radical stabilisation model in these systems could not be attributed to steric interactions that, as explained by Fukuda et al. [41], fall outside of the scope of this model. Indeed, for one of these two systems (PCS–PMOS), the terminal model was shown to provide an adequate description of the data and thus it would seem that the failure of the radical stabilisation model could not be attributed to other non-classical effects (such as solvent effects) as these should have resulted in the failure of the terminal model. Instead, it was argued that the failure of the radical stabilisation model in these two systems was likely to be the result of polar interactions which, as noted in Section 4.2, have been shown [47,48] to undermine the Evans–Polanyi rule [45,46]—one of the radical stabilisation model's principal assumptions.

4.3.6. Studies of solvent effects on monomer reactivity ratios

Evidence concerning the possible importance of polar interactions in free-radical propagation reactions can be found in studies of the solvent dependence of reactivity ratios. When polar interactions are important in the transition structure of the propagation reaction, the polarity of the solvent may affect the propagation rate. This may be explained as follows. As noted above (Section 4.2), polar interactions [43] are said to occur when the transition structure is stabilised by charge transfer between the reacting species. The amount of charge transfer, and hence the amount of stabilisation, is inversely proportional to the energy difference between the charge transfer configuration and the product and reactant configurations that combine to make up the ground state wavefunction of the transition structure. Now it is known that polar solvents can stabilise charged species, as seen in the favourable effect of polar solvents on both the thermodynamics and kinetics of reactions in which charge is generated [43]. Thus, when charge transfer in the transition structure is important, the relative stability of the charge-transfer configuration, and thus of the transition structure, will be affected by the polarity of the solvent. Hence, when polar interactions are important in a propagation reaction, a polar solvent can stabilise the transition structure and hence lower the reaction barrier.

When such effects are important, the polarity of the solvent affects radical selectivity as well as radical reactivity. This is because the extent to which charge-transfer stabilisation can occur, and hence the extent to which polar solvents can further enhance these effects, depends on both reacting species. For instance, in a free-radical copolymerisation, it is likely that polar interactions would be more important in the cross-propagations (when the monomer and radical bear different substituents and thus have different electronic properties) than in the homopropagations (when the monomer and radical bear the same substituents). Hence the effect of solvent polarity on the stability of the transition structure

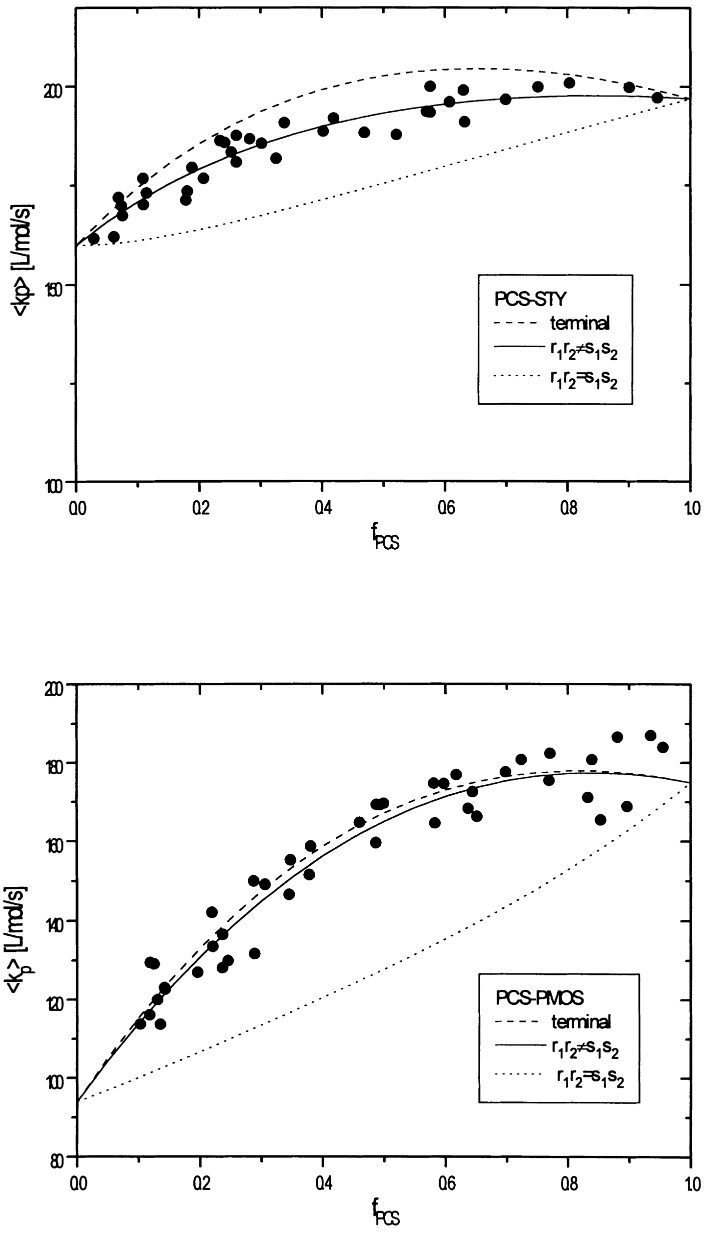

Fig. 4. Propagation rate coefficients for the copolymerisation of p-chlorostyrene (PCS) with styrene (STY) and p-methoxystyrene (PMOS) at 40°C. Also plotted are the corresponding terminal model predictions and the best-fits of the implicit penultimate model to the data both under the constraint that $r_1r_2 = s_1s_2$, and without the constraint that $r_1r_2 = s_1s_2$ (i.e. with $r_1r_2 \neq s_1s_2$) [73].

