Conformational Dependence of the Penultimate Unit Effect in Free-Radical Copolymerization

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Received March 31, 1999; Revised Manuscript Received June 4, 1999

ABSTRACT: The reaction barriers for the addition of various gamma-substituted propyl radicals to alkenes were obtained via ab initio molecular orbital calculations. The reactions studied were the additions of 3X-propyl ($X = H$, F) to $CH_2{=}CHF$, 3X-propyl ($X = H$, CN) to $CH_2{=}CHCN$, and 3X-propyl ($X = H$, CN) to $CH_2{=}CHNH_2$. The results indicate that the gamma substituent effect (i.e., penultimate unit effect) on the reaction barrier is strongly dependent on the conformations of the reacting radical and transition structure. The implications of these results for the penultimate unit effect in free-radical copolymerization are discussed.

Introduction

As is now well-known, the terminal model[1−3] cannot simultaneously describe the composition and overall propagation rate in the majority of free-radical copolymerization systems that have been studied to date.[4] Despite this result, the terminal model is still widely used for describing the composition and sequence distribution of such systems. The composition, triad/pentad fraction, and propagation rate equations of the terminal model all follow from the same basic assumption—namely, that the terminal unit of a polymer radical is the only unit affecting the rate of its propagation reaction with a given monomer. Thus, it would seem that the failure of the terminal model to describe the propagation rate of common copolymerization systems invalidates this assumption and hence the terminal model composition and triad/pentad fraction equations that follow from it.

To justify the continued use of the terminal model composition and triad/pentad fraction equations in systems for which the terminal propagation rate equation fails, the *implicit penultimate model* has been proposed.[5] A penultimate unit effect is said to occur when the rate of the propagation reaction is affected by both the terminal and penultimate units of the propagating radical. In the implicit penultimate model, it is assumed that the magnitude of this penultimate unit effect on the reactivity of a radical is independent of the type of monomer with which it is reacting. Under this special condition, the composition and triad/pentad fraction equations of the model collapse into their corresponding terminal model forms, and the penultimate unit effect (known as an implicit penultimate unit effect) thus appears only in the propagation rate equation. If, however, this special condition is not satisfied, the penultimate unit effect (known in that case as an explicit penultimate unit effect) causes the composition and triad/pentad fraction equations, as well as the propagation rate equation, to differ from their terminal model counterparts. This unrestricted penultimate model is known as the *explicit penultimate model.*[6]

From the above it will be seen that the failure of the terminal model to describe simultaneously the composition and propagation rate in a free-radical copolymerization may be attributed to either an explicit penultimate unit effect or an implicit penultimate unit effect. Under an explicit penultimate unit effect, the terminal model composition and triad/pentad fraction equations are invalid, but under an implicit penultimate unit effect they are valid. Thus, to determine whether the terminal model provides a physically realistic description of the composition and sequence distribution of common copolymerization systems, it is necessary to determine whether penultimate unit effects are implicit or explicit.

Attempts to discriminate between the implicit and explicit penultimate models on the basis of their ability to describe experimental composition and propagation rate data have not as yet been successful for common copolymerization systems such as styrene−methyl methacrylate. This is because both the implicit and explicit penultimate models contain monomer and radical reactivity ratios that are not independently measured but are instead treated as adjustable parameters as part of the model-fitting procedure. By selecting appropriate values for these adjustable parameters, any number of different models (regardless of their physical validity) can be made to fit the same set of data.[7]

A more promising means of discriminating between these alternative models is to examine their physical basis. As implied above, for a penultimate unit effect to be implicit, it is necessary that the magnitude of the penultimate unit effects in both the reaction barrier and frequency factor of the propagation reaction be independent of the coreactant. In this way, the penultimate unit affects the reactivity but not the selectivity of the propagating radical. Theoretical justifications of this assumption for both penultimate unit effects in the reaction barrier and the frequency factor have been proposed. Fukuda et al.[8] showed that this assumption could be justified for penultimate unit effects in the reaction barrier if the penultimate unit affected the stability of the propagating polymer radical and the Evans−Polanyi rule was satisfied for the propagation

10.1021/ma990468q CCC: $18.00

reaction. This is known as the radical stabilization model. In the case of penultimate unit effects in the frequency factor, Heuts et al.[9] showed via simple steric arguments that entropic penultimate unit effects on radical selectivity would always be smaller than their corresponding effects on reactivity. Hence, provided the reacting species were not too dissimilar, an “approximately” implicit penultimate unit effect could result. This is known as the entropic model.

