Penultimate Unit Effect in Free-Radical Copolymerization

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ABSTRACT: Based upon new insights into the dynamics of propagation reactions, a theoretical justification of the penultimate model in free-radical copolymerization kinetics is proposed. It is suggested that the penultimate unit effect may contain a large steric contribution (a different penultimate unit may affect the frequency factor for propagation by a factor typically between 1 and 10) and that the effect on activation energies is generally small. This implies that the stabilization energy model, where only differences in activation energies play a significant role, is valid only under unusual circumstances. Furthermore, a possible explanation is given for the occurrence of both the implicit and explicit penultimate unit effects. It is shown that mainly systems in which there is a large difference in the sizes of the substituents of both monomers are expected to exhibit an explicit penultimate unit effect. Finally, it is shown that neither a purely enthalpic effect, nor the steric effect proposed here, provides an adequate explanation why, experimentally, mainly radical reactivity ratios less than unity are found.

1. Introduction

The most contentious issue in free-radical copolymerization kinetics is the so-called penultimate unit effect. In most copolymerizations, the terminal model adequately describes the instantaneous copolymer composition and sequence distributions, but in certain systems, such as that of acrylonitrile and styrene,[1] these properties cannot be explained in terms of the terminal model.[2] Furthermore, propagation rate coefficients as a function of monomer feed composition, independently obtained with different experimental techniques, generally deviate significantly from the predictions of the terminal model.[3−8] Detailed studies illustrate that these characteristics of copolymerization are adequately modeled by a kinetic scheme which allows for the nature of the penultimate unit to be taken into account when considering the propagation of each radical.[1] Likewise, the observation that ESR signals of radicals depend on the nature of the penultimate unit[9] lends support to the supposition that the neighboring unit can significantly influence the radical. However, this does not necessarily imply that there should be a difference in reactivity of the radical that can be attributed to the penultimate unit. As such, other models are still being proposed and considered in an effort to explain systems that display deviations from the predictions of the terminal model.

In what follows, a new theoretical understanding[10] is employed to show that deviations from terminal kinetics can be attributed to the penultimate unit and that the origin of the deviations may also lie in steric (entropic) effects and not solely in electronic (enthalpic) effects, as proposed in the literature.[7] Highlighted first are the most important aspects of the terminal and penultimate models, together with a brief discussion the stabilization energy model,[6] which is the current theoretical justification of the penultimate model. Second, the assumptions underlying the stabilization energy model, which is solely based upon electronic arguments, will be discussed, followed by a separate discussion of the electronic and steric contributions to the penultimate unit effect. It will be shown that the steric effects are generally equally, if not more, important as the electronic effects. Taking these factors into account, the penultimate model is then analyzed and a possible alternative explanation for the implicit and explicit penultimate unit effects[7] is proposed. The final section of this paper consists of some case studies where we apply the proposed model in order to explain the behavior of some typical copolymerization systems.

(i) Terminal Kinetics. In the terminal model for copolymerization, four different propagation steps are described, in which the reactivity of the radical is solely determined by the terminal unit:[2]

$$\sim M_i^\bullet + M_i \xrightarrow{k_{ii}} \sim M_iM_i^\bullet \tag{1a}$$

$$\sim M_i^\bullet + M_j \xrightarrow{k_{ij}} \sim M_iM_j^\bullet \tag{1b}$$

$$\sim M_j^\bullet + M_i \xrightarrow{k_{ji}} \sim M_jM_i^\bullet \tag{1c}$$

$$\sim M_j^\bullet + M_j \xrightarrow{k_{jj}} \sim M_jM_j^\bullet \tag{1d}$$

Within the terminal model, the mole fraction of monomer i in the instantaneously formed copolymer, F_i, can be expressed as a function of the mole fraction of monomer i in the feed, f_i:

$$F_i = \frac{r_if_i^2 + f_if_j}{r_if_i^2 + 2f_if_j + r_jf_j^2} \tag{2}$$

where r_i and r_j are the monomer reactivity ratios given by

$$r_i = k_{ii}/k_{ij} \tag{3a}$$

$$r_j = k_{jj}/k_{ji} \tag{3b}$$

The expression for the average propagation rate coefficient, $\langle k_p\rangle$, is given by

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$$\langle k_p \rangle = \frac{r_i f_i^2 + 2 f_i f_j + r_j f_j^2}{\dfrac{r_i f_i}{k_{ii}} + \dfrac{r_j f_j}{k_{jj}}} \tag{4}$$

From eqs 2 and 4 it can be seen that both the instantaneous copolymer composition and the average propagation rate coefficient are expressed in terms of the monomer reactivity ratios. These ratios express the relative reactivity of a monomer toward a certain radical and they have been used in the past to develop schemes for the prediction of rate coefficients for propagation and chain transfer. Such schemes are based upon the Hammett equation,[11] in which the intrinsic reactivity of a molecule in a certain type of reaction is directly related to the electronic properties of the substituent. An early, and perhaps still the most popular, version of these schemes is the $Q-e$ scheme proposed by Alfrey and Price,[12] where the reactivities of the radicals and monomers are expressed in terms of the parameters Q and e. A significant improvement to the $Q-e$ scheme was made by Bamford and co-workers with their "patterns" treatment.[13] In this treatment, the following relationship was derived for the reaction rate coefficient, k, of a propagation or transfer reaction of a radical with a substrate:

$$\log k = \log k_{\mathrm{tr,T}} + \alpha\sigma + \beta \tag{5}$$

where $k_{\mathrm{tr,T}}$ is the rate coefficient for the transfer reaction with toluene (which should be virtually free of any polar substituent effects and is therefore a suitable reference for the general radical reactivity), α and β are constants for a given substrate (i.e., a monomer or chain transfer agent), and σ is the Hammett parameter for the substituent at the radical carbon center. Hammett parameters provide a quantitative measure for the electronic substituent effect, and the values for several different substituents (including the substituents in common vinyl monomers) are listed in Table 1. Both the $Q-e$ scheme and the "Patterns" treatment yield reasonably good results for monomer reactivity ratios, with the latter treatment having a sounder theoretical basis. The "Patterns" treatment and the σ values listed in Table 1 will be used in section 2(iii) for the discussion of electronic penultimate unit effects.

(ii) Nonterminal Behavior. It has been found that generally the terminal model is adequate to describe the instantaneous copolymer composition and sequence distributions[3] and that it has failed in only a small number of cases, such as the styrene/acrylonitrile system.[1] This, however, is not the case for the overall rate of propagation, which, in general, shows deviations from the predictions of the terminal model using monomer reactivity ratios obtained from composition data.[3] To give one of several examples, Maxwell et al.[8] showed that in order to simultaneously fit the copolymer composition and rate data in the styrene/methyl methacrylate system, only one extra adjustable parameter needed to be introduced into the terminal model in order to give an adequate fit, which explains the apparent success of all the proposed models. In this paper, we will confine ourselves to the penultimate model, as originally formulated by Merz et al.[14] and used by Fukuda and co-workers to explain the deviations from the terminal model in the styrene/methyl methacrylate system.[4,6,7] This model, which is one of the simplest in its formulation, adequately describes, simultaneously, both the copolymer composition and the rate of propagation. Also, recent work on the fundamental aspects that govern the propagation rate coefficient[10] suggests that the penultimate unit may significantly affect the propagation event, hence justifying the use of the penultimate model.