(and thus the propagation rate) would generally be expected to be greater in the cross than in the homopropagation reactions. Thus, there would be a net effect of solvent polarity on the reactivity ratios of the copolymerisation (regardless of whether or not these polar interactions are influenced by the penultimate unit, or merely by the terminal unit).

The idea of charge separation in the transition structure of the propagation step, as originally suggested by Price [74], was discounted by Mayo and Walling [75] and many subsequent workers [76]. The rejection of this idea was based on the absence of any unambiguous correlation between the reactivity ratios of a system and the dielectric constant of the solvent. For instance, in the copolymerisation of styrene with methyl methacrylate it was reported that the reactivity ratios were insensitive to small quantities of water, ethyl benzene, dodecylmercaptans, hydroquinone or the presence or absence of air [7,77,78], and were thus unaffected by the dielectric constant of the solvent. However, recent theoretical [47,48,79,81] and experimental [82,83] studies of the addition of small radicals to alkenes do indicate that polar interactions can be important in the transition structure of small-radical addition reactions, particularly when one reactant is highly electrophilic and the other highly nucleophilic. Indeed, a number of experimental studies have identified relationships between the reactivity ratios and solvent dielectric constants in specific systems—even in the styrene with methyl methacrylate system. For instance, Bonta et al. [84] noted a marked solvent effect on both of the terminal model reactivity ratios for the copolymerisation of styrene with methyl methacrylate in dioxane, acetone and *N*,*N*-dimethyl formamide. They found that this solvent effect could be correlated with the variation in the solvent dielectric constant. Ito and Otsu [85] noted that the reactivity ratios of this system in benzene, benzonitrile, benzyl alcohol and phenol were also subject to a significant solvent effect that could be correlated with the solvent polarity. Fujihara et al. [86] also observed a strong solvent effect on the reactivity ratios of this system in a variety of solvents. Correlations between the solvent dielectric constant and the monomer reactivity ratios have also been observed for other systems. For instance, correlations for the reactivity ratios of styrene with acrylonitrile have been reported by Sandner and Loth [87,88]. Further, other studies have found that the reactivity ratios of a copolymerisation are sensitive to the nature of the solvent, though no direct correlation between these ratios and the solvent dielectric constant was observed. For instance, Harwood [89] noted the solvent sensitivity of copolymerisations of styrene with methacrylic acid, with acrylic acid, and with acrylamide, while Klumperman and O’Driscoll [90] have noted the solvent sensitivity of the styrene with maleic anhydride system. Although the solvent sensitivity of these copolymerisations has in the past been attributed to other causes (such as a bootstrap effect [89]), it is nonetheless possible that solvent polarity plays a role in this solvent dependence, though the operation of additional types of solvent effect (such as a bootstrap effect) obscures a direct correlation.

Hence a number of studies suggest that the effects of solvent polarity can be important even in common copolymerisation systems such as styrene with methyl methacrylate, and this in turn suggests that polar interactions may be important in the transition structure of their propagation reactions. While such evidence polar interactions does not necessarily indicate that such effects are responsible for the penultimate unit effect in free-radical copolymerisation, evidence for these polarity effects nevertheless has important implications for the radical stabilisation model [41] since in this model it is assumed that the Evans–Polanyi rule [45,46] can describe the relationship between the reaction enthalpy and reaction barrier in the propagation reactions. As noted above (Section 4.2), theoretical studies of small radical addition reactions indicate that, when polar interactions are important in the transition structure, this rule is unlikely to hold [47,48]. Thus, the above evidence for polarity effects in systems such as the

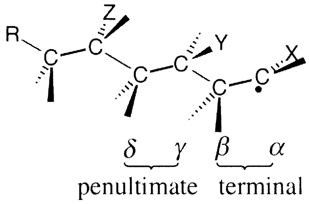

Fig. 5. Substituents on an alkyl radical.

copolymerisation of styrene with methyl methacrylate [84,86], implies that the radical stabilisation model is unlikely to be valid in these systems, as it indicates that one of its central assumptions is unlikely to hold.

4.3.7. Experimental studies of γ-substituent effects

One means of testing the alternative models is to measure the penultimate unit effect directly, via studies of γ-substituent effects on the reactivity and selectivity of alkyl radicals in addition reactions with alkenes. As seen in Fig. 5, these γ-substituents form the leading part of the penultimate unit of a polymer radical.