However, while it would thus seem to be theoretically possible for implicit penultimate unit effects to exist, recent studies indicate that, in practice, penultimate unit effects are more likely to be explicit. In calculations of the reaction barrier for the addition of a series of gamma-substituted propyl radicals to various alkenes, the observed gamma substituent (i.e., penultimate unit) effects were found to be strongly explicit and likely to be polar in origin.[10] Polar effects are said to occur when the transition structure is stabilized by charge transfer, which will occur when the charge-transfer configuration is sufficiently low in energy.[11] Not only are polar penultimate effects themselves strongly explicit (as can be confirmed by simple electrostatic arguments[12]), but polar interactions also undermine the Evans−Polanyi rule[11]—an essential assumption of the radical stabilization model. Further evidence for the importance of explicit polar penultimate unit effects has been obtained in a study of gamma substituent effects in the addition of 1,3-disubstituted propyl radicals to ethylene.[13] While for these radicals there were large penultimate effects on radical stability, these penultimate unit effects did not appear to carry over to any great extent into the reaction barrier. Where penultimate unit effects in the barrier were observed, it was impossible to rule out the participation of polar effects. Earlier experimental studies of gamma substituent effects on the selectivity of small radicals toward various alkenes also indicated an explicit penultimate unit effect that was polar in origin.[14−16] While these experimental and theoretical studies of gamma substituent effects in small radical addition reactions have involved only a limited range of monomers (including highly polar monomers such as acrolein and acrylonitrile), a recent pulsed laser polymerization study of the copolymerization of *p*-chlorostyrene with styrene and with *p*-methoxystyrene has provided some additional experimental evidence for shortcomings in the radical stabilization model.[17] 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 one another (i.e., $r_1r_2 \neq s_1s_2$)—a result which contradicts one of the predictions of the radical stabilization model (namely, that $r_1r_2 = s_1s_2$).

The above studies therefore indicate that penultimate unit effects in the reaction barrier are more likely to be explicit rather than implicit. While the existence of implicit penultimate unit effects in the frequency factor cannot be ruled out, if there are explicit penultimate unit effects in the reaction barrier, it follows that the penultimate unit effects in the overall propagation rate will also be explicit. Given that penultimate unit effects in the reaction barrier are likely to exist in common copolymerizations such as styrene−methyl methacrylate copolymerization,[18,19] it would therefore appear that the explicit penultimate model should be more appropriate for these systems, and thus the terminal model should not be appropriate for describing their composition and sequence distribution.

However, the above theoretical studies[10,13] have only examined gamma substituent effects in model reactions for which the conformations of the reacting radicals and transition structures were fixed across a series of reactions (though, of course, the geometries of all species were fully optimized within these conformations). In all cases, the model conformations selected were those fully extended conformations for which the substituents on the radical and monomer were as far away from one another as possible. In this way, it was hoped to estimate a lower bound to the penultimate unit effect. Nevertheless, these fully extended conformations do not necessarily provide the lowest energy pathway for a reaction, and thus the penultimate unit effects detected in this previous work may not be representative of the penultimate unit effects that might be expected in real reactions. Furthermore, it would be of interest to study the conformational dependence of the penultimate unit effect and thereby examine whether direct interactions involving the monomer and radical substituents are likely to contribute to the penultimate unit effect.

To address the above issues, in the present work we have taken some representative reactions from our previous studies[10,13] and examined the conformational dependence of the penultimate unit effect in these reactions. The reactions chosen for this study were the addition of 3X-propyl (X = H, F) to $CH_2{=}CHF$ (for which there was no penultimate unit effect in the model reaction), the addition of 3X-propyl (X = H, CN) to $CH_2{=}CHCN$ (for which there was a positive penultimate unit effect in the model reaction), and the addition of 3X-propyl (X = H, CN) to $CH_2{=}CHNH_2$ (for which there was a negative penultimate unit effect in the model reaction). In what follows, we present the results of the theoretical calculations and discuss their implications for copolymerization kinetics.

Computational Procedures

Standard ab initio molecular orbital calculations were performed using the Gaussian 94 suite of programs.[20] Geometries of all species were optimized at the HF/6-31G(d) level of theory, while improved energies were obtained at the QCISD/6-31G(d) level and corrected to QCISD/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.[21] The barriers were calculated for various (specified) conformations of the transition structures, while within a specified conformation, the geometry was fully optimized. In calculating the reaction barriers, the lowest energy structures for the reacting radicals were always used—regardless of the conformation of the reacting radical in the transition structure. In this way, a measure of the overall reaction barrier could be obtained. The lowest energy conformations of the reacting radicals were determined from energies calculated at the same level as the reaction barriers. Geometries (in the form of Gaussian archive files) for all species considered in the present work, together with their corresponding associated total energies, are provided in Tables S1−S16 of the Supporting Information. For two of the radicals, the **1c**/**1d**/**1e** conformations of the propyl radical[22] and the **1c** conformation of the 3CN-propyl radical,[11] the geometry was taken directly from earlier studies by Wong et al.