Table 1. Hammett σ Functions for Several Common Substituents in Vinyl Monomers[a]

substituent	σ	substituent	σ
CN[b]	+0.71	F[b]	+0.15
CHO	+0.47	Ph	+0.05
COOR[c]	+0.44	H[b]	+0.00
$CONH_2$	+0.31	$CH{=}CH_2$	−0.08
$OCOCH_3$	+0.31	NH_2[b]	−0.30

[a] The σ functions for para substitution were taken from ref 11b. [b] Substituents used in the ab initio molecular orbital calculations in ref 28. [c] R = H or an alkyl group.

In the penultimate model, the reactivity of a propagating radical is determined not only by the terminal unit but also by the penultimate unit. This leads to eight different propagation steps and evaluation of the kinetic equations leads to six different reactivity ratios (three per monomer), given by

$$r_i' = k_{iii}/k_{iij} \tag{6}$$

$$r_i'' = k_{jii}/k_{jij} \tag{7}$$

$$s_i = k_{jii}/k_{iii} \tag{8}$$

where a propagation rate coefficient k_{xyz} ($x,y,z = i$ or j) refers to the addition of monomer z to polymeric radical y, with x as penultimate unit in the chain. Examination of eqs 3 and 6−8 in more detail shows that r_i, r_i', and r_i'' are defined with respect to a common radical and s_i is defined with respect to a common monomer. For convenience we adopt the nomenclature proposed by Fukuda[3] and call r and s the monomer and radical reactivity ratios, respectively.

As in the terminal model, the instantaneous copolymer composition in the penultimate model is only determined by the monomer reactivity ratios:

$$F_i = \frac{\bar{r}_i f_i^2 + f_i f_j}{\bar{r}_i f_i^2 + 2 f_i f_j + \bar{r}_j f_j^2} \tag{9}$$

where

$$\bar{r}_i = \frac{r_i''(r_i' f_i + f_j)}{r_i'' f_i + f_j} \tag{10}$$

From eq 10, it can be seen that if $r_i' = r_i''$, eq 9 reduces to eq 2, i.e., the terminal model expression.

The main difference between the terminal and penultimate models lies in the introduction of the radical reactivity ratios in the expression for the overall propagation rate coefficient in the penultimate model:

$$\langle k_p \rangle = \frac{\bar{r}_i f_i^2 + 2 f_i f_j + \bar{r}_j f_j^2}{\dfrac{\bar{r}_i f_i}{\bar{k}_{ii}} + \dfrac{\bar{r}_j f_j}{\bar{k}_{jj}}} \tag{11}$$

where

$$\bar{k}_{ii} = \frac{k_{iii}(r_i' f_i + f_j)}{r_i' f_i + f_j/s_i} \tag{12}$$

From eq 12, it can be seen that in order to reduce the penultimate model expression for the average propagation rate coefficient to the terminal model expression (i.e., eq 4), not only the requirement $r_i' = r_i''$ needs to be satisfied but also the requirement $s_i = 1$ needs to be satisfied. Although introducing r_i' and r_i'' will result in a better overall fit, the better performance of the penultimate model in the simultaneous fitting of experimental composition and rate data effectively lies in the introduction of the two radical reactivity ratios in the average propagation rate coefficient.

(iii) Stabilization Energy Model. The stabilization energy model was the first attempt of a theoretical justification of the penultimate unit effect. This was based solely upon stabilization energy effects, i.e., on enthalpic and not steric effects.[6] We will briefly summarize and discuss the assumptions that form the foundation of this model:

(1) The Evans−Polanyi rule[15] is used to obtain a relationship between the activation energy, E_{ijm}, and the reaction enthalpy, ΔH_{ijm} for the addition reaction of monomer *m* to a polymeric radical with penultimate unit *i* and terminal unit *j*:

$$E_{ijm} = (E_{ijm})_0 - \rho(-\Delta H_{ijm}) \qquad (13)$$

where $(E_{ijm})_0$ and ρ are constants. This relationship seems to be applicable for the addition of $CH_3^{\bullet}$, $CH_2OH^{\bullet}$, and $C(CH_3)_3^{\bullet}$ radicals to a series of substituted ethylenes, with ρ values of −0.42, −0.56, and −0.50, respectively.[16] However, the relationship completely breaks down for the addition of $CH_2CN^{\bullet}$ radical to the same range of substituted ethylenes.[16] Hence, we may conclude that if we consider the additions of the *same radical* to a range of different monomers, the Evans−Polanyi rule is only applicable in specific cases.

In the case of the penultimate unit model, the additions of different radicals to the same monomer should be examined as well. Analysis of the results reported by Wong et al.[16] for the above-mentioned radical additions with respect to the *same monomer* clearly shows that in none of the reported cases a linear relationship between the barrier and reaction enthalpy can be obtained. Hence, in general, it may be concluded that analyses in terms of the Evans−Polanyi rule will at best only be qualitatively useful in very specific cases.

(2) The enthalpy of reaction is then expressed as a function of the stabilizing effects of the different substituents in the different monomer units of concern in this reaction:[17]

$$-\Delta H_{ijm} = -(\Delta H_p)_0 + U_{jm} - (U_{ij} + U_m) \qquad (14)$$

where $(\Delta H_p)_0$ is the reaction enthalpy for a propagation reaction without any substituent effects (i.e., the homopropagation of ethylene), U_{jm} is the stabilization energy of the product radical, U_{ij} is the stabilization energy of the reactant radical, and U_m is the stabilization energy of the monomer. Substitution of eq 14 into eq 13 yields a very convenient expression for the activation energy in which the substituent effects are explicitly taken into account.

(3) Finally, all constants and frequency factors are neglected and the penultimate propagation rate coefficients can then be written as[6]

$$k_{ijm} \sim \exp[\rho(U_{jm} - U_{ij} - U_m)] \qquad (15)$$

This proportionality is correct within this theoretical framework, but in Fukuda's elegant derivation that follows in order to obtain the well-known relationship of eq 16, the proportionality changes into an equality, which, as will be clear from the new theory presented in this paper, is not correct for the general case. The final and most important result of the stabilization energy model is the relationship between the monomer and radical reactivity ratios, which has been used extensively to analyze copolymerization rate data:[18]

$$r_1 r_2 = s_1 s_2 \qquad (16)$$

It should be noted that the validity of this relationship is limited to those cases in which enthalpic effects are indeed the major contributors to the penultimate unit effect, but as will be shown, it is likely that, in general, steric effects in the frequency factor are likely to be at least equally important. Since the frequency factors have been ignored in order to obtain eq 16 and the validity of the Evans−Polanyi rule in the cases of interest is at least questionable, it may be concluded that the physical meaning of eq 16 is very limited.

