Theoretical Study of Ethylene−Vinyl Acetate Free-Radical Copolymerization: Reactivity Ratios, Penultimate Effects, and Relative Rates of Chain Transfer to Polymer

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ABSTRACT: Ab initio calculations (UB3LYP/6-31G(d)// UHF/6-31G(d)) and transition state theory on the title polymerization provide relative kinetic information which show the following: that the hexyl group adequately represents the polymer chain, that theory predicts experimental reactivity ratios with reasonable accuracy, that the penultimate unit effect is small for this copolymerization, that inverted addition to give vicinal diacetoxy units should increase dramatically with polymerization temperature, and that the most favorable short chain branching reaction gives butyl braches as well as 1-acetoxybutyl branches, provided that inverted addition reactions place the acetoxy group six and four carbon atoms from the radical site, respectively. For primary radicals, the absolute values of the computed Arrhenius *A* factors are believed to be reliable, but the activation enthalpies are about 2 kcal/mol too low, based on a set of calibration reactions used to test the quality of our theoretical methods.

Introduction

Using ab initio molecular orbital calculations to predict polymer kinetics and composition is challenging because of the large size of polymer molecules and the large number of different reactions a propagating polymer can undergo. In the case of free-radical copolymerizations, the different reactivity of the growing polymer chain toward two different monomer molecules, and the possibility of chain transfer reactions further complicate the picture. Despite these difficulties, progress has been made in the theoretical understanding of free radical polymerizations[1−3] and the more general problem of the addition of radicals to unsaturated centers.[4−7] Of particular interest are papers dealing with the prediction of polymer propagation rate coefficients,[8] on theoretical studies of penultimate effects in copolymerizations,[9,10] and on short chain branching.[11]

These papers conclude that Arrhenius *A* factors and activation energies, as deduced by utilization of transition state theory (TST), generally follow trends that are in accord with qualitative ideas regarding the entropy and enthalpy of activation. Reactants substituted with large, complex groups generally have lower *A* factors than smaller reactants due to the relatively large amount of reorganization of the groups that occurs as the transition state is formed, while reactants with substituents that can stabilize radicals in the transition state have lower activation energies than unsubstituted reactants. Importantly, these studies attach quantitative values to polymer reactions which would be impossible to obtain experimentally. An interesting feature of studies of this type is the microscopic detail that can be achieved. For example, by analyzing the contributions of individual rotational partition functions to the *A* factors for polymerization of methacrylonitrile and acrylonitrile, it was found[8] that the difference calculated for the *A* factors for the two polymerizations was due to only three rotations in the monomer reactants.

While this kind of detail is crucial for a complete theoretical understanding of polymerization reactions, we have taken a less comprehensive but we hope useful approach to the problem, by selecting key polymerization steps for a single type of copolymerization and analyzing structure−reactivity relationships. We have used molecular structure calculations as a tool for obtaining entropies and energies of activation, without paying particular attention to the various contributions the molecular partition functions make to the overall entropy change. We have also not made an extensive study of how the level of theory affects the outcome of our computations, because cost-effective theoretical techniques that deliver reliable geometries[2] and energies[4] have been worked out on a large number of systems, which we adopted for our polymerization. Ultimately, a tradeoff is made between the level of theory and the size of the system under study, where the highest levels of theory are impractical for large multiheavy atom systems, due to the prohibitive cost of the calculations.[12] We have chosen an industrially important polymer (polyethylene-*co*-vinyl acetate, EVA) and examined some of the polymerization reactions that occur during its manufacture, with the aim of understanding how acetoxy substituents affect propagation rates in the growing polymer and how chain transfer to polymer rate coefficients compare with the calculated propagation rate coefficients. This information could ultimately be useful in understanding EVA reactions in general, and more specifically in modeling reactors in which EVA and ethylene-*co*-vinyl alcohol (EVOH) are manufactured. Note that EVOH is made from EVA by base-catalyzed removal of the acetate groups (saponification). Models that explicitly include chain transfer kinetics could lead to methods and practices that help prevent the buildup of undesirable scale in EVA reactors. Scale is polymer residue that is formed by complicated physical and chemical processes during the

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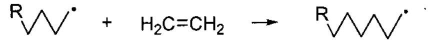
polymerization, which may be cross-linked by chain transfer reactions. The removal of scale is costly and involves lengthy reactor downtime.