The level of theory used for the present work, though selected in accordance with previous recommendations for the treatment of radical addition reactions,[23,24] is slightly lower than that recommended in a more recent study.[25] This new recommended level, CBS-RAD(QCISD,B3-LYP), could not be used to study the reactions of the present work owing to the computational expense. At the lower level of theory adopted for the present work it is likely that the errors in absolute reaction barriers will be significant; however, it is expected that the errors in the relative barriers will be relatively minor, particularly given the similarity of the reactions for which relative barriers are to be calculated. Two types of relative barriers will be studied. First, barriers for a specific radical adding to a specific monomer but via a variety of transition structure conformations will be compared. Second, barriers for the addition to a specific monomer via a specific transition structure conformation of radicals differing only in their gamma substituent will be compared. In each case, it is predicted that errors arising from spin contamination will be relatively constant within the sets of barriers being compared and can thus be expected to cancel to a large extent from the relative barriers.[26] Since in the present work we are only concerned with relative barriers, and do not intend to employ the absolute barriers for predicting reaction rates, the use of this lower level of theory can therefore be justified.

It should also be noted that the level of theory selected for the present work is slightly lower than that used in our previous studies of gamma substituent effects.[10,13] At the level of theory used previously, barriers were calculated using QCISD(T)/6-311G(d,p) energies, rather than QCISD/6-311G(d,p) energies. The additional errors introduced to our present results through the use of this slightly lower level of theory were assessed by calculating at both levels of theory the barriers for the addition of 3X-propyl radicals (X = H, F) to $CH_2{=}CHF$. The results obtained (listed in Table S17 of the Supporting Information) indicate that the difference in the absolute reaction barriers at the two levels of theory is around 5.5 kJ mol^{-1}. However, the maximum difference in the relative barriers is only 0.2 kJ mol^{-1}. Hence, the lower level of theory should be adequate for the study of relative reaction barriers, as in the present work. This result is consistent with an earlier study[23] which found that reaction barriers at the QCISD and QCISD(T) levels of theory for the addition of methyl radicals to various alkenes were highly correlated, having a correlation coefficient of 0.998.

Results

The conformations considered for the 3X-propyl radicals and their transition structures for addition to the appropriate alkenes are shown in Figures 1 and 2, respectively. For each gamma-substituted propyl radical, the relative energies of its different possible conformations (see Figure 1) are shown in Table 1. On the basis of these results, it appears that the gamma substituent (i.e., penultimate unit) can significantly influence the relative energies of the various radical conformations. For instance, the conformation with the highest energy for the 3F-propyl radical is conformation **1e**, while for 3CN-propyl it is **1a**. However, at least for the radicals considered in the present work, the lowest energy conformation for each of the 3X-propyl radicals is the same (i.e., **1d** for X ≠ H and the equivalent **1c**, **1d**, and **1e** conformations for X = H).

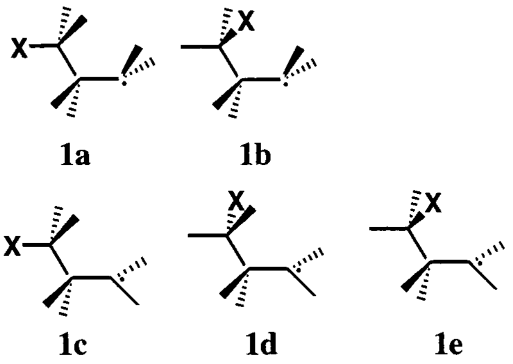

Figure 1. Possible conformations of the 3X-propyl radical.

