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Effect of the Penultimate Unit on Radical Stability and Reactivity in Free-Radical Polymerization

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ABSTRACT: Ab initio molecular orbital calculations have been used to study the effect of γ substituents ($X = H$, F, or CN) on the addition of 1-Y,3-X-disubstituted propyl radicals ($Y = F$ or CN) to ethylene. It is found that, although the γ substituent (i.e. penultimate unit) can exert a significant effect on the stability of the propagating radical, only a small fraction of this effect appears to carry over to the reaction barrier. Furthermore, it appears that when penultimate unit effects on radical stability are large enough to result in significant penultimate unit effects on the reaction barrier, polar interactions are also likely to be significant. The implications of these results for the implicit penultimate model in free-radical copolymerization are discussed.

Introduction

Copolymerization models are used to predict the overall propagation rate of a free-radical copolymerization reaction, and the composition and microstructure of the resulting copolymer, as a function of the feed ratio of the comonomers and a small set of characteristic parameters. To derive such models, it is necessary to characterize the rates of the different types of propagation reactions that may occur in a given copolymerization system. In theory, this task might seem impossible because countless different types of propagating radical (differing in their chain lengths, composition, and microstructure) are likely to be present in any given copolymerization. However, in practice, the task is greatly simplified by introducing assumptions as to the factors influencing the rate of the propagation step, which thereby reduces the number of different types of propagation reactions that need to be considered. For instance, in one of the simplest models, the *terminal model*,[1−3] it is assumed that only the terminal unit of the propagating radical influences its reactivity. Thus, in a given copolymerization system, it is necessary to consider only two types of radical (i.e. corresponding to the two types of terminal unit) and therefore to characterize only four different propagation reactions (i.e. corresponding to the additions of the two types of radicals to the two monomers) (see Figure 1).

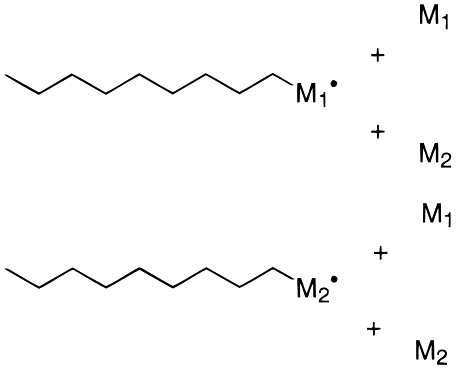

Figure 1. Reactions that need to be characterized in a free-radical copolymerization of monomers M_1 and M_2, under the terminal model.

For many years the terminal model was adopted as the basis of copolymerization kinetics, since it could successfully model the copolymer composition for most systems tested. However, since the composition equation of the terminal model has adjustable parameters, the ability of this model to be fitted to composition data is not sufficient evidence for its validity. A more critical test of the terminal model can be achieved by fitting the terminal model to the composition data of a given copolymerization system and using the parameters obtained to predict its propagation rate—which can then be compared with corresponding measured values. When, in 1985, Fukuda et al.[4] performed such a test—measuring the composition and propagation rate for the copolymerization of styrene with methyl methacrylate—they found that while the composition could be fitted by the terminal model, the propagation rate could not. Subsequent studies,[5] by several different groups, have reported similar behavior for this and several other comonomer pairs, and the frequent failure of the terminal model to describe simultaneously the composition and the propagation rate in free-radical copolymerization is now fairly well established.

An obvious refinement of the terminal model is the *penultimate model*[6] in which it is assumed that both the terminal and penultimate units of a polymer radical can affect its reactivity. Under the penultimate model, there are four different types of radical and thus eight different types of reaction that need to be characterized (see Figure 2). There is certainly evidence for penultimate unit effects (PUEs) in both theoretical[7] and experimental[8−10] studies of gamma substituent effects in the addition reactions of small radicals, and the majority of workers now adopt models based on PUEs for describing their copolymerization data.[5] However, while most workers now accept the existence of PUEs in free-radical copolymerization, there is dispute about