The paper is organized as follows. The first part deals with propagation rate coefficients for ethylene and vinyl acetate copolymerization, which includes the mixed rate coefficients for ethylene-terminated polymer radical reacting with vinyl acetate, and the vinyl acetate-terminated polymer radical reacting with ethylene (eqs 1−4). These rate coefficients are then used to compute reactivity ratios. We have chosen polymer fragments, however, that also make it possible to consider the effects of penultimate groups.[9] Penultimate groups are functional groups that are attached to the polymer one polymer unit away from the reactive radical site; hence, in eq 5, the acetoxy group in the reactant radical is a penultimate group. Finding reactivity ratios that take into account penultimate groups involves the computation of rate coefficients for the four additional reactions shown in eqs 5−8. These reactivity ratios will bear directly on the penultimate model of polymer reactivity.[13]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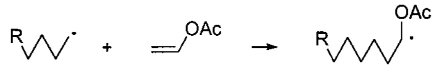
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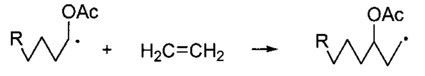
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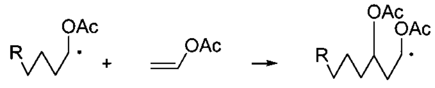
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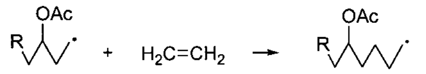
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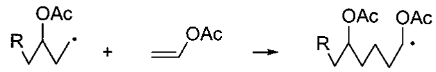
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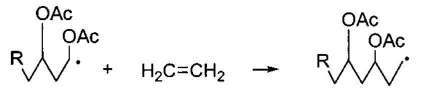
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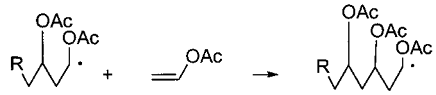
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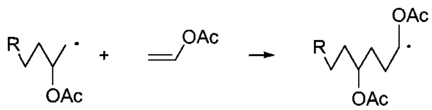
Next, we consider the inverted addition of vinyl acetate monomer to the growing polymer, since this is known to occur in vinyl acetate polymerization.[14] Equations 9 and 10 show the addition reactions that we consider in order to compare normal addition rate coefficients to inverted addition rate coefficients. Note that eqs 9 and 10 would give a 1,4-diol fragment and a 1,2-diol fragment (after saponification), respectively, which are the moieties attributable to inverted addition that can be detected by nuclear magnetic resonance (NMR) spectroscopy.[15] The rate coefficient for normal addition (eq 4 or 8) should be larger than the rate coefficients for inverted addition (eqs 9 and 10), since only about 2.4 mol % of polyvinyl acetate is formed from the inverted addition route.[14] This will provide an important test of the validity of our results. We do not consider penultimate effects in relation to inverted addition.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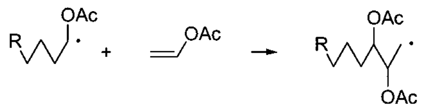
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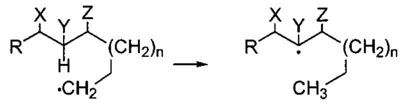
Finally, we examine chain transfer to polymer reactions that lead to short chain branching (SCB). SCB occurs during polymerizations when the radical at the end of the growing polymer intermolecularly abstracts a hydrogen atom from another site on the polymer, and the new radical center reacts with monomer units to produce a polymer chain at the branch point. The SCB reactions are shown in eqs 11−13, where X, Y, and Z are acetoxy groups or hydrogen, $n = 0$, 1, or 2, and R is an n-alkyl group such that the overall chain length is 12 carbon atoms long in eq 11. These fragments have been chosen on the basis of the favorable entropy associated with H atom transfers in small-ring transition states, balanced by the absence of strain in six- and seven-membered ring transition states (including the H atom in the ring).[16] Equation 11, $n = 0$, has been included to determine the effects of additional ring strain in the five-membered transition state on the relative rate. The rate coefficients for the analogous reactions leading to abstraction of an H atom from an acetyl group (eqs 12 and 13) are examined, since these rates should be competitive with the others, and this reaction is known to occur in vinyl acetate polymerizations.[17] This reaction is important industrially since the resulting branch point can be hydrolyzed away in the steps leading to EVOH.[18] For all the SCB reactions studied, reactants have been chosen such that the stabilizing effects of the acetoxy group on the newly formed radical products can be studied, and such that the correct ring size (either six- or seven-membered) is obtained in the transition states. The reactants have been chosen without regard to whether they themselves would have been formed from normal or inverted addition, but they have the same number of atoms so that their relative energies can be directly compared.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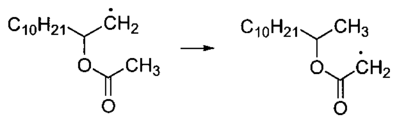
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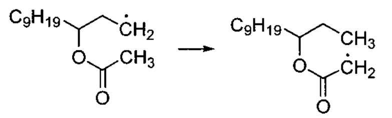
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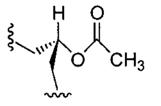
Theoretical Methods