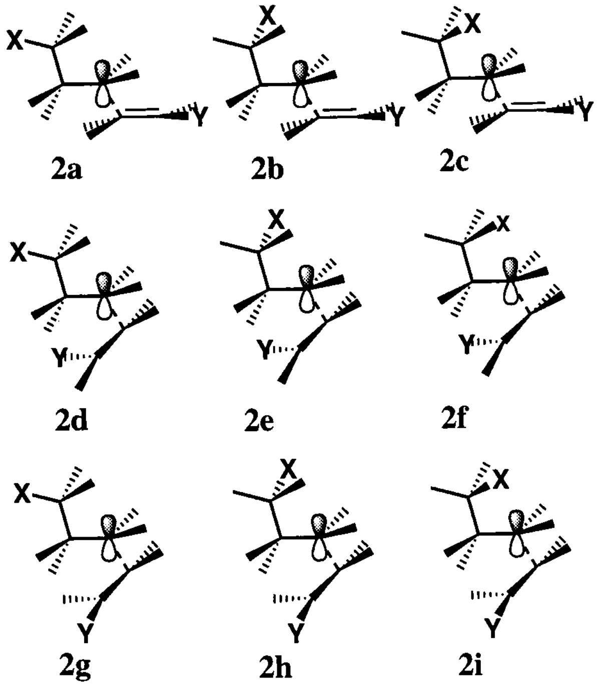

Figure 2. Possible transition structure conformations for the addition of a 3X-propyl radical to $CH_2{=}CHY$.

Table 1. Relative Energies (0 K, kJ mol^{-1})[a] of Conformations of 3X-Propyl Radicals ($XCH_2CH_2CH_2^{\bullet}$)

structure	X = H[b]	X = F	X = CN
1a	0	0	0
1b	0	0.55[c]	−0.59[c]
1c	−1.36	−0.67	−0.86
1d	−1.36	−1.23	−1.19
1e	−1.36	1.53[c]	−0.32

[a] Energies (relative to those of structure **1a**) correspond to estimated UQCISD/6-311G(d,p)//UHF/6-31G(d) values together with the incorporation of UB3-LYP/6-31G(d) ZPVE corrections; see text. [b] Note that, for the propyl radical, conformations **1a** and **1b** are equivalent and conformations **1c, 1d**, and **1e** are equivalent. [c] The ZPVE could not be calculated for these conformations as stable UB3-LYP/6-31G(d) geometries could not be located. Instead, it was assumed that the ZPVE for these conformations could be approximated as the ZPVE for the corresponding **1a** conformation.

Using the lowest energy conformation for each radical, the reaction barriers for the additions of 3X-propyl (X = H, F) radicals to $CH_2{=}CHF$, 3X-propyl (X = H, CN) radicals to $CH_2{=}CHCN$, and 3X-propyl (X = H, CN) radicals to $CH_2{=}CHNH_2$ were calculated for each of the transition structure conformations in Figure 2. The

Table 2. Reaction Barriers (0 K, kJ mol^{-1})^a for the Addition of 3X-Propyl Radicals (X = H, F) to $CH_2{=}CHF$ for Reaction via Various Possible Transition Structure Conformations

	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**
3F-propyl + $CH_2{=}CHF$									
absolute barrier	37.23	37.22	37.83	35.23	33.88	34.26	35.40	35.16	36.39
relative barrier	0	0.00	0.60	−2.00	−3.35	−2.96	−1.83	−2.07	−0.84
propyl + $CH_2{=}CHF$									
absolute barrier	37.44	37.44	37.44	34.93	34.93	34.93	35.73	35.73	35.73
relative barrier	0	0	0	−2.51	−2.51	−2.51	−1.71	−1.71	−1.71
PUE	−0.2	−0.2	+0.4	+0.3	−1.1	−0.7	−0.3	−0.6	+0.7

[a] Barriers correspond to estimated UQCISD/6-311G(d)//UHF/6-31G(d) values together with the incorporation of UB3-LYP/6-31G(d) ZPVE corrections; see text. Barriers are for the addition of the lowest energy alkene to the lowest energy radical via the optimized transition structure for each conformation in Figure 2. Relative barriers calculated in reference to the barrier for the same reaction but via transition structure conformation **2a**, while penultimate unit effects (PUEs) are calculated as the difference between the barriers for the addition of the two different 3X-propyl radicals (i.e., X = H and X = F) to the same monomer and via the same transition structure conformation. Note that, for propyl addition to $CH_2{=}CHF$, conformations **2a**, **2b**, and **2c** are equivalent, conformations **2d**, **2e**, and **2f** are equivalent, and conformations **2g**, **2h**, and **2i** are equivalent.