A number of studies have directly detected γ-substituent effects on radical selectivity (i.e. explicit penultimate unit effects) in small-radical addition reactions. For instance, Tirrell and coworkers [91,92] directly measured the relative rates of addition of γ-substituted propyl radicals to acrylonitrile and styrene. In their first study [91], they used Giese's [93] 'mercury method' and observed that the preference of 3-phenylpropyl for addition to acrylonitrile was reduced 3.5 fold when the phenyl-substituent was changed to a cyano-substituent. Later, they [92] repeated the work including a phenyl-substituent in the α-position of all of the radicals, and using an improved method for producing primary radicals. They reached the same conclusion, but their value for the penultimate unit effect of the CN unit was measured to be about 2.5, in agreement with the value obtained by Hill et al. [18] when they fitted the explicit penultimate model to the composition and sequence distribution data for copolymers of these two monomers. They further noted that the preference of an α-phenyl radical for reaction with styrene over acrylonitrile, was relatively unchanged when a γ-phenyl-substituent was exchanged for no penultimate unit at all (i.e. the 1-phenyl ethyl radical). In other words, the penultimate unit effect of the styrene unit was negligible. Since the highly resonance stabilised and very bulky phenyl-substituent had a negligible penultimate unit effect compared to the smaller and less stabilised cyano unit, the origin of the penultimate unit effect in this system is likely to involve some polar interaction between the attacking acrylonitrile monomer and the penultimate acrylonitrile unit.

Giese and Englebrecht [42] also detected polar penultimate unit effects on radical selectivity. They examined the effect of a series of polar β and γ substituents on the selectivity of alkyl radicals in addition reactions with alkenes. They found that these substituents do not influence the nucleophilicity of the radicals but do reduce their rate of addition to diethyl fumarate, and they thus concluded that the penultimate unit effect was polar in origin.

Busfield et al. [94] used a nitroxide radical trapping technique to study the competitive reaction of cyanoisopropyl radicals with styrene and acrylonitrile. They found that the primary cyanoisopropyl radicals preferred to add to styrene, and this preference was greatly increased for the second-generation cyanoisopropyl radical (i.e. bearing terminal and penultimate cyano groups). In other words, there was a penultimate unit effect on the selectivity of the radical. They also found that second-generation radicals that were terminated with a styrene unit reacted almost exclusively with acrylonitrile. The trends in their data were thus consistent with a polar origin for the substituent effects, since the radicals bearing electron withdrawing cyano substituents preferred the electron-rich styrene monomers, while the nucleophilic styrene terminated radicals preferred the electron-deficient acrylonitrile monomers.

However, another recent experimental study of substituent effects on primary radical addition reactions failed to detect significant penultimate unit effects. Using laser flash photolysis to measure the absolute rate constant, Avila et al. [95] showed that, while fluorination of *n*-alkyl radicals in the α and β position greatly increased their rate of addition to various styrene analogues, fluorination in the γ position had no effect. It has been argued [96,97] that these results suggest that electronic penultimate unit effects are small since the γ-fluoro substituent would have been expected to differ from a γ-hydrogen in its electronic, though not in its steric properties. However, while it would be expected to be larger than its steric effect, the electronic effect expected from a fluoro substituent (which has a Hammett parameter of only 0.05 [98]) would nevertheless be small. The absence of a penultimate unit effect in these reactions does not, therefore, necessarily indicate the general unimportance of electronic penultimate unit effects.

In summary, a number of studies have provided direct evidence for a γ-substituent effect on radical selectivity—that is, an explicit penultimate unit effect. In these studies, which typically involved polar substituents such as nitrile groups, the observed penultimate unit effects appeared to be polar in origin. However, studies of other common monomer pairs (such as styrene with acrylate or methacrylate derivatives) are required in order to confirm the generality of this result.

4.3.8. Direct measures of monomer reactivity ratios

Another means by which the implicit and explicit penultimate models can be tested is by comparing the terminal (and hence implicit penultimate) model monomer reactivity ratios for a given system, with corresponding values that are measured directly via experimental studies of small-radicals. Lyons and Senogles [99], using end-group studies, measured the relative reactivities of the 1-methyl-1-(methoxycarbonyl)ethyl radical toward a number of monomers, and compared the resulting (terminal model) monomer reactivity ratios with those estimated by fitting the terminal model to composition data. They found a substantial difference (a factor of 2.7) between their directly measured values and those estimated as fitted model parameters for the methyl methacrylate/acrylonitrile system; a small but significant difference (a factor of 1.4) for the styrene/methyl methacrylate system; and no difference in the methyl methacrylate/methyl acrylate system. These results would appear to provide direct evidence for a penultimate unit effect in the monomer reactivity ratios (i.e. an explicit effect) in the copolymerisations of methyl methacrylate with acrylonitrile and with styrene. However it should be acknowledged that the discrepancy between the small-radical and copolymerisation studies may (at least in part) be attributable to chain-length effects since (as noted in Section 2) the propagation rate coefficient of a monomeric radical differs from that of its corresponding macroradical. Although chain-length effects would be largely expected to cancel from reactivity ratios, the possibility that such effects are the cause of the small discrepancy in the styrene/methyl methacrylate system cannot be ruled out. Hence, further studies—in which the equivalent reactivity ratios are measured in slightly larger radicals—are required to confirm these results.