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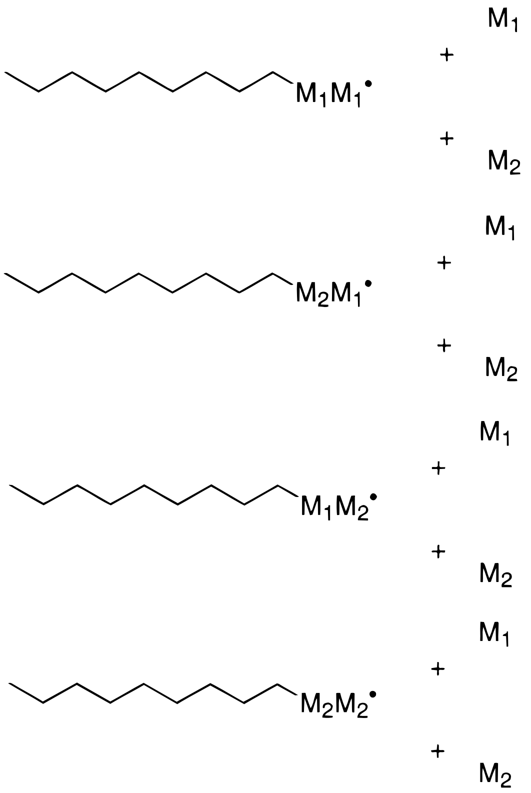

Figure 2. Reactions that need to be characterized in a free-radical copolymerization of monomers M_1 and M_2, under the penultimate model.

the type of penultimate model that should be used. Since the terminal model is capable of describing the composition data (though not the propagation rate) of the majority of copolymerization systems, Fukuda et al.[4] proposed a restricted form of the penultimate model, known as the *implicit penultimate model*. In this model, it is assumed that the magnitude of the PUE on radical reactivity is independent of the coreactant and that there is thus no PUE on the selectivity of the radical. A consequence of this assumption is that the implicit PUE affects only the overall propagation rate of a copolymerization and not the composition or microstructure of the resulting polymer—which can thus be fitted by the terminal model. While the implicit penultimate model has been widely adopted, and can be fitted to existing copolymerization data,[5] other models can also be fitted to existing data.[11] The most important of these alternative models is the *unrestricted* or *explicit penultimate model*[6] in which the PUE is allowed to affect both the reactivity and selectivity of the radical. Under the explicit penultimate model, both the propagation rate and the composition and sequence distribution are fitted by the penultimate model. A definitive discrimination between these two types of penultimate model has not as yet been achieved.

The main problem with using copolymerization data to discriminate between alternative models arises from the fact that these models include a number of characteristic parameters (such as reactivity ratios) which are not independently measured but are instead estimated as part of the model-fitting procedure. By selecting appropriate values of these adjustable parameters, any number of different models (regardless of their physical validity) can be made to fit the same set of data.[11−13] A more promising strategy for determining whether the implicit or the explicit penultimate model provides a physically valid description of copolymerization kinetics is to study the origin of the PUE. A number of different origins for the PUE have been proposed. These include (1) *the radical stabilization model*,[14] in which it is proposed that the penultimate unit affects the stability of the propagating radical (provided the Evans−Polanyi rule[15,16] holds, this results in an implicit PUE in the reaction barrier); (2) *the polar model*,[7,8] in which it is proposed that the penultimate unit affects the stability of the transition state by affecting the stability of its charge-transfer configuration (this results in an explicit PUE in the reaction barrier); and (3) *the entropic model*,[17] in which it is proposed that the penultimate unit affects the frequency factor of the propagation reaction (depending on the relative steric differences between the coreactants, this results in either an explicit or implicit PUE in the frequency factor).

It can therefore be seen that the origin of the PUE determines whether it will be implicit or explicit (or absent) in a given copolymerization system. Thus, by determining the relative importance of these possible causes of PUEs, it can also be determined whether the implicit or explicit penultimate model is likely to provide a physically valid description of the copolymerization kinetics.