Table 3. Reaction Barriers (0 K, kJ mol^{-1})^a for the Addition of 3X-Propyl Radicals (X = H, CN) to $CH_2{=}CHCN$ for Reaction via Various Possible Transition Structure Conformations

	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**
3CN-propyl + $CH_2{=}CHCN$									
absolute barrier	24.49	23.17	25.07	23.89	19.11	19.22	22.65	20.59	23.35
relative barrier	0	−1.32	0.58	−0.6	−5.38	−5.27	−1.84	−3.9	−1.14
propyl + $CH_2{=}CHCN$									
absolute barrier	21.20	21.20	21.20	19.32	19.32	19.32	19.96	19.96	19.96
relative barrier	0	0	0	−1.88	−1.88	−1.88	−1.24	−1.24	−1.24
PUE	+3.3	+2.0	+3.9	+4.6	−0.2	−0.1	+2.7	+0.6	+3.4

[a] Barriers correspond to estimated UQCISD/6-311G(d)//UHF/6-31G(d) values together with the incorporation of UB3-LYP/6-31G(d) ZPVE corrections; see text. Barriers are for the addition of the lowest energy alkene to the lowest energy radical via the optimized transition structure for each conformation in Figure 2. Relative barriers calculated in reference to the barrier for the same reaction but via transition structure conformation **2a**, while penultimate unit effects (PUEs) are calculated as the difference between the barriers for the addition of the two different 3X-propyl radicals (i.e., X = H and X = CN) to the same monomer and via the same transition structure conformation. Note that, for propyl addition to $CH_2{=}CHCN$, conformations **2a**, **2b**, and **2c** are equivalent, conformations **2d**, **2e**, and **2f** are equivalent, and conformations **2g**, **2h**, and **2i** are equivalent.

Table 4. Reaction Barriers (0 K, kJ mol^{-1})^a for the Addition of 3X-Propyl Radicals (X = H, CN) to $CH_2{=}CHNH_2$ for Reaction via Various Possible Transition Structure Conformations

	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**
3CN-propyl + $CH_2{=}CHNH_2$									
absolute barrier	28.52	28.89	28.64	24.77	24.31	25.05	25.39	24.99	25.10
relative barrier	0	0.37	0.12	−3.75	−4.21	−3.47	−3.13	−3.53	−3.42
propyl + $CH_2{=}CHNH_2$									
absolute barrier	33.09	33.09	33.09	30.58	30.58	30.58	30.53	30.53	30.53
relative barrier	0	0	0	−2.50	−2.50	−2.50	−2.55	−2.55	−2.55
PUE	−4.6	−4.2	−4.4	−5.8	−6.3	−5.5	−5.1	−5.5	−5.4

[a] Barriers correspond to estimated UQCISD/6-311G(d)//UHF/6-31G(d) values together with the incorporation of UB3-LYP/6-31G(d) ZPVE corrections; see text. Barriers are for the addition of the lowest energy alkene to the lowest energy radical via the optimized transition structure for each conformation in Figure 2. Relative barriers calculated in reference to the barrier for the same reaction but via transition structure conformation **2a**, while penultimate unit effects (PUEs) are calculated as the difference between the barriers for the addition of the two different 3X-propyl radicals (i.e., X = H and X = CN) to the same monomer and via the same transition structure conformation. Note that, for propyl addition to $CH_2{=}CHNH_2$, conformations **2a**, **2b**, and **2c** are equivalent, conformations **2d**, **2e**, and **2f** are equivalent, and conformations **2g**, **2h**, and **2i** are equivalent.

resulting absolute barriers for each of these reaction pairs are shown in Tables 2−4, respectively. On the basis of these absolute reactions barriers, two types of relative reaction barrier were calculated. First, to measure the effect of transition structure conformation on the barrier for a particular reaction, relative barriers corresponding to the various transition structure conformations for each individual reaction were calculated relative to the corresponding barrier for conformation **2a**. Second, to measure the gamma substituent (i.e., penultimate unit) effect on the reaction barrier for reactions proceeding via a given conformation, relative barriers corresponding to the addition of the various gamma-substituted propyl radicals to a specific monomer via a specific transition structure were calculated relative to the corresponding barrier for propyl addition. These two types of relative barrier are included in Tables 2−4 for each of the respective reaction pairs, where they are labeled relative barrier and PUE, respectively.