Table 2
Reaction barriers (barriers (0 K, kJ/mol) correspond to estimated UQCISD(T)/6-311G(d,p)//UHF/6-31G(d) values together with the incorporation of UB3-LYP/6-31G(d) ZPVE corrections. Barriers were computed for a model conformation in which a fully extended radical underwent anti-addition to the alkene. For more details of the calculations, the reader is referred to the original paper of Coote et al. [79]) for the addition of 3-X-Propyl radicals to various alkenes

X	$CH_2{=}CH_2$	$CH_2{=}CHF$	$CH_2{=}CHCHO$	$CH_2{=}CHCN$	$CH_2{=}CHNH_2$
H	30.3	30.8	17.8	14.6	25.7
F	30.0	30.6	20.0	16.8	23.1
NH_2	29.9	30.6	18.6	15.1	25.0
CN	29.6	30.2	20.7	17.8	21.1

4.3.9. Molecular orbital calculations of the reaction barrier

Ab initio molecular orbital calculations have also been used to study the penultimate unit effect in free-radical polymerisation. In an early study, Imoto et al. [100,101] calculated (at the UHF/STO-3G level) the reaction barriers for the primary homopropagation step for a series of common monomers, and found that the calculated and experimentally observed barriers were well correlated. However, similar calculations failed to explain the primary cross-propagation reactions, and hence the terminal model reactivity ratios. They attributed this failure to penultimate unit effects in the activation energy. However, it should be noted that the disagreement between their calculated results and the experimental results is likely to have been caused by the poor quality of the experimental data base of reactivity ratios (with which the results were being compared), chain length effects on the propagation rate coefficients in the first few propagation steps, and the substantial errors known to be present in Hartree–Fock level calculations of reaction barriers for radical addition reactions [102].

Recently, Heuts et al. [44,96,97] studied the penultimate unit effect directly, by measuring the effect of the γ substituent on the reaction barrier for the addition to ethylene of a series of γ-substituted propyl radicals (3X-propyl, $X = H$, F, CN, and NH_2). They also used a much higher level of theory to calculate the barriers (namely, UQCISD(T)/6-31G(d) energies based on UHF/6-31G(d) geometries with UHF/6-31G(d) zero-point vibrational energy corrections). They found that penultimate unit effects on the reaction barriers for these reactions were less than 2 kJ/mol, which would correspond to penultimate unit effects on the reaction rate (at room temperature) of less then 40%—much smaller than those observed experimentally. They argued that, given the wide range of Hammett parameters represented by the substituents, the reactions studied were likely to be representative, and they thus concluded that enthalpic factors were unable to account fully for the penultimate unit effect in copolymerisation. However, while this study clearly indicates that the penultimate unit effects in the barrier are small for the reactions that were studied, it should be noted that these reactions are not necessarily representative. In particular, they fail to consider: reactions with monomers other than ethylene, and thus the possible dependence of the penultimate unit effect on the reacting monomer; reactions of radicals bearing α substituents in addition to γ substituents, and thus the possible contribution to the penultimate unit effect of interactions involving these substituents; and substituents with a wider range of sigma-inductive properties. (The mesomeric properties of these substituents, to which the wide variation of their Hammett parameters can be mainly ascribed, would be unlikely to be significant at the γ position.)

More recently, Coote et al. [79,81] have extended the work of Heuts et al. [44,96,97] by examining

Table 3
Effect of gamma substituents (X) on the stabilities of 1-Y,3-X-Propyl radicals (calculated using RMP2/6-311 + G(3df,2p)//B3-LYP/6-31G(d) energies with scaled B3-LYP/6-31G(d) ZPVE corrections. For more details of the calculations see the original paper of Coote et al. [80])

X	Propyl	1-F-propyl	1-CN-propyl
H	0	0	0
F	0.1	−2.5	−4.5
CN	−1.4	−4.5	−9.2

gamma-substituent effects on the reaction barrier (and other related quantities) in a much wider range reactions. The main conclusions of this work can be summarised as follows:

1. *Polar penultimate unit effects.* Calculations [79] of the reaction barrier for the addition of a series of γ-substituted propyl radicals (3X-propyl; X = H, F, NH_2, CN) to various alkenes (CH_2=CHY; Y = F, NH_2, CN, CHO), indicated that the barrier was affected by the γ substituent X (i.e. there was a penultimate unit effect in the barrier), and that the magnitude and direction of this effect was strongly dependent on the nature of the alkene (i.e. the penultimate unit effect was strongly explicit). These results are summarised in Table 2. As seen in this table, replacing a γ CN substituent with a hydrogen was found to increase the reaction barrier by 4.6 kJ/mol in reactions with CH_2=$CHNH_2$, decrease the reaction barrier by 2.9 kJ/mol in reactions with CH_2=CHCN, and decrease the barrier by only 0.6 kJ/mol in reactions with CH_2=CHF. Furthermore, it was shown that the trends in the results were consistent with a polar origin for the observed penultimate unit effects [79]. (The importance of polar interactions in these reactions was later confirmed in an examination of the relevant charge-transfer energies [56].) In summary, the calculations provided direct evidence for explicit penultimate unit effects in the reaction barrier, and indicated that such effects were likely to be polar in origin.
2. *Radical stabilisation penultimate unit effects.* Calculations [80] of the radical stabilisation energy for a series of 1,3-disubstituted propyl radicals (1Y,3X-propyl; Y = F, CN; X = H, F, CN) indicated that the γ substituent (i.e. penultimate unit) could affect the stability of the propagating polymer radical (see Table 3). For instance, replacing a γ CN substituent with a hydrogen in the 1CN,3X-propyl radical, was found to stabilise the radical by 9.2 kJ/mol. However, although there were large penultimate unit effects on radical stability, when the reaction barriers for the addition of these radicals to ethylene were calculated, it was clear that the large penultimate unit effects on radical stability did not carry over to any great extent to the reaction barrier (see Table 4) [80]. For instance, although the γ CN substituent in the 1CN,3X-propyl radical destabilised the radical by 9.2 kJ/mol