Previous studies of the origin of the PUE have been inconclusive. ESR studies[18,19] of low molecular weight radicals derived from the addition of various initiator fragments to various alkenes indicate that substituents at the penultimate and even ante-penultimate positions can affect the stability of the propagating radical—evidence which would seem to support the radical stabilization model. However, Heuts et al.,[17] in a study of γ substituent effects in the addition of γ-substituted propyl radicals to ethylene, found no PUE in the reaction barrier. On the basis of a comparison of the frequency factors for ethyl and propyl addition to ethylene, they predicted that the PUE is largely entropic in origin. In contrast, in a recent pulsed laser polymerization study of styrene−methyl methacrylate copolymerization,[20,21] it was found that the PUE is temperature dependent and thus contains a significant enthalpic component. This conclusion was further supported by a theoretical study of the addition of γ-substituted propyl radicals to various alkenes.[7] These calculations indicated an explicit PUE in the reaction barrier that was likely to be polar in origin. Earlier experimental studies of γ substituent effects on the selectivity of small radicals toward various alkenes also indicated an explicit PUE that was polar in origin.[8−10]

The above studies do not exclude the possibility that entropic factors play a role in PUEs, but they do indicate that explicit PUEs in the barrier are likely to exist. However, it is important to note that if there is an explicit PUE in the barrier, it follows that the PUE in the propagation rate is also explicit—regardless of whether there is an implicit PUE in the frequency factor. Thus it would seem that the explicit model, rather than the more widely adopted implicit model, should be used in modeling copolymerization systems. However, this conclusion is based largely on studies of the addition reactions of γ-substituted propyl radicals. These radicals represent only a limited set of copolymerizations (i.e. those involving ethylene) and are not likely candidates for 1,3-interactions—a possible means by which PUEs on radical stability might occur. To test more critically for radical stabilization PUEs, reactions involving 1,3-disubstituted propyl radicals should be considered.

In the present work, we examine PUEs in the addition of 1-Y,3-X-disubstituted propyl radicals (Y = F, CN; X = H, F, CN) to ethylene in order to determine whether or not implicit PUEs in the reaction barrier are possible. To test for implicit PUEs in the reaction barrier, we examine in turn each of the assumptions of the radical stabilization model. That is, we first test for PUEs on radical stability by looking at the effect of the γ substituent on the stabilities of the 1-Y,3-X-disubstituted propyl radicals. We then determine whether any PUE in radical stability carries over to the reaction barrier. Finally we check whether the Evans−Polanyi rule[15,16] is likely to hold, to determine whether any PUE that may be observed can be implicit (rather than explicit). To do this, we test for polar effects in the addition reactions by examining the energy for charge transfer between the coreactants. When polar effects are present, the Evans−Polanyi rule is likely to break down[22] and the resulting PUEs would be expected to be explicit rather than implicit.[7] To maximize the probability of identifying systems that might display radical stabilization effects in the absence of polar effects, barriers were calculated for reactions with ethylene, an alkene which did not display polar PUEs in our previous studies.[7]

Computational Procedures

Standard ab initio molecular orbital calculations were performed using the Gaussian 94 suite of programs.[23] The effects of γ substituents on the stabilities of the 1,3-disubstituted propyl radicals (1-Y,3-X-propyl: Y = F, CN; X = H, F, CN) were calculated as the energy changes for the following reaction:

$$\mathrm{XCH_2CH_2CHY^{\bullet} + CH_3CH_2CH_3 \rightarrow XCH_2CH_2CH_3 + CH_3CH_2CHY^{\bullet}} \quad (1)$$

To assist in the qualitative rationalization of results, we also calculated the radical stabilization energies (RSEs) for the 1-Y-propyl radicals. These were computed as the energy changes for the following reaction:

$$\mathrm{CH_3CH_2CHY^{\bullet} + CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2Y + CH_3CH_2CH_2^{\bullet}} \quad (2)$$

For both reactions 1 and 2, the energy changes were computed at a level of theory selected in accordance with recent recommendations for the calculation of RSEs.[24,25] Geometries were optimized at the B3-LYP/6-31G(d) level of theory, and improved energies were obtained at the RMP2/6-311+G(3df,2p) level. The energies were corrected for zero-point vibrational energy (ZPVE) using B3-LYP/6-31G(d) harmonic vibrational frequencies, scaled by a factor of 0.9806.[26] The RSEs were calculated for the lowest energy conformations of the radicals and alkanes, the former being screened at the HF/6-31G(d) level of theory and the latter being screened at the RMP2/6-311+G(3df,2p)//B3-LYP/6-31G(d) level. For five of the seven radicals (the propyl radical and the 1-F,3-X-propyl and 1-CN,3-X-propyl radicals for X = H and CN), the lowest energy conformations were taken directly from previous studies by Wong et al.[22,27] The conformations used for the 1-F,3-X-propyl (**1**), 1-CN,3-X-propyl (**2**) radicals and 1-X-propanes (**3**) are shown schematically in Figure 3. Complete geometries for all species involved in the calculation of radical stabilities are given in the form of Gaussian archive files in Table S1 of the Supporting Information, with associated total energies in Table S2.