This conclusion is supported by the literature, where it is observed that agreement between experiment and eq 16 is not as good as may be hoped for.[3,19]

Recently, a more general version of the stabilization energy model was proposed by Fukuda et al.,[20] now incorporating terms accounting for penultimate unit effects in the frequency factors. Although this was done by factorizing the contributions to the frequency factor arising from the monomer and the radical (i.e., a very crude approximation, considering the fact that the internal modes in the transition state of the reaction arise from a specific interplay between both reactants; see below),[10] the physical meaning of the model has significantly improved.

2. Model Assumptions

(i) Previous Model Assumptions. In principle, the penultimate unit may affect the radical reactivity by electronic or steric effects. It is most likely that both effects play a role, but during the last decade, the stress has been on the electronic effects, as used in the stabilization energy model. A steric origin for the penultimate unit effect has been suggested by Bamford and Basahel,[21] based upon the observation that, when methyl methacrylate was the penultimate unit, the transfer reaction of styrene-terminated radicals with CBr_4 was significantly slower than the reactions in which styrene and methyl acrylate were the penultimate units. Although this point of view was not contested for this particular system, Fukuda et al.[7] argued against this explanation being applicable to most cases of propagation reactions. For the case of the implicit penultimate unit effect, where a penultimate unit effect is only observed in the rate of polymerization and not in the copolymer composition (i.e., $r_i' = r_i''$ and $s_i \neq 1$), it was suggested[7] that the origin of the penultimate unit effect lies in electronic factors. In the case of the explicit penultimate unit effect, in which case both the composition and sequence distributions cannot be adequately explained with the terminal model (i.e., $r_i' \neq r_i''$ and $s_i \neq 1$), it was argued that the origin may be more complex and may also lie in specific steric interactions.[7]

In the remainder of this section, we will consider that a steric interaction may be, at least, equally important in the penultimate unit effect as the electronic interac-

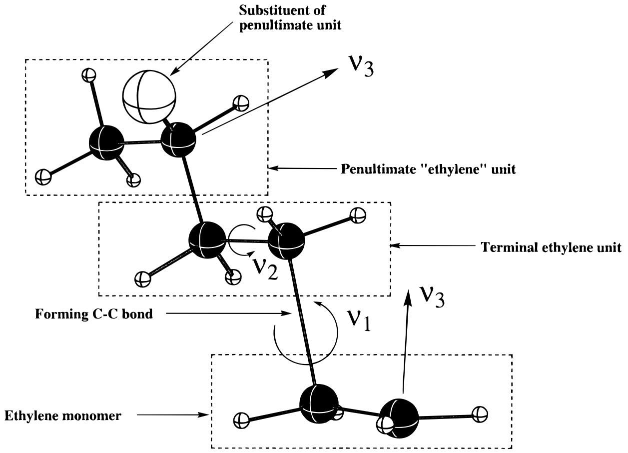


Figure 1. Schematic representation of the transition state for the addition reaction of a γ-substituted butyl radical to ethylene and the three most important internal motions, i.e., ν_1, ν_2, and ν_3, that will be affected most by differences in the substituents of the penultimate unit.

tions and that both the implicit and explicit penultimate unit effects have the same physical origin.

(ii) Steric Penultimate Unit Effects. In a previous paper,[10] the factors that govern propagation rate coefficients have been studied using high levels of ab initio molecular orbital and transition state theories. It was shown that a very important contribution (i.e., the one that will cause the main difference between different monomers) to the Arrhenius frequency factor is made by certain hindered internal motions in the transition state of the reaction. In Figure 1, these motions (i.e., ν_1, ν_2, and ν_3) are schematically shown for the transition state of a butyl radical (i.e., an ethylene dimer) propagatively adding ethylene, where one of the hydrogens in the radical is replaced by a larger group in order to indicate the substituent of the penultimate unit. The first motion (ν_1) corresponds to a rotation of the adding monomer unit about the forming C−C bond, the second motion (ν_2) corresponds to a rotation of the monomer + terminal carbon unit about the terminal C−C bond in the radical moiety, and the third motion (ν_3) corresponds to a simultaneous bending of the two reacting moieties. As can be seen, all three motions may be affected by the substituent in the penultimate unit, depending on its size and orientation within the radical (e.g., the γ-carbon in the radical may also be in a gauche conformation with the adding ethylene unit, instead of the depicted trans conformation). The size of the substituent determines the internal barriers (i.e., degree of hindrance) to these motions; the greater the hindrance, the smaller the Arrhenius frequency factor.[10]

A quantification of the above effect can be obtained by calculating the partition functions[22] of the hindered internal motions in the transition state, because the frequency factor is, to a first approximation, proportional to these partition functions, which in turn depend upon the potential energy function of these modes.[23] In Figure 2, an example is given of the effect of the rotational barrier, for a threefold cosine potential, on the partition function of a 1-dimensional rotor with a reduced moment of inertia of 10 amu bohr^2, which is comparable to the moment of inertia of ν_1 and ν_2 for the situation depicted in Figure 1. As can be seen from Figure 2, increasing the barrier to rotation decreases the rotational partition function and hence decreases the frequency factor.

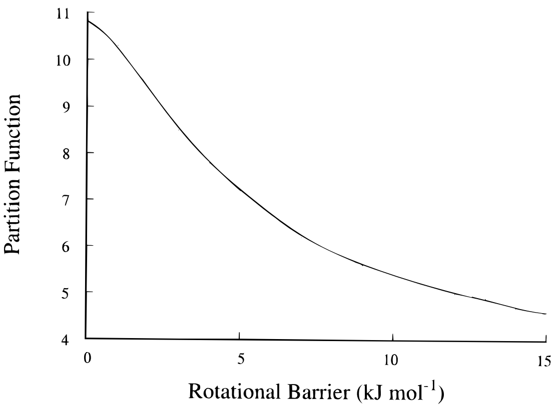


Figure 2. Calculated partition function (323 K) of a one-dimensional rotor, for which the potential is given by $V(\phi) = {}^1/_2V(1 - \cos 3\phi)$, where V is the rotational barrier, i.e., the variable of the x-axis, and ϕ is the angle of rotation (0−360°). The reduced moment of inertia of the rotor is 10 amu bohr^2.