Conformational and Stereochemical Analysis. The number of possible conformations that are energetically accessible at normal temperatures in long alkyl and substituted alkyl chains is enormous. In the reactions considered here, with the vinyl acetate monomer as reactant or already present in the polymer chain, the stereochemistry at the acetoxy carbon can also vary and give a number of stereoisomers. Prior to performing any calculations, it was necessary to arrive at reasonable criteria for constructing molecular models that could be used to generate starting geometries for the ab initio calculations. For each fragment, a model was constructed using the Chem3D program (CambridgeSoft Corp.), which made it possible to conveniently generate Cartesian coordinate input files for the Gaussian program. The elongated conformation was drawn, the stereochemistry of which could be controlled as the fragment was constructed, and its energy was minimized using Molecular Mechanics or AM1 software built into Chem3D. In this study, all reactants and products were in their lowest energy (elongated) conformation, and all the stereochemistry in the 1,3-substituted fragments was isotactic. Regarding the orientation of the acetoxy group with respect to the alkyl chain or the vinyl group, it was found that the lowest energy conformations (using AM1 calculations) had the carbonyl oxygen atom nearly eclipsing the H atom on the carbon atom to which the acetoxy group was attached, whether the carbon atom was part of an alkyl chain or a vinyl group. Hence, all acetoxy groups in this study were attached to other molecules as shown in **1** and **2**.



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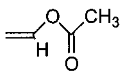

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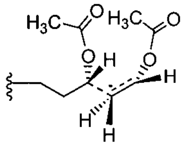
Transition States. Transition state searches were performed by using reasonable approximated geometries generated in Chem3D. In most cases, the incoming ethylene or vinyl acetate in the transition state approached the radical reactant in an elongated (anti) conformation, such that the incoming vinyl group had to undergo minimal relative motion to form the product radical. An example of an anti conformation is shown in the transition state for eq 4 in structure **3**. For the case of a vinyl acetate-terminated radical reacting with ethylene, it was found that the calculations would not converge unless the initial geometry of the transition state had a gauche conformation, as shown in structure **4**. This transition state geometry was found for eqs 3 and 7.



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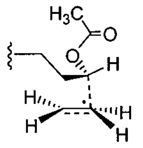

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Transition states for H atom transfers were approximated by performing ab initio calculations on initial geometries using the "opt=addredun" keyword in the Gaussian input file, by placing the H atom midway between the relevant C atoms and setting the C−H bond lengths to 1.35 Å. This forced the molecule to adopt the cyclic transition structure, whose Cartesian coordinates were used as inputs for the transition state search for the saddle point geometry.

The main criterion used in determining whether true transition states were obtained for each reaction was the presence of a single imaginary frequency in the output file of the appropriate magnitude.[19] Secondarily, the transition states were viewed in Chem3D to make sure they had reasonable structures.

Theory. Molecular orbital calculations were performed using the Gaussian 98 suite of programs.[20] All reactant, transition state, and product geometries were optimized at the UHF/6-31G(d) level of theory, and entropies were obtained using unscaled frequencies for reactants and transition states at this level as well. Energies were obtained for the optimized geometries using density functional theory (DFT) at the UB3LYP/6-31G(d) level.

Table 1. Arrhenius *A* Factors and Activation Enthalpies for Addition of Acetoxy Radical to Ethylene and Subsequent Addition of Substituted Ethyl Radicals to More Ethylene

ethylene units[a]	log A[b]	$\Delta H^{\ddagger}$ (kcal/mol)
1	8.97	4.65
2	7.92	5.04
3	7.68	5.08
4	7.68	5.13
6[c]	7.71	5.05

[a] The product radical for one ethylene unit is $AcOCH_2CH_2^{\bullet}$, for two ethylene units, it is $AcOCH_2CH_2CH_2CH_2^{\bullet}$, and so on. [b] Units of A for these and all other bimolecular reactions in this work are M^{-1} s^{-1}. [c] Product radical = 1-dodecyl.