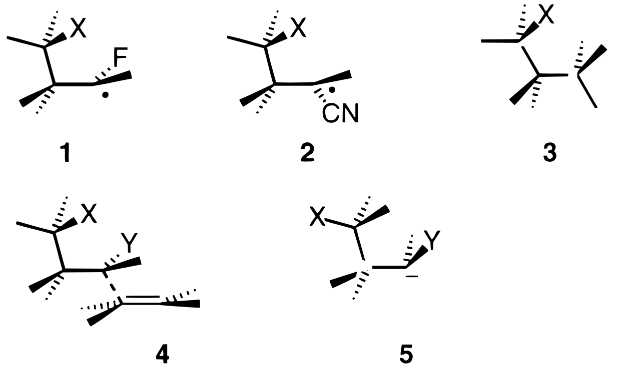

Figure 3. Conformations used for the 1-F,3-X-propyl radicals (**1**), the 1-CN,3-X-propyl radicals (**2**), the 1-X-propanes (**3**), the transition structures for radical addition to ethylene (**4**), and the 1-Y,3-X-propyl anions (**5**).

Reaction barriers were computed at a level of theory that was selected in accordance with previous recommendations for the treatment of radical addition reactions.[28,29] Geometries of all species were optimized at the HF/6-31G(d) level of theory, while improved energies were obtained at the QCISD(T)/6-31G(d) level and corrected to QCISD(T)/6-311G(d,p) using RMP2 energies and assuming the additivity of basis set and correlation effects. The barriers were corrected for zero-point vibrational energy (ZPVE) using B3-LYP/6-31G(d) harmonic vibrational frequencies, scaled by a factor of 0.9806.[26]

Since the main objective of the present work was to test whether implicit PUEs in the reaction barrier were possible, rather than to estimate the exact values of the PUEs in these specific reactions, we have not corrected the reaction barriers for temperature effects nor have we calculated the frequency factors for these reactions. Furthermore, as in our previous work,[7] rather than consider all possible conformations of the reacting radicals and transition structures, PUEs in the reaction barrier were measured for one combination of conformations. The conformation of the transition structure (**4**) in this model reaction is shown in Figure 3, while the lowest energy conformations were used for the 1-F,3-X-propyl (**1**) and 1-CN,3-X-propyl (**2**) radicals, and for ethylene (the D_{2h} structure). Complete geometries for all species involved in the calculation of reaction barriers are given in the form of Gaussian archive files in Table S3 of the Supporting Information, with associated total energies in Table S4.

To assess the likelihood of polar interactions in the addition reactions, charge-transfer energies were calculated from the ionization energies (IEs) and electron affinities (EAs) of the coreactants. Vertical IEs and adiabatic EAs were computed for the radicals at the G2-(MP2) level of theory,[30] while adiabatic IE and EA values for ethylene at the same level of theory were taken from a previous study.[22] In our previous work,[7] we computed vertical (rather than adiabatic) IEs for the 3-X-propyl radicals because the 1-propyl cation does not represent a minimum energy structure on its potential energy surface.[31] In the present work, we have computed vertical IEs for the 1-Y,3-X-propyl radicals, so as

Table 1. Effect of γ Substituents (X) on the Stabilities of 1-Y,3-X-Propyl Radicals[a]

X	propyl[b]	1-F-propyl	1-CN-propyl
H	0.00	0.00	0.00
F	0.25	−2.53	−4.47
CN	−1.54	−4.50	−9.21

[a] Calculated as the energy change (in kJ mol^{-1}) in reaction 1 and obtained from RMP2/6-311+G(3df,2p)//UB3-LYP/6-31G(d) energies with scaled UB3-LYP/6-31G(d) ZPVE corrections (see text). [b] From ref 7.