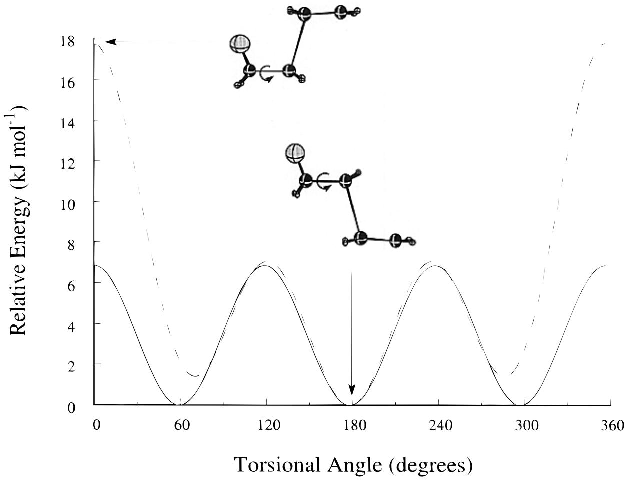


Figure 3. Calculated rotational potential (UMP2/6-31G*)[10] as a function of the rotational angle for the rotation about the terminal C−C bond in the radical moiety of the transition state of alkyl radical additions to ethylene. The gray "atom" denotes the two different substituents that were used: (—) H, i.e., the addition of an ethyl radical; (− − −) CH_3, i.e., the addition of a propyl radical. A torsional angle of 0° corresponds to an eclipsed conformation of the substituent and the forming C−C bond; an angle of 180° corresponds to an anti conformation.

A more concrete example of a steric substituent effect is shown in Figure 3, in which the rotational potentials are plotted for ν_2 (see Figure 1) in the cases of the addition of ethylene to, respectively, an ethyl radical and a propyl radical. This is a good example of a situation in which a hydrogen atom (i.e., from the ethyl radical) is replaced by a methyl group (i.e., from the propyl radical), both represented by the larger gray "atom" in Figure 3. It can be seen that upon rotation, starting from the minimum energy structure at 180°, the first maxima (i.e., where the rotating group is "eclipsed" with a hydrogen atom) are similar, but rotating more toward the substituent results, in the case of the propyl radical addition, in a higher energy than in the case of the ethyl radical addition. The energy of the situation in which the rotating group is eclipsed with the substituent leads to a barrier, which, in the case of a methyl substituent, is almost 3 times that for the case in which hydrogen is the substituent. This change in rotational potential upon exchanging the hydrogen atom by a methyl group reduces the calculated partition function by a factor of approximately 2. Although this is an example of only two small radicals adding to ethylene, the effect shown is a general one; i.e., it will also occur for longer (polymeric) radicals.[24] The given example may serve as a lower bound of the observed effect, as it is very likely that replacing a small substituent by a much larger substituent will result in a larger change than the one observed when replacing a hydrogen atom by a methyl group.

Direct evidence for these steric effects on the frequency factor of (small) radical addition reactions was found by Szwarc and co-workers.[25] It was found that for the addition of $CF_3^\bullet$ radicals to substituted ethylenes, the frequency factor decreases by a factor of approximately 5 when replacing the hydrogen atoms in ethylene by chlorine atoms or methyl groups. This effect was also attributed to a more hindered rotation in the transition state of the reaction.[25]

It is evident from the above that replacing the subsituent of the penultimate unit by another substituent can change the hindrance to the important motions as shown in Figure 1. Hence, we may conclude in general that

$$A_{iim} \neq A_{jim} \tag{17}$$

where A_{xym} (x, y, $m = i$ or j) is the frequency factor of the propagation rate coefficient of the addition of a monomer m to a radical with terminal unit y and penultimate unit x. This nonequality will be greater if the difference in size and shape of the two comonomers is greater and will be negligible if the differences are small. Since the penultimate unit may affect all three important motions shown in Figure 1, and the effect is a multiplicative one,[10,23b] the ratio A_{iim}/A_{jim} will typically have a value between 0.1 and 10.

(iii) Electronic Penultimate Unit Effects. It has been argued[6] that the main origin of the penultimate unit effect is an electronic effect, leading to different activation energies. Although an electronic effect must be present, we will show in the remainder of this section that it is conceivable that this effect is small, because the different substituents are two carbon atoms removed from the reaction site, and in most of the common polymeric radicals there is no other means for the transmission of substituent effects but through space or through the σ-electron skeleton. If this argument is valid, the following is true:

$$E_{iim} \approx E_{jim} \tag{18}$$

where E_{xym} (x, y, $m = i$ or j) is the activation energy of the propagation rate coefficient of the addition of a monomer m to a radical with terminal unit y and penultimate unit x.

This assumption is supported by a recent experimental study reported on the addition reactions of $CH_3CH_2CH_2CH_2CH_2^\bullet$ and $CF_3CF_2CF_2CF_2CH_2CH_2^\bullet$ radicals to styrene, α-methylstyrene, and 2,3,4,5,6-pentafluorostyrene.[26] It was found that the ratios of the addition rate coefficients of the unsubstituted alkyl radical and the fluorinated alkyl radical to the three different styrenes are about 0.92, 0.90, and 1.35, respectively. Since it is not likely that there is a large difference in the frequency factors of the reactions of the two radicals with one substrate,[10,22b] the relatively constant ratios can only be explained by relatively constant activation energies.

The assumption given by eq 18 is furthermore supported by high-level ab initio molecular orbital calculations[27] performed on the addition of γ-substituted propyl radicals (i.e., the smallest radical with a "penultimate" unit) to ethylene:[28]

$$X{-}CH_2CH_2CH_2^\bullet + CH_2{=}CH_2 \rightarrow X{-}(CH_2)_3CH_2CH_2^\bullet \tag{19}$$

where X is one of the following substituent groups: NH_2, H, F, or CN. These calculations indicate that the largest difference between the reaction barriers obtained for the several different radicals is only 2 kJ mol^{-1}, which can lead to a change in the rate coefficient by a factor of 2 at 298 K, but even in this case it is not possible to obtain values for s_i that are smaller than 0.5, as are reported in the literature.[3,4,19,29,30] This suggests that (steric) effects in the frequency factor must play a significant role and should not be ignored. In cases where the effect on the activation energy is very small, the steric effect must account for the major difference in the nonterminal behavior of the reactivity ratios.

A criticism of the quantum calculations mentioned above[28] could be that only very small substituents were used and not substituents such as phenyl or acrylic ester groups, typical of vinyl monomers. However, it is likely that the electronic effects of the range of substituents used in the calculations will cover nearly all the electronic substituent effects that are exhibited in a wide range of common vinyl monomers. This is indicated by the Hammett parameters for these subsituents (see Table 1, where it can be seen, e.g., that the σ-values for most monomer substituents fall between the values for CN and NH_2, which are used in the above-mentioned calculations). Since the Hammett σ-values are a quantitative measure of the electronic substituent effect (see eq 5), similar σ-values for the substituents in the quantum calculations and the substituents in the polymeric radicals should lead to similar behavior of the radicals toward the same substrate. This justifies the comparison of the quantum calculations with common copolymerization systems.