From an examination of Tables 2−4, it is apparent that, as was the case for the radicals, the relative energies of the various transition structure conformations depend on the nature of the penultimate unit. Consequently, the penultimate unit effect is strongly dependent upon the transition structure conformation. For instance, in the 3X-propyl (X = H, CN) additions to $CH_2{=}CHCN$, penultimate unit effects for the different transition structure conformations vary from +4.6 kJ mol^{-1} (for conformation **2d**) to −0.2 kJ mol^{-1} (for conformation **2e**). Furthermore, when the two reactions being compared have different transition structure conformations, even greater variation in the penultimate unit effect is possible. For instance, in the case of

Table 5. Barriers (0 K, kJ mol^{-1})[a] and Corresponding Penultimate Unit Effects (PUEs) for the Limiting Combinations of Conformations

case[b]	3X-propyl + CH_2=CHF			3X-propyl + CH_2=CHCN			3X-propyl + CH_2=$CHNH_2$		
	X = H	X = F	PUE	X = H	X = CN	PUE	X = H	X = CN	PUE
high, high	37.44	37.83	+0.4	21.20	25.07	+3.9	33.09	28.89	−4.2
high, low	37.44	33.88	−3.6	21.20	19.11	−2.1	33.09	24.31	−8.8
low, high	34.93	37.83	+2.9	19.32	25.07	+5.8	30.53	28.89	−1.6
low, low	34.93	33.88	−1.1	19.32	19.11	−0.2	30.53	24.31	−6.2
model[c]	36.08	36.00	−0.1	19.84	23.30	+3.5	31.72	27.33	−4.4

[a] Barriers correspond to estimated UQCISD/6-311G(d)//UHF/6-31G(d,p) values together with the incorporation of UB3-LYP/6-31G(d) ZPVE corrections; see text. [b] Each case corresponds to one of the four possible combinations of the lowest and highest barriers for each reaction pair, taken from the barriers for the individual transition structure conformations (see Tables 2−4). The resulting penultimate unit effects represent the range of overall penultimate unit effects possible for these reaction pairs, depending upon which transition structure conformations are entropically favored. [c] These are for the **1a** radical conformation and **2a** transition structure conformation.

3X-propyl (X = H, CN) additions to CH_2=CHCN, if the conformation giving the highest barrier for propyl addition (conformation **2a**/**2b**/**2c**) is compared with the conformation giving the lowest barrier for 3CN-propyl addition (conformation **2e**), the penultimate unit effect is −2.1 kJ mol^{-1}. If, however, the conformation giving the lowest barrier for propyl addition (conformation **2d**/**2e**/**2f**) is compared with the conformation giving the highest barrier for 3CN-propyl addition (conformation **2c**), the penultimate unit effect is +5.8 kJ mol^{-1}. The penultimate unit effect can therefore vary over a range of 8 kJ mol^{-1}, depending upon the conformation of the transition structure in each of the reactions. Table 5 summarizes the net penultimate unit effects possible when the conformations giving the highest or lowest reaction barriers are combined in the reaction pairs. From Table 5, it is clear that for each of the reaction pairs studied a wide range of penultimate unit effects are possible, depending upon the transition structure conformation. Thus, the penultimate unit effect in the overall reaction will be governed by the relative occurrence of the individual reaction pathways (i.e., radical and transition structure conformations).

Finally, it is of interest to compare the penultimate unit effects we obtained previously for the model reaction involving fully extended radical (**1a**) and transition structure (**2a**) conformations with those based on the lowest (and hence most favorable) reaction barriers. These “model” penultimate unit effects, recalculated at the same level of theory as used in the present work so as to allow meaningful comparisons, are included in Table 5. From an examination of Table 5, it can be seen that the model penultimate unit effects differ significantly from those “preferred” penultimate unit effects based on the lowest reaction barriers (described as “low, low” in the table). In the addition of 3X-propyl radicals to CH_2=CHF, the gamma-F substituent exerts negligible penultimate unit effect in the model reaction but a small negative penultimate unit effect in the preferred reaction. In the addition of 3X-propyl radicals to CH_2=CHCN, the gamma-CN substituent exerts a large positive penultimate unit effect in the model reaction but a negligible penultimate unit effect in the preferred reaction. In the addition of 3X-propyl radicals to CH_2=$CHNH_2$, the gamma-CN substituent exerts a large negative penultimate unit effect in the model reaction and a still larger negative penultimate unit effect in the preferred reaction. The present results thus indicate that, on the basis of the most favorable reaction barriers, the penultimate unit can affect the reaction barrier, though the trends in the penultimate unit effects observed in the present reactions differ significantly from those that were previously reported for the fully extended conformations.

Discussion

In the present work, we have shown that the relative energies of the various possible conformations for gamma-substituted propyl radicals and the transition structures for their addition to alkenes are strongly dependent upon the nature of the penultimate unit, and thus the penultimate unit effect in the reaction barrier is strongly dependent upon the reaction pathway (i.e., the radical and transition structure conformations). There are three important consequences of these results for free-radical polymerization kinetics.