Table 2. Barriers[a] for the Addition of 1-Y,3-X-Propyl Radicals to $CH_2{=}CH_2$

X	Y = H[b]	Y = F	Y = CN
H	30.3	26.3[c]	37.0
F	30.0	25.6	37.0
CN	29.6	25.4	34.5

[a] Barriers (in kJ mol^{-1}) at the UQCISD(T)/6-311G(d,p)//UHF/6-31G(d) level with scaled UB3-LYP/6-31G(d) ZPVE corrections (see text). [b] From ref 7. [c] The ZPVE correction to this barrier was calculated using a gauche addition transition structure since a first-order saddle point for the anti addition structure could not be located at the UB3-LYP/6-31G(d) level.

to enable the results for these radicals to be compared with our previous results for the 3-X-propyl radicals. The lowest energy conformations of the 1-F,3-X-propyl (**1**), 1-CN,3-X-propyl (**2**) radicals and their corresponding anions (**5**) were determined at the HF/6-31G(d) level of theory and are shown in Figure 3. Complete geometries for all species involved in the calculation of IE and EA values are given in the form of Gaussian archive files in Table S5 of the Supporting Information, with associated total energies in Table S6.

Results and Discussion

Penultimate Unit Effects on Radical Stability. The effects of the γ substituent (i.e. penultimate unit) on the stability of the 1-F,3-X-propyl and 1-CN,3-X-propyl radicals have been measured as the energy changes in reaction 1, giving the results shown in Table 1. Corresponding results for the γ-substituted propyl radicals, which were reported in our previous study,[7] are included in Table 1 for purposes of comparison.

Examination of these results shows that the γ substituent (X) does exert a significant effect on the stability of the 1-F,3-X-propyl and 1-CN,3-X-propyl radicals, but, as seen previously,[7] the effect is much smaller for the 3-X-propyl radical. The γ CN− and, to a lesser extent, F-substituents destabilize the radicals, as compared with the corresponding unsubstituted radicals. This destabilization effect is small in the 3-X-propyl radicals, larger in the 1-F,3-X-propyl radicals, and largest in the 1-CN,3-X-propyl radicals. These trends may be rationalized as follows. In the propyl radical, the ethyl group (attached to the radical carbon atom) helps to stabilize the radical by hyperconjugative electron donation to the singly occupied orbital at the radical center. This stabilizing effect is enhanced in the 1-CN- and, to a lesser extent, 1-F-propyl radical by the presence of electron-withdrawing groups in the α position. This may be seen in the RSEs for the 1-CN-propyl and 1-F-propyl radicals, which are 31.6 and 5.5 kJ mol^{-1}, respectively. When an electron-withdrawing group such as CN− or, to a lesser extent, F− is placed in the γ position of the radical, the donating power of the ethyl group is reduced, and thus the radical is destabilized, relative to the corresponding unsubstituted radical. The destabilizing effect of the γ substituent is largest when the stabilizing effect of the corresponding unsubstituted ethyl group is largest, and thus the largest γ substituent effects occur for the 1-CN,3-X-propyl radical, while smaller effects occur for the 1-F,3-X-propyl radicals.

The present results, together with the earlier ESR studies[18,19] thus support the proposition of Fukuda et al.[14] that the penultimate unit can affect the stability of the propagating radical.

Penultimate Unit Effects in the Reaction Barriers. Having identified radicals for which there are PUEs on radical stability, it is then of interest to see whether these PUEs appear in the reaction barrier. To do this, we have calculated the reaction barriers for the addition of these radicals to ethylene. The results obtained are given in Table 2, together with the barriers for addition of the γ-substituted propyl radicals to ethylene from our previous study,[7] included for purposes of comparison. Examination of the barriers in Table 2 shows that although there are significant PUEs on radical stability, penultimate unit effects in the reaction barriers are small. The largest PUE, the effect of the γ CN substituent in the 1-CN,3-X-propyl addition reactions, is only 2.5 kJ mol^{-1}—approximately 27% of the corresponding PUE on radical stability.

It therefore appears that only a small fraction of the PUE on radical stability carries over to the reaction barrier. We note that, under the radical stabilization model,[14] the PUE in the reaction barrier is predicted to be *proportional* to the PUE in reaction enthalpy (and thus radical stability). The size of this proportionality constant depends on how late or early the transition state is. If, on one hand, the transition state is similar to the product radical (i.e. late), the proportionality constant will be close to unity, and most of the PUE in enthalpy will appear in the barrier. If, on the other hand, the transition state is very similar to the reactants (i.e. early), the proportionality constant will be small, and only a small fraction of the PUE in enthalpy will appear in the barrier. The present results indicate a small proportionality constant and thus an early transition state in these reactions. This conclusion is consistent with what is generally expected for highly exothermic reactions such as these and with the large forming carbon−carbon bond lengths (around 2.2−2.4 Å) which are calculated for the transition structures of these reactions.