Since the "Patterns" treatment (eq 5) basically only considers the terminal unit, it is important to investigate whether a similar treatment is applicable to the electronic substituent effect of the penultimate unit. It is an established fact that the electronic substituent effect decreases upon increasing the distance between the reaction site and a substituent in the molecule.[31] Generally, two possibilities for the transmission of substituent effects exist: an electrostatic effect through space, i.e., the field effect, and a transmission through the bonds of the molecule. The relative importance of these two effects has been part of a longstanding discussion in physical organic chemistry, but, for simplicity, we will use the through-bond model, which seems to describe adequately the effects in a large number of test cases.[31c] Equation 13 shows the relationship between the "effective" Hammett parameter, σ_{eff}, for a substituent which is n bonds removed from the reaction site:[31c,32]

$$\sigma_{\text{eff}} = \sigma\epsilon^n \tag{20}$$

where ϵ is the transmission factor, which was found to be approximately 0.36.[31c] According to eq 20, the effective Hammett parameter of the penultimate unit "felt" at the reaction site is directly proportional to and smaller than its orginal value. This implies that the σ-values listed in Table 1 are a direct measure for the electronic substituent effect of the penultimate unit.

Hence, we may conclude that most electronic substituent effects should be encompassed by the chosen range of substituents in the quantum calculations of ref 28.

(iv) Summary of Model Assumptions. In this section we have shown that different substituents in the penultimate unit may have significantly different effects on the hindrances of the important internal motions in the transition state of the reactions and that dependent on this difference, the Arrhenius frequency factor may be affected by a factor typically between 1 and 10. We have also shown that it is unlikely that different substituents will affect the activation energy by more than 2 kJ mol^{-1}, provided that there are no specific interactions between the substituents of the terminal and the penultimate units (see section 4 of this paper). These results indicate that the penultimate unit effect in the activation energy is relatively small as compared with the penultimate unit effect in the frequency factor and should not be ignored for most comonomer systems.

3. Analysis of the Penultimate Unit Model

(i) Penultimate Unit Effects in Monomer Reactivity Ratios. The observation that the instantaneous copolymer composition of most common copolymerizations can be adequately fitted by the terminal model suggests the following:

$$r_i' \approx r_i'' \tag{21}$$

which in turn implies

$$r_i' \approx r_i'' \approx r_i \tag{22}$$

In terms of the Arrhenius equation, this leads to

$$\frac{A_{iii}\exp\left(-\frac{E_{iii}}{RT}\right)}{A_{iij}\exp\left(-\frac{E_{iij}}{RT}\right)} \approx \frac{A_{jii}\exp\left(-\frac{E_{jii}}{RT}\right)}{A_{jij}\exp\left(-\frac{E_{jij}}{RT}\right)} \approx \frac{A_{ii}\exp\left(-\frac{E_{ii}}{RT}\right)}{A_{ij}\exp\left(-\frac{E_{ij}}{RT}\right)} \tag{23}$$

This result indicates the absence of an explicit penultimate unit effect,[7] and can be easily explained by the model proposed in this paper, as follows:

Firstly, the main energetics of the reaction are determined by the nature of the radical terminus and the adding monomer. Electronic effects by the penultimate unit, i.e., by a substituent on the γ-carbon atom of the radical chain, are likely to be very small, as discussed in the previous section. As such, if two possible penultimate units are of the same size so that there is no significant difference in "steric" contribution to the activation energy,[33] the following is very likely to be true:

$$E_{iii} - E_{iij} \approx E_{jii} - E_{jij} \approx E_{ii} - E_{ij} \tag{24}$$

From eq 23, it now follows that

$$\frac{A_{iii}}{A_{iij}} \approx \frac{A_{jii}}{A_{jij}} \approx \frac{A_{ii}}{A_{ij}} \tag{25}$$

This result can be explained if we consider the fact that hindered internal motions in the transition state govern the frequency factors (see section 2(ii), where it was shown that in general the penultimate unit will affect the frequency factor). However, in the case of eq 25, where we consider *ratios* of frequency factors, the effect of the hindrance of the penultimate unit may cancel if the two comonomers are not too dissimilar in size and shape, since both the numerator and denominator involve the same penultimate unit. However, if the two comonomers are very different in size, the effect will be greater and will not cancel, in which case we have the situation of the explicit penultimate unit effect.[7]

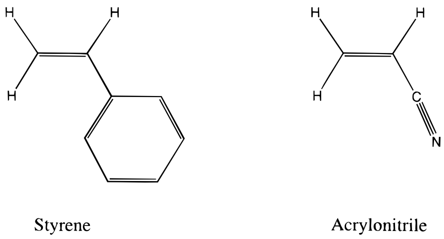
We will now attempt to explain the result of an implicit penultimate unit effect only in enthalpic terms. It is a well-known fact that nucleophilic radicals react more easily with electrophilic monomers than nucleophilic monomers and vice versa.[34] Let us now consider a radical with terminal unit i. If penultimate unit i has an (enthalpic) rate-enhancing effect on the addition of monomer j, then $k_{iij} > k_{jij}$. Additionally, the effect of the same penultimate unit i on the addition of monomer i will be to decrease the rate, or in a best case scenario, it will not affect the rate: $k_{iii} \leq k_{jii}$ (e.g., if i is an electrophilic penultimate unit, then this penultimate unit is not likely to increase the rate of the addition of an electrophilic monomer i, as compared with the same addition in the absence of penultimate unit effects). In terms of monomer reactivity ratios, this implies that (if all values were initially equal, for simplicity)

$$r_i'' > r_i' \qquad \left(\text{or } \frac{k_{jii}}{k_{jij}} > \frac{k_{iii}}{k_{iij}}\right) \tag{26}$$

The result of eq 26 implies that an enthalpic penultimate unit effect may only cancel in the monomer reactivity ratios if the penultimate unit does not affect the activation energy to a great extent. However, as outlined before, the enthalpic penultimate unit effect is even smaller for the radical reactivity ratios than for the monomer reactivity ratios. This is in disagreement with the observation that the penultimate unit effects (in the case of an implicit penultimate unit effect) are generally larger in s_i than r_i. Hence, the use of only enthalpic arguments to explain the observed implicit penultimate unit effect leads to inconsistent results.