Table 4
Barriers (barriers (in kJ/mol) at the QCISD(T)/6-311G(d,p)//HF/6-31G(d) level with scaled B3-LYP/6-31G(d) ZPVE corrections. For more details of the calculations the reader is referred to the original paper of Coote et al. [80]) for the addition of 1-Y,3-X-Propyl to CH_2=CH_2

X	Propyl	1-F-propyl	1-CN-propyl
H	30.3	26.3	37.0
F	30.0	25.6	37.0
CN	29.6	25.4	34.5

(relative to the γ hydrogen), it only lowered the reaction barrier for its addition to ethylene by 2.5 kJ/mol. This small proportionality constant in the relationship between penultimate unit effects on radical stability (i.e. reaction enthalpy) and their corresponding reaction barriers is indicative of an early transition structure—a result that is likely to be general, given the highly exothermic nature of the propagation step in most free-radical polymerisation reactions.In the same study [80], it was noted that, in the reactions where significant penultimate unit effects in the barrier were observed, the charge-transfer energies indicated that polar interactions were likely to be significant. This was despite the fact that the barriers had been calculated for reactions with ethylene—a monomer which was relatively insusceptible to polar interactions—even under the most unfavourable circumstances. In other words, it appeared that for radical stabilisation effects to exert significant penultimate unit effect in the reaction barrier, the substituents involved needed to be so strongly electron donating or accepting that they would simultaneously susceptible to polar interactions. It was thus concluded that radical stabilisation effects were unlikely to result in significant penultimate unit effects in the reaction barrier, without the simultaneous interference of polar interactions. Since (as noted in Section 4.2) polar interactions undermine the Evans–Polanyi rule (one of the radical stabilisation model's central assumptions) and are themselves responsible for explicit rather than implicit penultimate unit effects, these results suggest that, where penultimate unit effects in the reaction barrier are significant, they are likely to be explicit rather than implicit.

3. *Conformational effects.* A further study [81] of the conformational dependence of the reaction barriers for the addition of various gamma substituted propyl radicals to alkenes revealed that the penultimate unit effect in the reaction barrier was strongly dependent on the conformation of the reacting radical and transition structure. This indicated that direct interactions involving substituents on the penultimate unit and the monomer, mediated perhaps by the substituents on the terminal unit and/or the unpaired electron, were likely to be contributing to the penultimate unit effect in the reaction barrier. This importance of direct interactions further indicates that penultimate unit effects are likely to be explicit rather than implicit, since it would be expected that the magnitude of the penultimate unit effect would not be independent of the nature of the species with which it was directly interacting. It also meant that the penultimate unit effect in the overall reaction barrier of a reaction would depend on the relative contribution of the individual pathways (i.e. radical and transition structure conformations), and hence on the barriers and frequency factors of these individual pathways. In other words, the penultimate unit effect in the overall reaction barrier would depend in part on entropic factors. Finally, the results also indicated that the penultimate unit would affect the relative contribution of the different reaction pathways to the overall reaction and hence there would be a penultimate unit effect on the tacticity of the resulting polymer—a result which is supported by a recent NMR study [103] (see below).

In summary, recent ab initio molecular orbital calculations [56,79,81] of γ-substituent effects in small-radical addition reactions have provided direct evidence for explicit penultimate unit effects in the reaction barrier, and suggest that polar interactions and direct interactions are likely to be important in determining this behaviour. The calculations also indicate that significant penultimate unit effects on radical stability are possible, though (owing to the early transition structure in these highly exothermic reactions) only a small fraction of these effects carry over to the reaction barrier. As a result, where such effects are significant they are unlikely to occur independently of (explicit) polar interactions; hence penultimate unit effects in the barrier are likely to be explicit rather than implicit.

4.3.10. Molecular orbital calculations of the frequency factor

Heuts et al. [44,96,97] also used ab initio molecular orbital calculations, in conjunction with transition state theory, to study penultimate unit effects in the frequency factors of the propagation reaction. Based on a study of ethyl and propyl addition to ethylene, they argued that the penultimate unit would be able to hinder certain internal motions in the transition structure, including:

- the rotation of the adding monomer unit about the forming carbon–carbon bond;
- the rotation of the monomer and terminal carbon units about the terminal carbon–carbon bond;
- the simultaneous bends of the reacting moieties.

As these motions were important in determining the frequency factor of the propagation reaction, and since any penultimate unit effects in these individual motions would be multiplicative, they argued that entropic penultimate unit effects in the range 0.1–10 were possible. However, it should be noted that this prediction was based on differences between ethyl and propyl propagation (i.e. a β-substituent effect). Direct evidence for entropic penultimate unit effects (i.e. γ-substituent effects) is required in order to verify this prediction.

4.3.11. ESR studies of model radicals

ESR studies of low molecular weight compounds by Sato et al. [104] and Tanaka et al. [50], have experimentally detected penultimate unit effects on radical stability. In experiments with di-*n*-butyl itaconate (DBI) with benzoyl peroxide initiator, Sato et al. [104] found that only one type of propagating radical was produced. However, when azobisisobutyronitrile (AIBN) was used as an initiator, an additional low molecular weight non-propagating radical was produced. This was assumed to be the product of addition by AIBN to the DBI radical. They proposed that the cyano group at the penultimate position stabilises the DBI radical, suppressing further propagation. Thus, there was a penultimate unit effect on radical stability. In another ESR study, Tanaka et al. [50] observed that substituents in the penultimate and even anti-penultimate positions affect the spin distribution and conformation of the radicals. They also noted that, of the substituents that they had studied, the penultimate units bearing nitrile groups had a large effect on the spin distribution, but those that were simply alkyl or acrylate groups did not.