Transition state theory was used to utilize the entropies and enthalpies of activation to obtain Arrhenius *A* factors and rate coefficients for the reactions, as shown in eq 14 ,[21] where **k** is

$$k = \mathbf{k}T/h \exp(\Delta S^{\ddagger}/\mathrm{R}) \exp(-\Delta H^{\ddagger}/RT) \tag{14}$$

the Boltzmann constant, T is the temperature, and h is Planck's constant. For all reactions, the electronic energies obtained from single point UB3LYP calculations on the UHF geometries was corrected by the recommended thermal and zero point energy corrections[22] to obtain the enthalpies of reaction leading to transition states. Overall reaction enthalpies were also obtained this way. Conversion from gas-phase units (partial pressures), as obtained from the Gaussian program, to condensed phase units (molarity) was accomplished as explained by Benson.[23] Solvent effects were not considered. It is important to stress that only relative kinetic data are reported here, and calibration reactions (i.e., ethyl on ethylene) suggest that the calculated results vary systematically from true experimental numbers. Hence, the reported kinetics are useful for understanding structure−reactivity relationships for EVA polymerization, as well as for use in models in which key rate coefficients, such as propagation rate coefficients,[24] are obtained from experimental data.

Results and Discussion

Choice of Polymer Fragments. At the outset of this work, a primary goal was to establish computationally how the reactivity of the polymer changed as the polymer chain length grew, with an aim being to determine how large a molecule would be needed to model the polymer chain adequately. To this end, results were obtained for the acetoxy radical adding to ethylene, and for the resultant radical adding to successively more ethylene units, up to a chain length of eight carbon atoms (four ethylene units). It was found that the largest *A* factor and the lowest activation energy were calculated for the addition of the acetoxy radical to ethylene, and that subsequent additions had very nearly the same *A* factors and activation enthalpies. Small changes were noted as the chain length grew, as can be seen in Table 1. From Table 1, it was concluded that when a 1-butyl radical (three ethylene units in the product) or 1-hexyl radical (four ethylene units in the product) adds to an ethylene molecule, it makes little difference what is attached at the ω position on the alkyl radical chain, whether it is an acetoxy group or a 2-acetoxyethyl group, since nearly the same Arrhenius parameters were found.

Other theoretical work on free radical polymerization has taken the approach that a polymer chain can be modeled by single atom of very high mass.[8] We felt that some of the entropy change associated with polymeri-

Table 2. Comparison of Theory (UB3LYP/6-31G(d)//UHF/6-31G(d)) and Experiment for Calibration Reactions

	this work		experiment^a	
reaction	log A	ΔH	log A	ΔH
methyl + E	8.1	4.74	9.3	7.51
ethyl + E^b	7.75	5.30	8.2	7.3
tert-butyl + E	6.25	5.78	7.9	6.60
hydroxymethyl + E	8.14	4.63	7.9	7.27
methyl + VA	8.25	4.12	7.4	4.52
ethyl + VA^b	7.88	4.70	7.89	6.9
tert-butyl + VA	6.43	5.19	7.2	4.90
hydroxymethyl + VA	8.33	4.21	7.7	6.60

[a] Key: methyl, ref 25; ethyl, ref 28; *tert*-butyl, ref 26; hydroxymethyl, ref 27. [b] Gas phase. For a discussion of the relatively small differences observed for gas and liquid-phase reactions, see ref 4.

Table 3. Geometries, Arrhenius *A* Factors, Activation Enthalpies, Calculated Rate Coefficients, and Reactivity Ratios for the Reactions Found in Eqs 1−8, Where 1 = Ethylene and 2 = Vinyl Acetate

eq	PU^a	geometry^b	log A	$\Delta H^‡$ (kcal/mol)	k_{298} (M^{-1} s^{-1})	r_1	r_2
1	1	0.0 (109.7)	7.71	5.05	9800		
2	1	0.6 (110.2)	7.84	4.28	48000	0.20	
3	1	116.1 (109.4)	7.30	4.46	10000		
4	1	27.8 (110.7)	6.80	3.82	9700		0.97
5	2	2.1 (109.5)	8.37	5.74	14000		
6	2	1.9 (110.0)	8.45	5.18	43000	0.32	
7	2	117.4 (109.5)	6.61	4.00	4600		
8	2	33.8 (111.1)	6.14	3.52	3500		0.76

[a] PU = penultimate unit. [b] Dihedral angle (C- - -C=C angle), both in degrees.

zation reactions could be manifested in low frequency rotations in the alkyl chain. Therefore, the hexyl group was chosen to model the polymer chain, on the grounds that it is long enough that its fragments would show reactivity essentially identical to that of fragments composed of longer chains, and hexyl-based fragments are not so large that they cannot be treated computationally at reasonable cost. To produce the fragments found in eqs 1−13, other monomer units (ethylene or vinyl acetate) were appended onto the hexyl chain, as appropriate. The simplest such fragments can be seen in eq 1, and the kinetic parameters for this reaction are also included in Table 1. It can be seen that the longer alkyl chain has little effect on the kinetic parameters. However, we have kept the hexyl part of the molecules throughout this study, to be able to compare reactions using the same fragment size as a model for the polymer.