Considering the inconsistencies in the use of a purely enthalpic argument to explain the implicit penultimate unit effect, it could be argued that the experimental data are simply too insensitive to distinguish between the penultimate and terminal model, and hence an enthalpic argument cannot be ruled out on the basis of existing data. Indeed, Moad et al.[35] showed that differences between r_i' and r_i'' of up to a factor of 2 did not show a significant improvement, when fitting styrene/methyl methacrylate composition data to both the penultimate and terminal models. This suggests that the apparent implicit penultimate unit effect may just be the result of insensitive measurements and that there may be a significant enthalpic penultimate unit effect on the monomer reactivity ratios. However, Maxwell et al.[8] showed that penultimate unit effects could not be observed in the triad sequences of styrene/methyl methacrylate, whereas in the system styrene/acrylonitrile a significant penultimate unit effect was observed in the triad sequences.[1] In the latter system, use of the penultimate model resulted in a significantly better fit, yielding an r_i' and r_i'' only differing by factors of 2−3. This latter observation does not support the assertion of Moad et al.[35] that differences between r_i' and r_i'' of a factor of 2−3 are not observed/detected. Therefore, the implicit penultimate unit effect cannot be explained by an enthalpic penultimate unit effect on the monomer reactivity ratios which is not detected by modeling of experimental data.

Chart 1



More importantly, the results of section 2 and this section suggest that the observed implicit penultimate unit effect is not a result of enthalpic effects, and must therefore be due to entropic effects. In this respect, the work by Moad et al.[35] does support our steric explanation of an implicit penultimate unit effect, because the steric effects need only approximately cancel to give an implicit penultimate unit effect. This will be elaborated further upon below.

(ii) Penultimate Unit Effects in Radical Reactivity Ratios. Neither the terminal nor the penultimate model contains radical reactivity ratios in the expressions for the copolymer composition and sequence distribution. However, in contrast to the terminal model, the two radical reactivity ratios do appear in the penultimate model expression for the overall propagation rate coefficient (eq 11). With the use of these two extra parameters, the overall propagation rate coefficient in combination with the copolymer composition can be modeled adequately within the (implicit) penultimate model.[7] This result can be explained by using considerations of the Arrhenius parameters analogous to those developed in section 3(i). The radical reactivity ratio s_i can be expressed as

$$s_i = \frac{A_{jii}\exp\left(-\frac{E_{jii}}{RT}\right)}{A_{iii}\exp\left(-\frac{E_{iii}}{RT}\right)} \tag{27}$$

As before, it is not likely that the activation energies will be greatly affected by the penultimate unit; hence

$$s_i \approx A_{jii}/A_{iii} \tag{28}$$

We now return to the consideration of the hindered internal motions in the transition state for propagation reactions. Both the terminal and monomer units are the same in the denominator and numerator of eq 27, the only difference being the nature of the penultimate unit. Now, the effect of the penultimate unit in the denominator need not cancel with the effect in the numerator, which explains why systems that *do not* show a penultimate unit effect in composition and sequence distributions *can* show a penultimate unit effect in the rate of polymerization, i.e., an implicit penultimate unit effect.

4. Discussion

In the previous section, we analyzed the penultimate model using a new theoretical understanding of the dynamics of propagation reactions. It was shown that steric factors can be very important in determining the extent to which a penultimate unit effect is observed. We deliberately focused on this steric effect and assumed the energetic effects to be comparatively small, which is in accord with the early ideas of Bamford and Basahel[21] but in contrast with the more recent ideas of Fukuda and co-workers.[3,6,7] We have shown that energetic effects do not adequately explain the observed implicit penultimate unit effect and that, using our steric argument, the parameter which is most sensitive to a possible penultimate unit effect is s_i, which is not surprising. If there is a penultimate unit effect in s_i, there will also be a penultimate unit effect on the individual rate coefficients in r_i' and r_i'', but since the *ratios* of rate coefficients with the same penultimate units are being considered, the penultimate unit effect on r_i' and r_i'' may cancel if the two comonomers are of similar size and if there is not a very large effect on the activation energies.

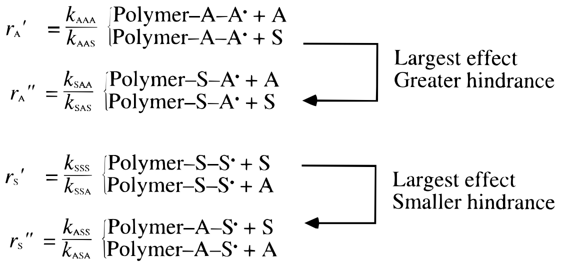
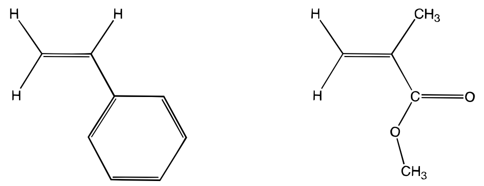


Figure 4. Schematic representation of the reactions involved in the monomer reactivity ratios of the styrene−acrylonitrile copolymerization. Changing the penultimate unit from acrylonitrile (A) to styrene (S) has the largest effect when the attacking monomer is styrene.

(i) Case Studies. In this section, we will discuss in some detail three typical copolymerization examples in the literature: styrene/acrylonitrile,[1] styrene/methyl methacrylate,[4,5] and styrene/*p*-methoxystyrene.[29] The behavior of these systems has previously been explained in terms of electronic effects, which seems to be consistent in view of the σ-values of the different monomers (see Table 1). *In what follows, we discuss the behavior of these systems, using only our alternative steric arguments.* It will be shown that this also leads to a consistent explanation of all the observed phenomena.

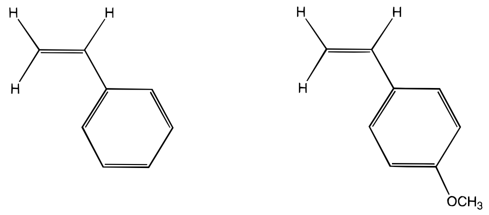
(a) Styrene/Acrylonitrile. The styrene/acrylonitrile copolymerization (see Chart 1) is one of the first and few systems studied that displays an explicit penultimate unit effect and will be seen to be a good illustration of the theory presented in this paper. In this section, we will restrict ourselves to the discussion of the monomer reactivity ratios, and we will discuss the recently reported radical reactivity ratios[20] in section 4(ii) (see below). In Figure 4, the eight reactions involved in the four monomer reactivity ratios of the styrene/acrylonitrile copolymerization are schematically represented. In this figure, we use the abbreviations S and A for styrene and acrylonitrile, respectively. First, we discuss the two monomer reactivity ratios of acrylonitrile, r_A' and r_A''. If we restrict ourselves to the two reactions in which acrylonitrile is the monomer, we may conclude that from a steric point of view, the reaction with styrene in the penultimate unit will be slower. This penultimate unit effect, however, will be relatively small, because acrylonitrile is a relatively small monomer and will therefore not be affected greatly by the penultimate unit (Note: in this discussion we consider only *relative* effects in the reactions). On the other hand, examination of the two reactions involving the styrene monomer shows that changing the small acrylonitrile for the bulky styrene in the penultimate unit will have a more distinct effect than in the case of the acrylonitrile monomer, because the large styrene monomer will "feel" the effect of the penultimate unit more