These studies therefore support the proposition by Fukuda et al. [41] that the penultimate unit can affect the stability of the propagating radical—a result that is also supported by the ab initio molecular orbital calculations outlined above [80]. However, the penultimate unit effects detected were for groups bearing nitrile substituents and, as seen in the small-radical studies [42,91,92,94] and ab initio molecular orbital calculations [79,80] outlined above, such substituents are simultaneously responsible for explicit (polar) penultimate unit effects. Further studies are thus required in order to demonstrate that significant radical stabilisation effects can occur independently of polar interactions.

4.3.12. Stereochemical evidence

Studies of polymer tacticity have also been used to examine the penultimate unit effect. For instance, Moad et al. [105] claim to have found stereochemical evidence for a penultimate unit effect in the homopolymerisation of methyl methacrylate. While, in a homopolymerisation, there is only one type of penultimate unit, it could nevertheless influence the propagation reaction. Although this penultimate unit effect would not, of course, be detectable in the propagation kinetics or the composition or sequence distribution of the polymer, it could be detectable in the polymer tacticity. Moad et al. [105] argued that if the addition reaction was completely random, irreversible, and determined solely by the nature of the

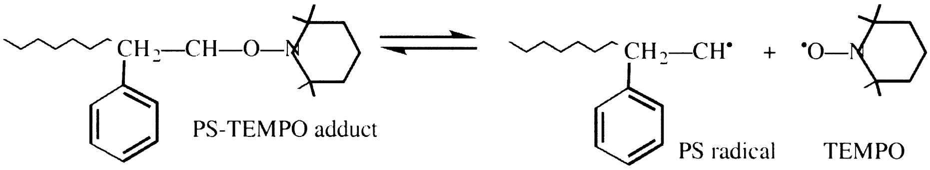

Fig. 6. Living free-radical polymerisation of styrene [106].

terminal unit, free-radical homopolymers should be atactic. That is, the probability of finding a meso dyad should be 50% ($P(m) = 0.5$). However, in their NMR study of poly(methyl methacrylate) homopolymers, they found that in fact $P(m) = 0.202$ and $P(m|m) = 0.159$. In other words, there is a preference for the new chiral centre to adopt a configuration that is opposite to that of the previous one, and hence form a new racemic dyad—thus the conformation of the penultimate unit influences the conformation of the attacking monomer in the transition structure. Furthermore, they found that antepenultimate unit effects also operate, since the probability of finding a meso dyad is reduced by a further 20% if the preceding dyad is also meso.

Although the above study shows that the conformation of the penultimate unit affects the conformation of the monomer, it cannot show whether or not this influence varies with the nature of the penultimate unit (that is, whether or not there is a penultimate unit effect on the polymer tacticity). This is because, in a homopolymerisation, there is only one type of penultimate unit. However, in a more recent NMR study, Yamamoto et al. [103] have identified a penultimate unit effect on the tacticity of copolymers of vinyl acetate with vinyl pivalate. In the same study they noted that the tacticities of poly(vinyl acetate-*co*-vinyl propionate) and poly(vinyl acetate-*co*-vinyl decanoate) were well described by the terminal model.

The above studies therefore indicate that the conformation of the penultimate unit can affect the conformation of the reacting monomer, and the size of this effect can, at least in some cases, vary with the nature of the penultimate unit. This further supports the above theoretical evidence for the existence of penultimate unit effects in the propagation reaction [56,79–81], and in particular supports the conclusion [81] that direct interactions involving substituents on the penultimate unit and the monomer, mediated perhaps by the substituents on the terminal unit and/or the unpaired electron, contribute to this effect.

4.3.13. Evidence from ‘living’ free-radical polymerisation

Recent experimental evidence for an electronic penultimate unit effect has emerged from the unlikely field of ‘living’ free-radical polymerisation. Fukuda et al. [106] has noted that ‘living’ free-radical copolymerisation of monomers, for which ‘living’ free-radical homopolymerisation is not possible, may be induced if the comonomer undergoes ‘living’ free-radical polymerisation. This behaviour may be attributed to the penultimate unit effect of the comonomer. For instance, ‘living’ free-radical polymerisation of styrene is possible in the presence of the stable free-radical TEMPO. The ‘living’ behaviour has been attributed to the equilibrium that is established between the TEMPO and a styrene terminated radical, and the corresponding TEMPO adduct (see Fig. 6). TEMPO does not cause ‘living’ free-radical behaviour for other monomers such as acrylonitrile, methyl acrylate, ethyl acrylate and 9-vinyl carbazole, and this has been attributed to the failure of these monomers to establish a similar equilibrium with TEMPO. However, when these monomers are copolymerised with styrene, ‘living’ behaviour does occur, provided that the concentration of styrene in the reacting mixture is not too low. Fukuda et al. [106] argued that the ability of styrene to cause ‘living’ free-radical behaviour in these monomers is evidence for a penultimate unit effect, exerted by the styrene penultimate unit on the strength of the carbon–oxygen bond in the above equilibrium. However, the possibility that this is merely a medium effect cannot be ruled out.

