Accurate ab initio prediction of propagation rate coefficients in free-radical polymerization: Acrylonitrile and vinyl chloride

Ekaterina I. Izgorodina, Michelle L. Coote *

Research School of Chemistry, Australian National University, Science Road, Canberra, ACT 0200, Australia

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Dedicated to Professor Noel Hush on the occasion of his 80th birthday

Abstract

A systematic methodology for calculating accurate propagation rate coefficients in free-radical polymerization was designed and tested for vinyl chloride and acrylonitrile polymerization. For small to medium-sized polymer systems, theoretical reaction barriers are calculated using G3(MP2)-RAD. For larger systems, G3(MP2)-RAD barriers can be approximated (to within 1 kJ mol\(^{-1}\)) via an ONIOM-based approach in which the core is studied at G3(MP2)-RAD and the substituent effects are modeled with ROMP2/6-311+G(3df,2p). DFT methods (including BLYP, B3LYP, MPWB195, BB1K and MPWB1K) failed to reproduce the correct trends in the reaction barriers and enthalpies with molecular size, though KMLYP showed some promise as a low cost option for very large systems. Reaction rates are calculated via standard transition state theory in conjunction with the one-dimensional hindered rotor model. The harmonic oscillator approximation was shown to introduce an error of a factor of 2–3, and would be suitable for “order-of-magnitude” estimates. A systematic study of chain length effects indicated that rate coefficients had largely converged to their long chain limit at the dimer radical stage, and the inclusion of the primary substituent of the penultimate unit was sufficient for practical purposes. Solvent effects, as calculated using the COSMO model, were found to be relatively minor. The overall methodology reproduced the available experimental data for both of these monomers within a factor of 2.

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1. Introduction

Radical polymerization processes are complex processes involving many different reactions [1]. Even in a simple homopolymerization, initiation, propagation, and termination steps occur, and in the majority of systems the propagating species may also undergo a variety of chain transfer processes. In more complex systems, such as copolymerization or controlled radical polymerization, the process might involve as many as 20 or more (kinetically distinct) chemically controlled reactions, not to mention the chain length dependent termination reactions. The absolute and relative rates of these individual steps govern the overall rate of polymerization, and the molecular weight, chain architecture, and (in copolymerization) composition and sequence distribution of the resulting polymer. The ability to measure the rates of these individual reactions, and study their mechanisms and structure-reactivity relationships, is extremely important, as it allows us to develop better kinetic models and (ultimately) better methods for controlling free-radical polymerization.

Owing to its complexity, the measurement of the rate coefficients of the individual reactions in radical polymerization processes is not straightforward. In recent years, the development of techniques such as pulsed-laser polymerization (PLP) and single-pulse PLP has made possible the measurement of the individual rate coefficients for the prin-
principal reactions in a simple free-radical homopolymerization in a relatively model-free manner [2–5]. However, a number of problems remain. Even in homopolymerization, the direct measurement of the individual rate coefficients may be hampered if, for example, there is a large degree of chain transfer to monomer, or if the monomer absorbs significantly at the wavelength of the PLP experiments. In more complex situations, such as copolymerization or controlled radical polymerization, the inclusion of additional reactions in the kinetic scheme renders the direct (i.e., model-free) measurement of the individual rate coefficients difficult, if not impossible. This situation is exemplified by the recent controversy surrounding the causes of rate retardation in RAFT polymerization. At the center of this controversy are alternative experimental values for the fragmentation rate coefficient in cumyl dithiobenzoate (CDB) mediated polymerization of styrene at 60 °C that differ by six orders of magnitude, a discrepancy that arises (at least in part) in the alternative model-based assumptions implicit in their measurement [6–9]. Likewise, in free-radical copolymerization, the rates (and associated reactivity ratios) of the individual types of propagation reaction cannot be measured directly, and are instead estimated by fitting some assumed kinetic model to the available experimental data. As a result, any number of kinetic models can be fitted to the same experimental data, and model discrimination is not always possible [10].