Chart 2



Styrene Methyl Methacrylate

Chart 3



Styrene *p*-Methoxy Styrene

distinctly than the small acrylonitrile monomer. Hence, we may conclude that for the acrylonitrile monomer reactivity ratios, a styrene penultimate unit will decrease the frequency factor of a styrene addition more than the frequency factor of an acrylonitrile addition, leading to $r_A'' > r_A'$. This was also found in the literature, where r_A'' is reported to be approximately 2−3 times higher than r_A'.[1] A similar examination of the styrene monomer reactivity ratios leads to the conclusion that $r_S'' > r_S'$, which is also in accordance with the literature, where again this difference is a factor of 2−3, indicating that similar factors play a role as in the case of the AN monomer reactivity ratios.[1]

It is important to note that solvent effects play a significant role in this system[1e] and that they should not be ignored in the analyses of the experimental data. However, in the study reported by Klumperman and Kraeger,[1e] the apparent reactivity ratios in different solvents were found to behave as predicted with our steric argument (i.e., $r'' > r'$), and the variation in the apparent reactivity ratios with solvent could be explained in terms of the Bootstrap model.[36]

(b) Styrene/Methyl Methacrylate. For the previously discussed styrene/acrylonitrile system, the large difference in the sizes of the two monomers causes the penultimate unit effect to be visible in the composition and sequence distribution data. If the sizes of the two monomers are very similar, this effect will be much less and it is possible that a penultimate unit effect is observed only in the propagation rate coefficient. This is the case in the styrene/methyl methacrylate system (see Chart 2).[4,5] Discussion of this type of system is not as straightforward as in the case of styrene/acrylonitrile, for here, subtle differences in geometries can be significant in the monomer reactivity ratios (as discussed in section 3 of this paper). Examination of the substituents in both monomers shows that the ester and phenyl groups are of a similar size and that the effect of replacing a methyl methacrylate penultimate unit by a styrene penultimate unit in the case of the monomer reactivity ratios is thus likely to be negligible. This can be explained by the fact that both monomers are fairly large and that the important internal modes are hindered to the same extent in the reactions of concern in the monomer reactivity ratios given by eqs 6 and 7, where the same penultimate unit occurs in the denominator and numerator of the reactivity ratios. Examination of the radical reactivity ratios shows that the monomer and the terminal unit in the two reactions of concern are the same and that the penultimate units are different. Here, the extra methyl group and the greater flexibility of the ester group as compared with the phenyl group may just be important enough to cause a penultimate unit effect, which is indeed reported in the literature.[4,5] The reason that the effect of the extra methyl group is only observed in the radical reactivity ratios and not in the monomer reactivity ratios probably lies in the fact that the other two substituents (i.e., the acrylic ester group in methyl methacrylate and the phenyl group in styrene) are large compared to the methyl group and that this is a hindered system to begin with.

It is expected that a second penultimate methyl substituent in a monomer can cause a significant penultimate unit effect in the monomer reactivity ratios (i.e., $r' \neq r''$) if the first substituents in the two monomers are of similar size to the methyl group, e.g., cyano substituents, and hence cause an explicit penultimate unit effect. A more extensive experimental study on this kind of system is therefore required for a more definite statement.

(c) Styrene/*p*-Methoxystyrene. Finally, if the two monomers are very similar in size, the propagation rate coefficient can be predicted by the terminal model. This is the case for the styrene/*p*-methoxystyrene system (see Chart 3).[29] Here, the extra methoxy group on the phenyl substituent will not contribute significantly to the barriers to rotation and there can only be a very small contribution from the somewhat higher mass of the *p*-methoxyphenyl group.[10] Since the same penultimate unit appears in the denominator and numerator of the monomer reactivity ratios, this very small effect will definitely cancel and no penultimate unit effect will be observed in the copolymer composition. In this particular case, the mass effect is not large enough to cause a significant difference in the frequency factors of the reactions that are involved in the radical reactivity ratios, because the penultimate unit is too far removed from the reaction site and the difference in masses of a phenyl group and a *p*-methoxyphenyl group is too small.[10] Hence, we may conclude that such a copolymerization system will not even show an implicit penultimate unit effect, which is in accordance with the literature.[29]

(d) Case Study Summary. In conclusion, we agree with the statement by Fukuda et al.[3,7] that the implicit penultimate unit effect is a very general phenomenon and that both the explicit penultimate unit effect and the case without any significant penultimate unit effect are reasonably rare phenomena. The occurrence of either of both cases is easier to predict than the occurrence of an implicit penultimate unit effect, and the latter may therefore be expected to be generally present in cases where there is not a great dissimilarity or great similarity between the two comonomers. However, it is not likely that the implicit and explicit penultimate unit effects are caused by different physical phenomena, which is in contrast to what is suggested in the literature.[7] The implicit and explicit penultimate unit effects are caused by the same effects, but in many cases the penultimate unit effect may cancel in the monomer reactivity *ratios* leading to the implicit penultimate unit effect.

(ii) Implications. In the previous sections, we outlined the theoretical foundations for a steric penultimate unit effect and ended with the discussion of some typical copolymerizations. Here, we will discuss some of the implications of the model.

An important result of the model is eq 28, which states that a radical reactivity ratio may be approximated by the ratio of the two frequency factors. This indicates that radical reactivity ratios should be virtually temperature-independent. Even if there is an electronic penultimate unit effect resulting in a difference of 2 kJ mol^{-1} in activation energies (our estimate for the maximum difference in many common copolymerizations), the effect will be less than a 15% change upon increasing the temperature from 0 to 50 °C. The temperature independence of the radical reactivity ratios seems to be in accordance with the literature, although no conclusive evidence exists, considering the large confidence intervals of the radical reactivity ratios.[19a]

The stabilization energy model[6] does *not* seem to be able to explain why few radical reactivity ratios greater than unity have been observed.[20,37] Although it is claimed that a different penultimate unit will stabilize the radical, there is no reason to assume that a different penultimate unit cannot *increase* the reactivity of a radical, which should be the case if one of the monomers has an electron-withdrawing and the other an electron-donating substituent. Recently, Jenkins and O'Driscoll[38] proposed that a particular interaction between the substituents in the penultimate and terminal units may lead to the stabilization of the radical and that absence of these interactions will not lead to any changes in the stability of the radical. In itself, this may be a suitable explanation for some particular systems, but this argument is not likely to be valid for the general case. If, for example, a favorable interaction between the substituents in the homopolymer existed, then replacement by a different penultimate unit will disrupt this stabilizing effect and make the radical more reactive, leading to radical reactivity ratios greater than unity.