4.4. Assessment of the penultimate models

The above studies provide extensive evidence for the existence of significant penultimate unit effects in the propagation step of free-radical polymerisation. Independent studies have shown that the penultimate unit can affect the selectivity of small-radicals in addition reactions with alkenes, the spin distribution and conformation of small-radicals, the tacticity of certain copolymers, and the transfer constants in certain transfer-dominated copolymerisations. In addition, ab initio molecular orbital calculations indicate that penultimate unit effects are significant in both the barrier and frequency factors of the propagation reaction, and can influence both the stability of the propagating radical and the relative ease of charge transfer between the coreactants. Penultimate unit effects appear likely to be general in free-radical polymerisation, and a penultimate model should thus replace the terminal model as the basis of free-radical copolymerisation kinetics.

While the model discrimination studies based on model-fitting to co- and terpolymerisation data have been largely unsuccessful in discriminating between the implicit and explicit penultimate models, the mechanistic studies outlined above (in particular the ab initio molecular orbital calculations) suggest that an explicit penultimate model is likely to provide a more physically realistic description of free-radical copolymerisation kinetics. This conclusion is based largely on the theoretical evidence [79,80] that, owing to the early transition structures in these reactions, (significant) implicit radical stabilisation effects are unlikely to occur independently of explicit polar effects. Hence, where penultimate unit effects in the reaction barrier are significant, they will be explicit and not implicit. The experimental studies outlined above provide indirect support for this idea in more common systems such as the copolymerisation of styrene with methyl methacrylate. In this system, the study of temperature effects [24,25] indicated that penultimate units in the barrier were significant, while the studies of solvent effects [84,86] indicated that polar interactions were likely to be important in this system. Furthermore the experimental studies of *para*-substituted styrene copolymerisations [73] provide direct evidence against the radical stabilisation model for these system, a failure that is likely to be the result of polar interactions. The small-radical studies [42,91,92,94] also provide direct experimental evidence for explicit penultimate unit effects that are likely to be polar in origin.

The studies reviewed above also indicate that, in addition to polar interactions, a number of other factors are likely to contribute to the penultimate unit effect in free-radical polymerisation. Both the theoretical [81] and experimental [103] studies suggest that direct interactions are likely to contribute to the penultimate unit effect—particularly in the more crowded conformations. The theoretical [80] and experimental [50,104] studies also suggest that radical stabilisation penultimate unit effects are possible, though as noted above, such implicit effects are unlikely to occur independently of explicit polar effects. Finally theoretical studies indicate that entropic factors are also likely to contribute to the penultimate unit effect—both directly (as a penultimate unit effect in the frequency factor [44]), and indirectly (by governing the relative contributions of the individual reaction pathways to the overall reaction, and thereby determining the penultimate unit effect in the overall reaction barrier [81]).

5. Conclusions and implications for copolymerisation kinetics

In conclusion, the studies reviewed in this paper indicate that the explicit penultimate model should replace the terminal model as the basis of copolymerisation kinetics. It should be acknowledged that, for common copolymerisation systems such as the bulk copolymerisation of styrene with methyl methacrylate, the direct evidence for this result is still somewhat limited and an experimental study of γ-substituent effects in a small-radical model of this system is required to confirm this result. However, while there is only circumstantial evidence for the explicit penultimate model in systems such as the bulk copolymerisation of styrene with methyl methacrylate, there appears to be no evidence for the implicit penultimate model in such systems. Hence existing evidence appears to favour the explicit penultimate model over the implicit penultimate model, as a more physically realistic description of copolymerisation kinetics. It might be objected that the evidence against the implicit model is not yet strong enough to outweigh the fact that this model should be favoured on methodological grounds (i.e. “Occam’s Razor”) owing to its simplicity—its having six parameters to the explicit model’s eight. However, despite its having fewer parameters than the explicit model, the implicit model involves us in an additional theoretical commitment—namely, the need to justify why the penultimate unit, unlike the terminal unit, should affect only the overall propagation rate coefficient and not the composition or sequence distribution. The explicit model avoids this additional commitment, and is thus, in chemical rather than mathematical terms, the simpler model. Hence, contrary to the above objection, Occam’s Razor would in fact suggest that we adopt the explicit rather than the implicit penultimate model, until there is sufficient evidence for the implicit model’s additional assumption—particularly in the light of the indirect evidence against it, as reviewed in this paper.

The conclusion that the explicit (rather than implicit) penultimate model should be adopted as the basis of free-radical copolymerisation kinetics has important implications. In particular it implies that the large numbers of terminal model monomer reactivity ratios that have been and continue to be published have limited physical meaning. Although these parameters are crudely correlated with average radical reactivity, they do not reflect their proposed physical meaning and can thus lead to false predictions of the other copolymerisation properties which depend upon them—as indeed they are already known to do in the case of propagation rate coefficients. Not only does this imply that such parameters should not be used in quantitative studies of radical reactivity, but it also suggests that the ‘measured’ sequence distribution data for systems such as styrene with methyl methacrylate which rely on fitted coisotacticity factors may be incorrect, since these have been fitted to the (incorrect) terminal model. In addition, as penultimate unit effects are significant in most copolymerisations, we recommend that the optimisation of statistical methods for the estimation of terminal model reactivity ratios should not be subjected to intense study as an incorrect model is being applied to the experimental data. The conclusion that penultimate unit effects are widespread in free-radical copolymerisation also undermines the theoretical basis for the *Q*–*e* or Patterns schemes as these are based on the (incorrect) terminal model and thus neglect contributions from penultimate unit effects.