Importance of Direct Interactions. First, the dependence of the penultimate unit effect upon the transition structure conformation suggests that direct interactions involving substituents at the radical’s penultimate position and substituents on the monomer, mediated perhaps by the formally singly occupied orbital at the reaction center, may be contributing to the penultimate unit effect. This can be seen in the following arguments.

For each of the reactions studied in the present work, though there is some variation among the individual reactions, the lowest energy transition structure conformations are those gauche-addition transition structures in which the monomer substituent is close to both the gamma substituent of the propyl radical and the unpaired electron. Not only are these conformations significantly lower in energy than the corresponding fully extended conformations, but within a reaction pair they are also relatively lower for reactions of the gamma-substituted propyl radical compared with those of the propyl radical. Thus, while there is a large positive penultimate unit effect for the gamma-CN substituent in the addition of 3X-propyl (X = H, CN) radicals to CH_2=CHCN for the fully extended conformation, for the more crowded conformations the penultimate unit effect is negligible. While the penultimate unit effect for the gamma-F substituent in the addition of 3X-propyl (X = H, F) radicals to CH_2=CHF is negligible for the fully extended conformation, for the more crowded conformations there is a small negative penultimate unit effect. While there is already a large negative penultimate unit effect for the gamma-CN substituent in the addition of 3X-propyl (X = H, CN) radicals to CH_2=$CHNH_2$ for the fully extended conformation, for the more crowded conformations this negative penultimate unit effect is still larger in magnitude. The present results therefore indicate that, in the conformations in which the gamma substituent, monomer substituent, and unpaired electron are close together, the gamma substituent has a relative stabilizing effect on the reaction transition structure.

Given the importance of direct interactions involving monomer and radical substituents in determining the reaction barrier, it would seem that predictions of reaction barriers that are based solely upon the properties of the individual reactants may be subject to considerable uncertainty. For instance, in previous work[10,13] we showed that the relative magnitudes of the penultimate unit effects for fully extended conformations could be explained in terms of the properties of the individual reactants (such as the ionization energies and electron affinities of the radicals and monomers and the radical stabilization energies). On the basis of these properties, we predicted a negligible penultimate unit effect in the addition of 3X-propyl (X = H, F) radicals to $CH_2{=}CHF$, a large positive penultimate unit effect for the addition of 3X-propyl (X = H, CN) radicals to $CH_2{=}CHCN$, and a large negative penultimate unit effect for the addition of 3X-propyl (X = H, CN) radicals to $CH_2{=}CHNH_2$.[10] While these predictions hold for the conformations for which direct interactions between the monomer and radical substituents are unlikely (such as in conformation **2a**), when the substituents can interact (such as in conformations **2e** and **2f**) the penultimate unit effects differ significantly from these predictions. Not only does this highlight the possible danger associated with predicting penultimate unit effects solely from the isolated properties of the coreactants, it also suggests that predictions of monomer reactivity ratios based solely on the parameters for the isolated reactants (such as they are in the Q−e or Patterns schemes) may be likewise compromised by direct interactions between the coreactants. Furthermore, when direct interactions between the monomer and radical substituents are important, it seems unlikely that penultimate unit effects could be independent of the monomer with which they are directly interacting. Hence, these results would seem to further undermine the general applicability of the implicit penultimate model, an essential assumption of which is that the penultimate unit effect is independent of the reacting monomer.

Entropic Dependence of Overall Enthalpic Penultimate Unit Effects. Second, since the penultimate unit effect in the barrier for an individual conformation depends on the conformation of the transition structure, the penultimate unit effect on the overall reaction barrier will depend on the relative frequency factors for these individual pathways. This can be seen in the following arguments.

In general, the lowest energy pathway (i.e., corresponding to the addition of the lowest energy radical to the lowest energy alkene via the lowest energy transition structure) would be expected to dominate a reaction. However, provided they are close enough in energy to the lowest energy pathway, the other reaction pathways may also contribute significantly to the overall reaction—especially when they are favored entropically. In the reactions of the present work, several alternative transition structure conformations for a given reaction lie within 1−2 kJ mol^{-1} of their corresponding lowest energy conformations. Thus, depending on the frequency factors of the individual reaction pathways, many of these alternative pathways could participate in the overall reaction. Under such circumstances, the overall reaction barrier consists of a weighted average of the barriers for the individual reaction pathways, in which these individual pathways are weighted by the amount that they contribute to the overall reaction. An important consequence of this result is that, since the relative contributions of the alternative pathways depend on their frequency factors, the overall reaction barrier also depends on the frequency factors of the individual pathways.