Computational quantum chemistry offers a potential solution to this problem, as it allows the individual reactions within a complex process to be studied directly, without recourse to empirical data (other than the fundamental physical constants) or model-based assumptions (other than the laws of quantum mechanics) [11]. Moreover, quantum chemistry also provides access to useful related data (such as radical stabilization energies, charge distributions and transition state geometries) that can assist in the interpretation of the results. However, quantum chemistry is not without its own problems. As is well known, the many-electron Schrödinger equation has no analytical solution, and in order to solve it, various numerical approximations need to be made. Although accurate methods exist, these are computationally intensive and their computational cost scales exponentially with the size of the system. Thus, although “chemical accuracy” has been achieved for small molecules using high-level composite procedures such as W1 and G3 [12–14], these procedures cannot be practically applied to large polymeric molecules. In order to study polymeric systems, one needs either to adopt less computationally intensive methods and/or to model the polymeric propagating radical using much smaller species. These approximations are a potentially significant source of error.

Despite these problems, computational chemistry has already made some important contributions to our understanding of radical polymerization. For instance, high-level ab initio molecular orbital calculations of small prototypical systems have provided an insight into the mechanism of radical reactions such as addition to C═C bonds [15,16], C═S bonds [17,18], hydrogen atom abstraction reactions [19–21], and bond dissociation energies and associated radical stabilities [22,23]. The mechanistic insights from these studies are applicable, at least in a qualitative manner, to the polymeric versions of these reactions (e.g., propagation, addition fragmentation in the RAFT process, chain transfer), and indeed more directed studies of model polymeric systems have been used to identify reaction mechanisms and model and interpret structure–reactivity trends in conventional and controlled radical polymerization processes [6,24–47]. Quantum-chemical studies have, among other things, provided evidence for the penultimate unit effect in free-radical polymerization [26,29–31], identified a new fragmentation pathway in RAFT polymerization [38], and recently led to the first computer-designed RAFT agent [43,48].

To date, these successful applications of quantum chemistry in free-radical polymerization have been largely restricted to situations in which qualitative mechanistic information, (such as accurate geometries and reasonably accurate relative values of rate and equilibrium constants), is sufficient for practical purposes. However, with recent and continuing increases in computer power, and the concurrent development of efficient algorithms and methods, the prediction of accurate absolute rate and equilibrium constants is now within reach. This offers the exciting prospect of using computational chemistry as a substitute for experiment, in situations where the model-free measurement of individual rate coefficients is difficult, dangerous or impossible. However, it is first essential to develop a well-defined, practical methodology for modeling polymerization rate coefficients, and demonstrate through systematic studies that the predictions are not only accurate, but yield “the right answer for the right reason”.

The first systematic attempts to predict accurate absolute rate coefficients in free-radical polymerization date to the mid-1990s when Heuts et al. studied the propagation of ethylene [24,25]. They suggested rate coefficients could be calculated via simple transition state theory, provided the low frequency torsional modes were treated as simple one-dimensional hindered internal rotations. More recently, the accuracy of this one-dimensional approach has been verified by Van Speybroeck et al., who compared the calculated rate coefficients for radical addition reactions (and also the heats of formation of n-alkanes) under this model with a more accurate two-dimensional method [49,50]. In their original work, Heuts et al. [24,25] studied the chain length dependence of the calculated propagation rate coefficient, showing that it had largely converged by hexyl radical stage, and that convergence to the long chain limit could be induced at the propyl radical stage if a gamma-hydrogen were to be replaced with a “heavy hydrogen”, having a mass of 9999 amu. This work offered hope that the kinetics of propagation reactions could indeed be studied using relatively small models of the propagating radical. However, the ethylene system represents a rather special case, since the polymeric chain lacks substituents
that might affect the barrier height and the various rotational potentials associated with the low frequency torsional modes. Moreover, one might expect ethylene to be much less sensitive to the selected level of theory than substituted monomers (such as styrene or acrylonitrile) in which the radical is highly delocalized.