However, the adoption of the more physically realistic explicit penultimate model may not offer a substantive solution to the above problem. For, even in the two-parameter fits of the terminal model to composition data, or of the implicit penultimate model (with fixed monomer reactivity ratios) to propagation rate coefficients, the uncertainties in the fitted model parameters are large. Given this, it is clear that the *six* reactivity ratios estimated when fitting the explicit penultimate model to the data are likely to be indeterminate. Indeed, it has recently been shown that, under the explicit penultimate model, multiple sets of monomer reactivity ratios can describe with reasonable accuracy the composition data from styrene with methyl methacrylate copolymerisations [107]. It is important to note that this does not mean that these parameters are superfluous—merely that they should not be estimated by fitting models to data. Instead, these parameters should be measured directly via, for example, experimental or theoretical studies of small-radical models of the various types of the propagation reactions.

In conclusion, the present work indicates that the various reactivity ratios that have been estimated from copolymerisation data using the terminal or implicit penultimate models are likely to convey only limited physical meaning. Provided these parameters are only used to reproduce the data to which they have been fitted (and assuming of course that the model is able to provide a reasonable fit to the data), this is not a problem—although this job could be performed equally well using any third order polynomial with *A*, *B*, *C* and *D* as constants. However, such parameters are not suitable for making independent predictions, or for quantitative studies of radical reactivity. Unfortunately, the parameters estimated by fitting the explicit penultimate model to the data are also likely to convey only limited physical meaning—owing to the enormous uncertainty in their point estimates—and thus the further development of direct means of measuring these parameters is important.

Acknowledgements

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Appendix A. Radical stabilisation model derivation

Assuming that the Evans—Polanyi Rule holds, if the penultimate unit affects radical stability, this results in an implicit PUE in the barrier. This can be shown as follows.

An implicit PUE occurs if

$$r_i\left(=\frac{k_{iii}}{k_{iij}}\right)=r'_i\left(=\frac{k_{jii}}{k_{jij}}\right)\text{ but }s_i\left(=\frac{k_{jii}}{k_{iii}}\right)\neq 1$$

For PUEs in the reaction barrier this amounts to the following:

$$E_{iij}-E_{iii}=E_{jij}-E_{jii}\text{ but }E_{iii}-E_{jii}\neq 0$$

Consider the following propagation step:

$$RM_aM_b\cdot+M_c\overset{(E_{abc})}{\rightarrow}RM_aM_bM_c\cdot$$

The enthalpy of this reaction could be written as:

$$-\Delta H_{abc}=-\Delta H_{\mathrm{p}_0}+U_{bc}-(U_{ab}+U_c) \tag{A1}$$

where ΔH_{p_0} is a constant representing the enthalpy in the absence of substituent effects, and U_{c}, U_{bc}, and U_{ab} are the substituent effects on the enthalpy arising from substituents in the monomer, and product and reactant radicals, respectively. Note $U_{abc} \equiv U_{bc}$ assuming there are no ante—PUEs Under the Evans–Polanyi rule, the barrier and enthalpy are related as follows:

$$E_{abc} = E_{\mathrm{p}_0} - \alpha(\Delta H_{abc}) \qquad \text{(where } E_{\mathrm{p}_0} \text{ and } \alpha \text{ are constant)} \tag{A2}$$

Substituting Eq. (A1) into Eq. (A2):

$$E_{abc} = E_{\mathrm{p}_0} + \alpha(-\Delta H_{\mathrm{p}_0} + U_{bc} - (U_{ab} + U_c)) = \text{const} + \alpha(U_{bc} - U_{ab} - U_c) \tag{A3}$$

Thus, using Eq. (A3):

$$E_{iij} = \text{const} + \alpha(U_{ij} - U_{ii} - U_j) \tag{A4}$$

$$E_{iii} = \text{const} + \alpha(U_{ii} - U_{ii} - U_i) \tag{A5}$$

$$\therefore E_{iij} - E_{iii} = \alpha(U_{ij} - U_{ii} + U_i - U_j) \tag{A6}$$

$$E_{jij} = \text{const} + \alpha(U_{ij} - U_{ji} - U_j) \tag{A7}$$

$$E_{jii} = \text{const} + \alpha(U_{ii} - U_{ji} - U_i) \tag{A8}$$

$$\therefore E_{jij} - E_{jii} = \alpha(U_{ij} - U_{ii} + U_i - U_j) \tag{A9}$$

Thus, from Eqs. (A6) and (A9) we have

$$E_{iij} - E_{iii} = E_{jij} - E_{jii} \tag{A10}$$

Also using Eq. (A3):

$$E_{jii} = \text{const} + \alpha(U_{ii} - U_{ji} - U_i) \tag{A11}$$

$$E_{iii} = \text{const} + \alpha(U_{ii} - U_{ii} - U_i) \tag{A12}$$

$$\therefore E_{jii} - E_{iii} = \alpha(U_{ii} - U_{ji}) \neq 0 \tag{A13}$$

for, as there is a PUE on radical stability, $U_{ii} \neq U_{ji}$). Thus from Eq. (A13) there is a PUE in the barrier, and from Eq. (A10) this PUE is implicit.

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