Can Penultimate Unit Effects in the Reaction Barrier be Implicit? The present results indicate that the penultimate unit can significantly affect the stability of the propagating radical but that only a small fraction of this PUE carries over to the reaction barrier. Nevertheless it does appear that, provided the PUEs on radical stability are sufficiently large (as in the case of the 1-CN,3-X-propyl addition reactions), significant radical stabilization PUEs in the reaction barrier are possible. However, for these PUEs to be implicit (rather than explicit) it is necessary that they occur independently of polar effects. This is because polar interactions undermine the Evans−Polanyi rule,[22] one of the assumptions of the radical stabilization model,[14] and, as seen in our previous work,[7] polar PUEs are strongly explicit.

Thus, to determine whether the PUEs observed in the present work are likely to be implicit, we have examined the reactions of the present study for polar interactions. Since charge calculations for systems as large as those

Table 3. Vertical IE and Adiabatic EA Values for the 1-Y,3-X-Propyl Radicals[a]

	propyl[b]		1-F-propyl		1-CN-propyl	
X	IE	EA	IE	EA	IE	EA
H	8.40	0.01	8.48	0.23	9.12	1.39
F	8.68	0.40	8.78	0.58	9.33	1.78
CN	9.06	0.68	9.01	0.90	9.54	2.05

[a] In eV, calculated at the G2(MP2) level based on conformations screened at the UHF/6-31G(d) level. [b] From ref 7.

Table 4. Charge-Transfer Energies (IE−EA)[a] **for the Interaction of 1-Y,3-X-Propyl Radicals with $CH_2{=}CH_2$**

	donor alkene			acceptor alkene		
X	Y = H	Y = F	Y = CN	Y = H	Y = F	Y = CN
H	10.6	10.4	9.2	10.3	10.3	11.0
F	10.2	10.0	8.8	10.5	10.6	11.2
CN	9.9	9.7	8.5	10.9	10.9	11.4

[a] In eV, calculated from G2(MP2) vertical IE and adiabatic EA values for the radicals, taken from Table 3, together with the adiabatic IE and EA values for ethylene of +10.58 and −1.86 eV, respectively, taken from ref 22.

of the present study are computationally expensive, we have adopted a semiquantitative test for polar effects, based on the work of Wong et al.[22] They showed that, in the addition of substituted methyl radicals to various alkenes, polar effects become important when the charge-transfer energy, calculated as the difference between the ionization energy (IE) of the donor and the electron affinity (EA) of the acceptor, drops below about 9−9.5 eV. Thus, to test for polar effects in our reactions, we have calculated the charge-transfer energy for the coreactants from their IE and EA values. The IE and EA values for the radicals are given in Table 3, while the IE and EA values for ethylene (at the same level of theory) have been taken from the earlier work of Wong et al.[22] Our previously published[7] results for the 3-X-propyl radicals are included in Table 3, for comparison. On the basis of the IE and EA values of Table 3, the energies for both possible directions of charge transfer between the radicals and ethylene were calculated and are given in Table 4.

From the charge-transfer energies in Table 4, it is evident that polar effects are likely to be present in the 1-CN,3-X-propyl reactions since the charge-transfer energies do drop below 9−9.5 eV. Since these reactions are the only reactions in which a significant PUE was observed, it would seem that significant PUEs in the reaction barrier are unlikely to occur independently of polar effects. This conclusion is further strengthened when it is remembered that, to satisfy the implicit penultimate model in free radical copolymerization, polar effects need to be absent in all possible propagation reactions involving the two comonomers. For instance, the reaction of 1-CN,3-X-propyl (X = H, CN) radicals with ethylene represents a small radical model of the copolymerization of ethylene with acrylonitrile. For this copolymerization to obey the implicit (rather than explicit) penultimate model, the PUEs in all four reaction pairs (see Figure 4) must be implicit, and thus polar interactions must be absent from all of these reactions. Not only do the present results indicate that polar interactions are likely to be significant in the addition of the 1-CN,3-X-propyl (X = H, CN) radicals to ethylene (reaction pair (b) in Figure 4), but our previous results[7] indicate that there are strong polar interactions in the addition of the 3-X-propyl (X = H, CN) radicals to acrylonitrile (reaction pair (c) in Figure 4). Indeed, comparison of the PUEs for the addition of the 3-X-propyl (X = H, CN) radicals to ethylene (reaction (d) in Figure 4) and acrylonitrile (reaction (c) in Figure 4) reveals that the PUE in these reactions is strongly explicit. Thus, introducing a γ-CN substituent into the propyl radical results in a 0.7 kJ mol^{-1} decrease in its reaction barrier for addition to ethylene, but a 3.2 kJ mol^{-1} increase in its reaction barrier for addition to acrylonitrile (see Table 1 of ref 7).