Calibration. Because of the size of the fragments in this study, use of very high levels of theory for the determination of geometries and energies was impractical, due to the expense of the calculations. It is therefore appropriate to consider the accuracy of our calculations. To do this, we have compared computed Arrhenius parameters to experimental literature values for model reactions involving four different radicals reacting with ethylene or vinyl acetate. These reactions were chosen because most of their kinetic parameters have been recently measured,[25−28] and because the radicals bear some resemblance to the radicals in eqs 1−8. Since our goal is to obtain reactivity trends for the title polymerization, we have compared our computational results to the literature values, with the aim of determining whether there are systematic corrections that we can apply to our computational results.

In Table 2 are collected data for the calibration reactions. It can be seen that for the ethyl and hydroxymethyl reactions, the *A* factors are computed with reasonable accuracy, while the *A* factors for the methyl and *tert*-butyl reactions are off by close to an order of magnitude. For the activation enthalpies, the computed ethyl and hydroxymethyl values are low by 2.0−2.6 kcal/mol (average 2.3), while the scatter is worse for the other radicals. These results suggest that there is a systematic error in our calculations for primary radicals (excluding methyl) close to 2 kcal/mol low for the activation energy for their addition to ethylene or vinyl acetate. The electronic influence of oxygen lone pairs on the radical center in hydroxymethyl is reasonably predicted by our level of theory, making it likely that similar predictions will hold for the acetoxy substituted radicals in the polymerization. Unfortunately, the vinyl acetate-terminated polymer units are secondary radicals, and experimental values are not available for calibration purposes.[29] This leaves open the important question of whether the *A* factors and activation enthalpies for the secondary radicals in this work will follow the same trends as the primary radicals, with regard to accuracy and systematic errors. Nevertheless, the values in Table 2 suggest that relative reactivity can be computed for primary radicals reacting with ethylene and vinyl acetate. For more substituted radicals, the *A* factors become less accurate while the activation energies are off by less than 2 kcal/mol, suggesting that the polymerization reactions considered here involving secondary radicals may have less accurate *A* factors and activation energies that need to be corrected by less than 2 kcal/mol. Thus, we feel confident making reactivity comparisons within a structurally related group of reactions only.

Geometries. The dihedral angles for the transition states found for eqs 1−8 are found in Table 3 along with the bond angles defined by the carbon atom bearing the incoming radical and the vinyl carbon atoms. Note that a dihedral angle of 0° and a C- - -C=C angle of 109.5° have been found computationally for the transition state of the methyl plus ethylene reaction.[4] For reactions 4 and 8, the transition states are in anti conformations (see structure **3**), with the vinyl acetate rotated such that its acetoxy group is rotated away from the acetoxy group on the radical. For reactions 3 and 7, the transition states are in gauche conformations (see structure **4**), with the ethylene rotated toward the acetoxy group of the incoming radical. Low-energy gauche transition states have been found computationally for other radical additions to vinyl compounds,[9] although not for simple ethylene reactions.

Reactivity Ratios and Penultimate Effects. The reactivity ratios for ethylene-vinyl acetate copolymerization have been measured by a number of workers, as listed in ref 30. These values are collected from the literature dating from 1963 to 1979 and vary from $r_1 =$ 0.13 to 0.88 and $r_2 =$ 0.72 to 3.74, where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, and the subscripts refer to the type of monomer unit at the radical end of the polymer chain and the reactant monomer (1 for ethyl, 2 for vinyl acetate in this case). Reactivity ratios are sensitive to reaction temperature, pressure and media, which accounts in part for the broad range reported. More recent high pressure (2000 atm, ca. 200 °C) terpolymerization results [31,32] place the value of r_1 close to 0.9 and the value of r_2 in the range 0.9−1.7.

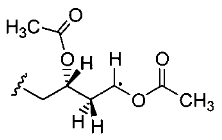
Using computational data for the polymer fragments in eqs 1−8, we were in a position to compute reactivity

Table 4. Reactivity Ratios at Various Temperatures for Ethylene−Vinyl Acetate Co-Polymerization, Where 1 = Ethylene and 2 = Vinyl Acetate

T (°C)	r_1	r_2	ref
60	0.16	1.12	33[a]
80	0.18	1.05	33
135	0.49	1.02	33
not reported	0.16	0.72	30[b]
60	0.23/0.36[c]	0.83/0.70	this work
80	0.25/0.37	0.79/0.67	this work
135	0.29/0.42	0.70/0.61	this work

[a] Pressure = 100 atm of ethylene. [b] Recalculated. [c] The first value has the penultimate unit (PU) = ethylene, the second value has PU = vinyl acetate.