This important shortcoming of the stabilization energy model does *not* seem to be overcome by the model proposed in this paper either, although it is likely that the radical reactivity ratios will not greatly exceed unity. The penultimate unit effect will be greatest when the difference in monomer size is large and in this case *one* of the radical reactivity ratios will be greater than unity:

$$s_{\text{big}} = \frac{k_{\text{small big big}}}{k_{\text{big big big}}} \tag{29}$$

where the subscript "big" is used for the larger monomer and the subscript "small" for the smaller monomer, using the same definitions as for eqs 3–5. The smaller penultimate unit in the numerator will decrease the hindrance in the transition state and hence will increase the propagation rate coefficient, leading to $s_{\text{big}} > 1$. This effect will be smaller if the larger molecule is very bulky, in which case the monomer will be shielded from the penultimate unit by the bulky terminal unit and hence will not "feel" its presence; in that case, s will approach 1 from above, as the bulky unit becomes larger.

Using this argument, our prediction for the radical reactivity ratios in the copolymerization of styrene/acrylonitrile would be $s_S > 1$ and $s_{AN} < 1$, which is the opposite of what is reported by Fukuda et al. (i.e., $s_S = 0.74$ and $s_{AN} = 1.65$ in bulk at 40 °C).[20] We cannot think of an obvious explanation for this disagreement, but the fact that a reasonable fit of the data was obtained by using $s_S = s_{AN} = 1$[39] suggests that the optimized radical reactivity ratios may only have a limited physical meaning.

We have shown in this section that both enthalpic and entropic arguments fail to predict one apparently general experimental result, i.e., the observation that few radical reactivity ratios found to date are greater than unity, which should be a much more general phenomenon according to both models. The uncertainties in the experimental data are not large enough to account for the failure of both models, so the question arises: *What is causing this very important discrepancy between theory and experiment?* One possibility is an incorrect description of the actual physical processes that take place. This possibility, however, is very unlikely, because the entropic factors presented here are based upon a rigorous theory (i.e., transition state theory)[23b,40] and this theory has proven its value in many different types of reactions.[41] Also, using enthalpic arguments to describe penultimate unit effects (not to be confused with the stabilization energy model!), as was done previously in this section, are based upon our general understanding of reactivity in organic chemistry. Hence, we may conclude that it is not likely that our microscopic picture of the reaction dynamics is wrong. But, why then do our microscopic models not predict what is observed macroscopically? A possible reason could be that there is one parameter too many to be fitted in the expression for the average propagation rate coefficient, as was realized previously by, e.g., Fukuda et al.[3] and Maxwell et al.[8] This may lead to sets of radical reactivity ratios that might represent an adequate statistical fit to the experimental data, but which do not necessarily need to have a real physical meaning; the large confidence intervals[3] for these parameter sets may be a possible indication for this possibility.

Another, and a very likely, possibility might be that other effects, such as preferential complexations,[1e,3,36,42] need to be taken into account, together with the penultimate unit effects.

In summary, we can state that penultimate unit effects exist, but they may not completely account for the overall effect that is observed macroscopically. Independent experiments need to be designed for the determination of radical reactivity ratios and possible deviations from the predictions of the penultimate model (using these independently obtained radical reactivity ratios) should be explained by other models, which take into account complexation of the radicals or monomers[3,42] or local concentration effects.[3,36] One promising experimental approach would be a similar one to the one taken in end-group studies.[43] In these studies, initiator-derived monomeric radicals are used to initiate a mixture of monomers A and B, yielding the monomer reactivity ratios r_A and r_B. An approach for the present problem might be the use of two radicals with the same terminal unit, but a different penultimate unit; such an approach was taken by Tirrell and co-workers[1b–d] in order to determine r' and r'' for styrene/acrylonitrile.

An important advantage of the new model presented in this paper is that it has, in contrast with current models, some qualitative predictive value with respect to the occurrence of an implicit or explicit penultimate unit effect. Below, we offer some predictions of the model, which can be tested. If the copolymerization of acrylonitrile and acrolein (AC) is considered, then these two monomers have similar sizes and hence should not show an explicit penultimate unit effect. Another system that could be tested is styrene/acrolein. This system resembles styrene/acrylonitrile from a steric point of view, but styrene/methyl acrylate (MA) from an electronic one ($\sigma_{\mathrm{AC}} \approx \sigma_{\mathrm{MA}}$; see Table 1). If our steric argument is valid, then styrene/acrolein should display an explicit penultimate unit effect. Furthermore, systems such as styrene/vinylpyridine should not show a large penultimate unit effect at all, because the comonomers have very similar geometries. However, in systems such as this, solvent effects may play an important role, as the hydrophilic properties of both monomers differ significantly.

5. Conclusions

The first conclusion that can be drawn is that penultimate unit effects exist on a molecular level and they should be invoked *first* in order to explain deviations from the predictions of the terminal model. Possible corrections for solvent effects or complexations[3] should be made after application of the penultimate unit model.

A more important conclusion of this paper is that the penultimate unit effect in most comonomer systems may contain a large steric contribution and not, as has been assumed, solely an enthalpic one. This steric penultimate unit effect can arise if certain internal motions in the transition state are hindered by the substituent in the penultimate unit. If there is a large difference in size between the two comonomers, the penultimate unit effect is likely to be large and it can even be so large that it is observed in the monomer reactivity ratios and give rise to an explicit penultimate unit effect; the implicit and explicit penultimate unit effects have the same origin, but the penultimate unit effect may cancel in the monomer reactivity *ratios* to give an implicit penultimate unit effect.

Furthermore, it was shown that the major result of the stabilization energy model,[6] i.e., the relationship that the product of the monomer reactivity ratios equals the product of the radical reactivity ratios, only has a physical meaning if the penultimate unit effect has mainly an enthalpic origin. Having shown that this will only be the case in very few systems, this relationship should not be seen as a physical reality, but merely as a handy tool in fitting polymerization rate data. The latter suggestion was first realized by Fukuda et al., who showed that the assumption $s_i = s_j = s$ leads to less scatter in the fit results for styrene/methyl methacrylate.[3]

The work in this paper also suggests that systems in which the two comonomers have similar sizes (e.g., styrene/methyl methacrylate) are not likely to display an explicit penultimate unit effect, but that this is only the case in systems where the two monomers are very different in size (e.g., styrene/acrylonitrile). More experimental investigations (e.g., propagation rate coefficient measurements with pulsed laser polymerization)[44] could be performed in order to check these predictions. Furthermore, increasing computer resources will make it possible to investigate the effect on the activation energy in more complicated systems by means of ab initio quantum calculations.

Finally, it was shown that neither an enthalpic nor an entropic consideration of the reactants leads to an explanation for the fact that mainly radical reactivity ratios less than unity are observed experimentally. Therefore it is possible that preferential solvation or complexation might play an important role in copolymerization.

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(32) The transmission of electronic substituent effects in the through-bond model will take place via more than one pathway, if the molecule contains branches or ring systems. In those cases, eq 20 will contain a summation over all possible pathways, but, since there is only one possible pathway in most common copolymerization reactions, the summation was omitted from eq 20 for reasons of clarity.

(33) Here, the "steric" contribution to the activation energy is the extent to which the addition reaction is hindered by substituents and *not* to what extent the rotations in the transition state are hindered.

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