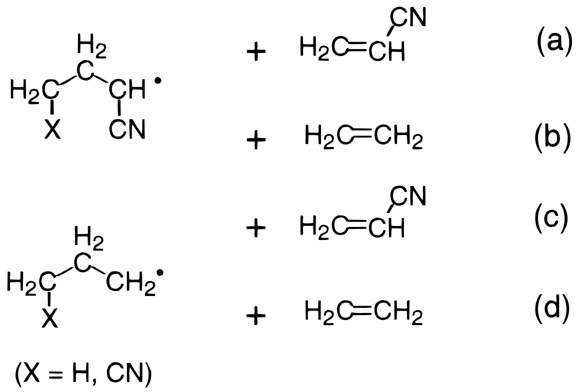

Figure 4. Eight possible propagation reactions (under the penultimate model) in a small radical model of the copolymerization of ethylene with acrylonitrile. The PUEs of the X = CN substituent (relative to X = H) on the barriers for these reactions are −2.5 kJ mol^{-1} for (b), +3.2 kJ mol^{-1} for (c)[7] and −0.7 kJ mol^{-1} for (d).[7] Reaction pair (a) was not examined because of the computational expense.

The present results therefore suggest that where PUEs on radical stability are sufficiently large to result in significant PUEs in the reaction barrier, these effects are unlikely to occur independently of polar interactions. This is probably because the radical substituents associated with large PUEs on radical stability are strong electron donors or acceptors and are thus simultaneously associated with strong polar interactions—especially when these substituents appear on the monomer, as they would in the cross-reactions of a free-radical copolymerization. Since polar interactions undermine the Evans−Polanyi rule,[22] an essential assumption of the radical stabilization model,[14] and are themselves associated with strongly explicit PUEs,[7] it may therefore be concluded that where PUEs on the reaction barrier are significant, they are likely to be explicit and not implicit. *Thus it appears that the explicit penultimate model should, in general, provide a more physically valid description of copolymerization kinetics than the more widely adopted implicit penultimate model.*

Of course, further testing of these models is required in order to confirm this result. In particular, it should be noted that theoretical studies have not, as yet, considered phenyl substituents—for which radical stabilization effects may be somewhat larger than those considered thus far. However, some experimental support for the invalidity of the radical stabilization model is provided by a recent pulsed laser polymerization study of the copolymerization of *p*-chlorostyrene with styrene and with *p*-methoxystyrene.[32] For both of these monomer pairs, it was shown that, within a 95% level of confidence, the monomer and radical reactivity ratio products were not equal to each other (i.e. $r_1r_2 \neq s_1s_2$)—a result which contradicts one of the predictions of the radical stabilization model (namely, that $r_1r_2 = s_1s_2$). Hence, on the basis of existing evidence, the explicit rather than the implicit penultimate model should be adopted for analyzing copolymerization data, which in turn implies that the terminal model should not be used for analyzing the composition data of common copolymerization systems. This is important, since the parameters obtained by fitting a physically invalid model to kinetic data will not reflect their proposed physical meaning and will thus yield incorrect results when used to predict other copolymerization properties such as the microstructure of a polymer.