In the present work, it was shown that the penultimate unit effect in the barrier varies significantly among the individual pathways. Given this, the penultimate unit effect in the overall barrier depends on the relative contribution of the different pathways to the overall reaction barrier. Now, as noted above, the contributions of the individual pathways to the overall reaction barrier will depend on both their relative frequency factors and their relative barriers. Therefore, the penultimate unit effect in the overall reaction barrier will also depend on the relative frequency factors for the individual pathways. Hence, if the relative frequency factors for the individual pathways depend on the reacting monomer, the penultimate unit effect in the overall reaction barrier will also depend on the reacting monomer. Even if the penultimate unit effect in the reaction barrier for every individual reaction pathway is independent of the reacting monomer, if the relative contributions of these individual pathways change with the reacting monomer, the penultimate unit effect in the overall reaction barrier will also change. Given this situation, it seems unlikely that implicit penultimate unit effects could be a general phenomenon in free-radical addition reactions.

Penultimate Unit Effects on Polymer Tacticity. Third, the dependence of the relative barriers for the different reaction pathways on the penultimate unit would suggest that the tacticity of the resulting polymer also depends on the nature of the penultimate unit. This may be explained as follows.

The polymerization of a monomer which bears two different substituents on the same vinylic carbon (for example $CH_2{=}CXY$, where $X \neq Y$) results in the formation of chiral centers at alternate carbons throughout the polymer backbone. The relative occurrence of the various possible sequences of the different stereoisomers that can be formed is known as the tacticity of the polymer and is determined by the relative contributions of the different transition structure conformations to the overall reaction. As noted above, the relative contributions of these different conformations are governed by their relative frequency factors and their relative reaction barriers. Since, as the present results indicate, the relative reaction barriers are affected by the penultimate unit, the tacticity of the resulting polymer is also affected by the penultimate unit. Thus, in a copolymerization, not only is there a penultimate unit effect on the rate of the propagation reaction but also there is a penultimate unit effect upon the stereochemistry of the resulting copolymer. Penultimate unit effects on copolymer tacticity have been detected experimentally. For instance, Yamamoto et al.[27] reported a penultimate unit effect on the tacticity of copolymers of vinyl acetate with vinyl pivalate.

The existence of a penultimate unit effect in polymer tacticity would have important consequences for analyzing the NMR spectra of copolymers. Information on the tacticity of the copolymer is frequently required in order to extract triad and pentad fraction data from NMR spectra. This information is typically contained in a single coisotacticity factor, which is assumed to be constant as a function of the composition of the given type of copolymer. However, if there is a penultimate unit effect on the tacticity of the copolymer, the tacticity of the polymer would clearly be dependent upon copolymer composition (being, as it is, dependent upon the nature of the penultimate unit). Under these circumstances, the sequence distribution information extracted from NMR spectra may be subject to considerable systematic error.

Conclusions

Our study of the gamma substituent effects in the barriers for the addition of various gamma-substituted propyl radicals to alkenes confirms our earlier findings that penultimate unit effects in the reaction barrier are possible. The penultimate unit effects observed are strongly dependent upon the conformation of the transition structure. On the basis of these results, it is shown that (1) direct interactions involving the monomer and radical substituents may play an important role in determining the penultimate unit effect in certain conformations; (2) the penultimate unit effect in the overall reaction barrier depends on the relative contributions of the individual pathways (i.e., radical and transition structure conformations) to the overall reaction, and thus upon both the relative frequency factors and the relative barriers for these individual pathways; and (3) the penultimate unit may influence the tacticity of the resulting polymer and, under such circumstances, the use of a composition-independent coisotacticity factor in the analysis of NMR spectra may be invalid. Finally, given (1) and (2) above, it is argued that the implicit penultimate unit effect in free-radical copolymerization seems unlikely to be a general phenomenon.

Acknowledgment. We gratefully acknowledge a generous allocation of time on the Fujitsu VPP300 and SGI Power Challenge computers of the Australian National University Supercomputer Facility, useful discussions with Dr. Hans Heuts and Dr. Tony Scott, support from the Australian Research Council, and the award (to M.L.C.) of an Australian Postgraduate Award.

Supporting Information Available: Tables (S1−S16) listing Gaussian archive entries, giving the geometries of all species considered in the present work, and showing their associated total energies. Also included (Table S17) is a comparison of the results obtained using QCISD and QCISD(T) energies to calculate absolute and relative reaction barriers in the addition of 3X-propyl (X = H, F) to CH_2CHF. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA990468Q