ratios which also explicitly included penultimate effects. These data are reported in Table 3, from which it can be seen that the reactivity ratios, calculated for room temperature, fall within the range of reported values for EVA polymerization. While the differences seen for r_1 and r_2 in going from the penultimate group being ethyl to vinyl acetate might suggest there is a small penultimate effect for this polymerization, it is interesting to note that the rate coefficients for eqs 7 and 8 fall by more than a factor of 2 compared to eqs 3 and 4, while the same comparison for eqs 1 and 2 vs eqs 5 and 6 reveal that these rate coefficients are within 30% of each other. Upon closer inspection, the similarity in the reactivity ratios seen in Table 3 is the result of the penultimate acetoxy group having the same relatively large effect on the A factor for reactions 7 and 8, in which the penultimate acetoxy group is next to the acetoxy group linked to the radical center in the reactant. Since the activation enthalpy actually drops (eqs 3 and 4 compared to eqs 7 and 8), the drop in the rate coefficients is all due to the drop in the A factor, suggesting that there is a strong entropic effect, relating to the alignment of the carbonyl dipoles in the more ordered transition state as compared to the reactants. This is clearly seen upon examination of the Gaussian output geometries in the ground-state radical reactants (carbonyl groups not aligned), compared to the transition states (carbonyl groups aligned). These structures are diagramed in **5** (reactant radical) and **6** (transition states, X = H or OAc). Clearly, the terminal acetoxy group in **5** must swing out of the way and align itself with the penultimate acetoxy group in the transition state for the reaction to proceed. This alignment contributes to the large negative entropy of activation (small A factor) for eqs 7 and 8.



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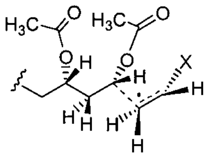

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A more detailed examination of the reactivity ratios in the literature reveals that r_1 and r_2 in Table 3 compare most favorably with the data of Ratzsch et al.,[33] work that involved measuring EVA polymer composition at early reaction times in the absence of solvent at various temperatures and pressures. The relevant reactivity ratios are collected in Table 4, along with data for eqs 1−8 using rate coefficients that were computed from the Arrhenius A factors and activation enthalpies in Table 3 at the temperatures indicated. It is of some interest to note that the temperature trends observed in the literature are reproduced by our results, although the absolute values of the reactivity ratios are off by a considerable amount, up to 70%. This is probably due in part to the fact that our calculations are for gas-phase reactions at 1 atm and also due to the uncertainty in the quality of our geometry optimizations at the relatively low level of theory used here.

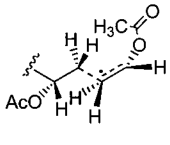
Table 5. Arrhenius A Factors, Activation Enthalpies, and Calculated Rate Coefficients at Room Temperature and at 135 °C for the Inverted Addition Reactions Found in Eqs 9 and 10

eq	log A	$\Delta H^{\ddagger}$ (kcal/mol)	k_{298} (M^{-1} s^{-1})	k_{408} (M^{-1} s^{-1})
9	7.84	4.51	33000	260000
10	6.88	11.4	0.031	5.9

Two conclusions can be drawn: our computational data reproduce the reported reactivity ratios reasonably well, and the acetoxy group exerts a small enough penultimate effect that it can probably be ignored when one considers the range of measured reactivity ratios in EVA.

Inverted Addition. As early as 1948,[14] it was discovered that inverted addition occurs in the polymerization of vinyl acetate. More recent work has further characterized the different groupings that occur in the inverted portions of the polymer. Specifically, NMR data[15] has shown that coupled 1,2- and 1,4-diol structures exist in polyvinyl acetate and in EVA with ethylene contents up to 13 mol %. For higher ethylene mole fractions, the authors see only 1,4-diol structures, which they attribute to the intervention of an ethylene unit between a normal vinyl acetate unit and an inverted vinyl acetate unit.

The results of our calculations are shown in Table 5. The dramatically different Arrhenius parameters for the two reactions must be attributed to the profound influence of the acetoxy substituent on the stability of the transition state for eq 10, since eq 9 is close to “normal,” in that it involves an unsubstituted terminal radical reacting with vinyl acetate, and eq 10 has a “normal” A factor, but a dramatically higher activation enthalpy, for an acetoxy substituted radical reacting with vinyl acetate. These results can be seen clearly by comparing the Arrhenius parameters of eq 9 to those of eqs 2 and 6, and by comparing those of eq 10 to those of eqs 3 and 7. The transition states for eqs 9 and 10 are diagramed in structures **7** and **8**, respectively, which show the orientations of the acetoxy groups, and emphasize that the radical can be delocalized into the acetoxy group in **7** but that the radical cannot be delocalized to the same extent into the acetoxy group in **8**, because the carbonyl group is rotated out of the plane of the vinyl group, which was seen upon examination of the Gaussian output geometry in Chem3D. Thus, to the extent that vinyl acetate is conjugated in eq 9 in both the ground state and **7**, this stabilization energy is preserved throughout the reaction, and a relatively low barrier to reaction is found. In contrast, ground-state vinyl acetate