Conclusions

In the present work we have shown that the γ substituent (or penultimate unit) can significantly affect the stability of substituted propyl radicals. This, together with the earlier ESR studies,[18,19] supports the proposition of Fukuda et al.[14] that there is a PUE in the stability of the propagating polymer radical. However, in contrast to the earlier arguments of Fukuda et al.,[14] this penultimate unit effect on radical stability does not appear to any great extent in the reaction barrier for the addition of these radicals to ethylene, and, in cases where significant penultimate unit effects are observed, polar interactions are likely to be important. Based on these results, it appears that the assumptions of the radical stabilization model cannot be satisfied for these reactions, and thus the explicit rather than implicit penultimate model should provide a more physically realistic description of copolymerization kinetics. However, it should be noted that this conclusion is based on the behavior of a limited number of systems, including those involving highly polar monomers such as acrylonitrile. Further evidence for other systems, particularly those involving more common monomers such as styrene and methacrylate or acrylate monomers, is required to confirm the generality of this result.

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Supporting Information Available: Tables listing Gaussian archive entries, giving the geometries of all species involved in the calculation of radical stabilities, the reaction barriers, and the IE and EA values and showing their corresponding total energies (13 pages). Ordering and Internet access information is given on any current masthead page.

References and Notes

(1) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.
(2) Jenkel, E. *Z. Phys. Chem. Abt. A* **1942**, *190*, 24.
(3) Alfrey, T.; Goldfinger, G. *J. Chem. Phys.* **1944**, *12*, 205.
(4) Fukuda, T.; Ma, Y.; Inagaki, H. *Macromolecules* **1985**, *18*, 17.
(5) For a review of this work, see: Fukuda, T., Kubo, K., Ma, Y.-D. *Prog. Polym. Sci.* **1992**, *17*, 875.
(6) (a) Merz, E.; Alfrey, T., Jr.; Goldfinger, G. *J. Polym. Sci.* **1946**, *1*, 75. (b) For a derivation of the propagation rate equation for this model, see ref 4.
(7) (a) Coote, M. L.; Radom, L.; Davis, T. P. *J. Mol. Struct. (THEOCHEM)*, in press. (b) Note that a conformation model that is slightly different from that of the present study was used in this work.
(8) Giese, B.; Engelbrecht, R. *Polym. Bull.* **1984**, *12*, 55.
(9) Jones, S. A.; Prementine, G. S.; Tirrell, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5275.
(10) Cywar, D. A.; Tirrell, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 7544.
(11) Maxwell, I. A.; Aerdts, A. M.; German, A. L. *Macromolecules* **1993**, *26*, 1956.
(12) Schweer, J. *Makromol. Chem., Theory Simul.* **1993**, *2*, 485.
(13) Moad, G.; Solomon, D. H.; Spurling, T. H.; Stone, R. A. *Macromolecules* **1989**, *22*, 1145.
(14) Fukuda, T.; Ma, Y.; Inagaki, H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 495.
(15) Evans, M. G. *Discuss. Faraday Soc.* **1947**, *2*, 271.
(16) Evans, M. G.; Gergely, J.; Seaman, E. C. *J. Polym. Sci.* **1948**, *3*, 867.
(17) (a) Heuts, J. P. A. Ph.D. Thesis, University of Sydney, 1996. (b) Heuts, J. P. A.; Gilbert, R. G.; German, A. L.; Radom, L. To be submitted for publication.
(18) Tanaka, H.; Sasai, K.; Sato, T.; Ota, T. *Macromolecules* **1988**, *21*, 3534.
(19) Sato, T.; Inui, S.; Tanaka, H.; Ota, T. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 637.
(20) Coote, M. L.; Zammit, M. D.; Davis, T. P.; Willett, G. D. *Macromolecules* **1997**, *30*, 8182.
(21) Coote, M. L.; Johnston, L. P. M.; Davis, T. P. *Macromolecules* **1997**, *30*, 8191.
(22) Wong, M. W.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 6284.
(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision B.3; Gaussian Inc.: Pittsburgh, PA, 1995.
(24) Parkinson, C. J.; Mayer, P. M.; Radom, L. *Theor. Chem. Acc.*, in press.
(25) Parkinson, C. J.; Mayer, P. M.; Radom, L. To be submitted for publication.
(26) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
(27) Wong, M. W.; Pross, A.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 415.
(28) Wong, M. W.; Radom, L. *J. Phys. Chem.* **1995**, *99*, 8582.
(29) Heuts, J. P. A.; Gilbert, R. G.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 18997.
(30) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.
(31) Koch, W.; Liu, B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 3479.
(32) Coote, M. L.; Davis, T. P. *Macromolecules*, in press.

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