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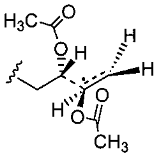

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Table 6. Arrhenius *A* Factors, Activation Enthalpies, Reaction Enthalpies, and First-Order Room Temperature Rate Constants for the SCB Reactions Found in Eqs 11−13

entry	eq	transn state ring size	X, Y, Z, *n*	log *A*	$\Delta H^{\ddagger\,a}$	ΔH_{reacn}	k_{298} (s^{-1})
1	11	5	H, OAc, H, 0	10.85	19.9	−3.8	0.00037
2	11	6	H, OAc, H, 1	10.24	16.6	−4.9	0.010
3	11	7	H, OAc, H, 2	9.83	16.4	−4.8	0.0057
4	11	6	OAc, H, H, 1	10.40	13.5	−4.0	2.9
5	11	6	H, H, OAc, 1	10.67	13.3	−2.9	7.6
6	12	6	n/a	11.01	20.9	−5.6	0.000042
7	13	7	n/a	10.71	19.8	−4.3	0.00014

[a] Enthalpies in kcal/mol.

still enjoys stabilization via delocalization in eq 10, but the reduced delocalization in the transition state results in a higher barrier for the reaction.

It is important to note that **8** would lead to a nonisotactic polymer. An input orientation similar to **8** was chosen to minimize steric enthalpy barriers to reaction which would have undoubtedly been significant had a transition state been found that led to isotactic product (that is, with both acetoxy groups on the same side of the chain). Also, the absence of conjugation in **8** would suggest this is a late transition state, in contrast to the rest of the exothermic additions, which would be expected to have early transition states.

The observation in the literature that 1,2-diol units are coupled to 1,4-diol units is significant in the context of the calculated rate coefficients in Table 5. Namely, the slow formation of 1,2-diacetoxy units via eq 10 gives the reactive inverted product radical, which has the same structure in the vicinity of the radical as the reactant radical in eq 9. The inverted product radical would react with vinyl acetate rapidly, with a rate coefficient similar to that for eq 9, to give the 1,2-diacetoxy unit coupled to the 1,4-diacetoxy unit. Note that if the reactivity of the system were reversed (that is, eq 10 faster than eq 9), or if the rate coefficients were about equal for these two reactions, then one would expect to see isolated 1,2-diol units in poly(vinyl alcohol), in disagreement with experiment.

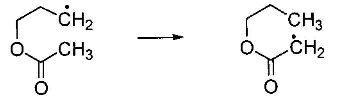
The same caution as mentioned earlier regarding the magnitude of the differences for the values in Table 3 also applies here, that neglect of solvent effects and pressure, and the quality of the energy calculations, probably influence our results. It is notable, however, that the ratio of the rate coefficients in Table 5 drops from $k_9/k_{10} = 10^6$ at room temperature to $k_9/k_{10} = 10^{4.6}$ at 135 °C, suggesting that more inverted addition should be observed at higher temperatures for this polymer.

Chain Transfer to Polymer. The literature on chain transfer to polymer in the poly-vinyl acetate and EVA systems is somewhat contradictory. For chain branching in EVA, it has been found by some authors [16,18] that H atom abstraction from acetoxy-substituted carbon atoms in the polymer does not occur, while others[17] have observed branching at these tertiary sites (but not at methylene sites) in poly(vinyl acetate).

Our results for SCB reactions in eqs 11−13 are collected in Table 6. These results can be compared to theoretical work on ethylene SCB,[11] which found *A* factors higher than ours using shorter chains at the same level of theory. This suggests that including longer chains to model the polymer could be important for the theoretical prediction of *A* factors. The reactant radicals all had ground-state energies within 0.3 kcal/mol of each other, indicating that the position of the acetoxy group had little effect on the stability of the 1-dodecyl radical, as expected. It can be seen that the overall exothermicities of the reactions do not vary greatly, making it difficult to evaluate the relative stabilities of the product radicals in eqs 11−13. However, the situation is different for the kinetic parameters. For entries 1−3, as the ring size in the transition state increases, the *A* factors drop, reflecting the less favorable entropy of activation in the larger ring transition states. At the same time, the enthalpy of activation is greatest for the smallest ring transition state, indicating there is more strain in the five-membered ring transition state. For the six- and seven-membered ring transition states, the enthalpy of activation is about the same for the two reactions, but the higher *A* factor for the six-membered transition state results in the largest rate coefficient for entry 2 among entries 1−3.

Comparison of entry 2 to entries 4 and 5 shows that while the overall exothermicity for transfer of an H atom from an acetoxy-substituted carbon atom to the terminal position is somewhat greater than for an unsubstituted site, the barrier for the latter reactions (entries 4 and 5) is very much less. The *A* factors are about the same for all three reactions, which would be expected for reactions that all have the same size ring in the transition state. The resultant rate coefficients are much greater for entries 4 and 5, consistent with the authors who do not observe chain branching from tertiary sites. The large rate coefficient found for entry 4 is consistent with the predicted formation of butyl branches in EVA,[34] but entry 5 would give a 1-acetoxyl butyl branch, which may be difficult to identify by NMR.[16] The small rate coefficient for entry 2 can be understood in terms of the greater steric barrier that would exist for this reaction, in which the terminal radical site must approach the tertiary site bearing the relatively bulky acetoxy group. We note that for vinyl acetate homopolymerizations in which normal addition occurs, the terminal radical will have an acetoxy group attached to it, making its approach to the tertiary H atom in the six-membered transition state even less favorable. However, it should be noted that both butyl and 1-acetoxybutyl branch formation require inverted additions to place the acetoxy group on the appropriate carbon atom for entries 4 and 5.

The reactions in which hydrogen atoms are transferred from acetoxy groups via SCB (entries 6 and 7) have normal *A* factors, but much larger enthalpies of activation compared to the other reactions in Table 6. This difference is difficult to rationalize, since there do not appear to be significant steric barriers to reaction. It would appear that the carbonyl group destabilizes the radical in the transition state. To test this, we performed higher level optimizations on a simpler model reaction, shown in eq 15. The transition state geometry was optimized at the UHF/6-31G(d) and the UB3LYP/6-31G(d) level; the higher level optimization lowered the energy of the reactant, the transition state, and the product by close to the same amount (ca. 2.0 kcal/mol), indicating that the UHF optimization was able to compute the relative delocalization energy as well as



(15)

the DFT method. Preliminary results on H atom abstraction via an eight-membered transition state indicate that the activation enthalpy of the reaction does not drop as the ring size increases, suggesting that unusual ring strain from the sp^2-hybridized carbonyl carbon or the ester group in this system is not a major factor. Hence, no satisfactory explanation emerges for the high activation enthalpies for entries 6 and 7 at these levels of theory. Solvent effects could play a significant role in the stabilization of the transition state in this case, due to the close proximity of the polar carbonyl group to the radical center.

It is appropriate to consider briefly the effects of quantum mechanical tunneling on the SCB reactions. Generally, hydrogen atom tunneling becomes significant at low temperatures (up to room temperature) and when barriers are large for hydrogen atom transfer reactions.[35−37] Hence, tunneling is probably significant for SCB reactions. While tunneling will probably increase the absolute SCB rates, and therefore the relative amount of SCB observed over propagation in EVA, it should have the same relative effect on the reactions shown in Table 6. In this case, the above conclusions remain unaltered. On the other hand, there is the possibility that tunneling will have a leveling effect on all of the SCB reactions, and cause all of the rates to become competitive. In this case, hydrogen atom abstraction from the tertiary site (entry 3, Table 6) could predominate, in agreement with some experiments.[17]

Conclusion

We have performed ab initio calculations on a variety of radical fragments that undergo chain propagation and chain transfer to polymer reactions for the copolymerization of ethylene and vinyl acetate. Polymer reactivity can be adequately modeled using a hexyl group to represent the polymer chain. Reactivity ratios for EVA are reproduced by our computations, and show that there is a relatively small penultimate unit effect, if any, for this copolymerization. Inverted addition to give 1,2-diacetoxy units occurs very slowly according to our calculations, and we predict that the extent of inverted addition should increase dramatically with temperature. Short chain branching should be most pronounced for abstraction of a hydrogen atom next to an acetoxy group, to give butyl and 1-acetoxybutyl branches, provided that inverted addition reactions place the acetoxy group six and four carbon atoms from the radical site, respectively. Finally, for primary radicals in this study, the computed A factors are believed to be reliable, while the activation enthalpies for the addition reactions are about 2 kcal/mol too low, based on calibration reactions determined at the level of theory we used for the large fragments in this work. These kinetic parameters, utilizing corrected activation enthalpies, can be used in more elaborate models for EVA polymerizations. However, the difficult job reconciling all of the factors that influence polymerization kinetics, such as reaction vessel inhomogeneities, long chain branching, and hydrogen atom tunneling, remain.

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