More recently, studies of substituted monomers have been published. For instance, Huang et al. [27] calculated the propagation rate coefficients of acrylonitrile and methacrylonitrile using a "heavy" unimer. They noted that the frequency factor of methacrylonitrile showed excellent agreement with experiment, but the barrier was highly sensitive to the chosen level of theory. Although at the highest level of theory the barrier was in reasonable agreement with experiment, the authors noted that this agreement may have been fortuitous, given that the highest level of theory considered was only QCISD/6-31G(d). These concerns are indeed justified when the data for the other monomer in their study, acrylonitrile, are compared with a more recent experimental study of this system at 75 °C [51]. Using the Arrhenius parameters of Huang et al. [27] the calculated propagation rate coefficient is just 12 L mol$^{-1}$ s$^{-1}$ at 75 °C, the corresponding experimental value is over 2 orders of magnitude greater at 5.30 × 10$^5$ L mol$^{-1}$ s$^{-1}$ (for the unimer, or 4.60 × 10$^3$ L mol$^{-1}$ s$^{-1}$ for the long chain limit) [51]. When high levels of theory are used, the results have been more encouraging. We have recently reproduced the exact experimental value for the propagation of methyl acrylate, using reliable high-level composite methods for the electronic structure calculations, but only a unimeric model of the propagating radical and the harmonic oscillator approximation [40]. We have also reproduced (to within a factor of 1.1) the experimental values of vinyl chloride, again using high-level composite procedures in conjunction with the harmonic oscillator approximation, and this time a dimer model for the propagating species [35].

Our recent studies of vinyl chloride and methyl acrylate offer tantalizing evidence that the accurate prediction of propagation rate coefficients is now possible. However, it cannot yet be ruled out that this agreement is due to a fortuitous cancellation of error. Although the electronic structure calculations are based on chemically accurate methods, we have adopted only the harmonic oscillator approximation, and we have not yet systematically demonstrated that the rate coefficients calculated with the small radical models have converged to their long chain limits. Moreover, other questions remain. What are the most cost-effective electronic structure methods for delivering chemical accuracy in these radical reactions? For instance, can we avoid using expensive composite procedures on the larger oligomeric reactions via an ONIOM-based [52] approach? Are any of the new generation hybrid DFT methods (such as KMLYP [53], MPW1B95 [54], BB1K [55] and MPWB1K [54]) suitable for these systems? What is the minimum-sized chemical model that can reliably approximate the rate coefficients of the polymeric systems? Is it necessary to replace all low-frequency torsional modes by hindered internal rotations, or is the simple harmonic oscillator approximation sufficient?

In this work we investigate these outstanding issues, with a view to developing and evaluating an accurate cost-effective methodology for the general treatment of propagation reactions in radical polymerization. For this purpose we consider the propagation of two different monomers, vinyl chloride (VC) and acrylonitrile (AN). They were chosen as, like ethylene, they are relatively small (compared with the methacrylates or styrene) and could thus be studied with high levels of theory such as G3(MP2)-RAD. However, unlike ethylene, their substituents were likely to have stronger (and contrasting) remote substituent effects on the propagation rate. Moreover, in the case of acrylonitrile, the electronic structure calculations are expected to be much more sensitive to the selected level of theory and to reflect more accurately the sensitivity of "problem" monomers such as styrene. In what follows, we study the effects of the electronic-structure methods, the harmonic oscillator approximation (compared with the low-mode hindered rigid-rotor model), the chain length and solvent on the calculated rates and Arrhenius parameters, and we benchmark our results against experimental data for the corresponding oligomeric and polymeric systems.

2. Computational procedures

2.1. Models of the propagation step

Rate coefficients and corresponding Arrhenius parameters were calculated for the propagation of two monomers, vinyl chloride (CH$_2$=CHCl) and acrylonitrile (CH$_2$=CHCN). In each case rate coefficients were calculated for increasingly larger portions of the propagating radical, so as to establish the chain length at which the propagation rate coefficient converges. These models of the propagation reactions are displayed in Scheme 1 for the first three propagation steps of CH$_2$=CHX. For acrylonitrile propagation X = CN, while for vinyl chloride propagation X = Cl. To distinguish the various model sizes, we have assigned integer labels to the propagation reactions of the unimer (n = 1), dimer (n = 2), and trimer (n = 3) propagating radicals, and corresponding fractional values to the intervening radicals (e.g., n = 0.5 for CH$_2$X, n = 1.5 for CHX-CH$_2$-CH$_2$X, and not merely those that differ in whole unimeric units (i.e., n = 1, 2, 3, ...). It should be noted that the aim of the present work is not to model the first few propagation steps in a real polymerization system, which may vary considerably depending upon the nature of the initiation step. Rather, we are attempting to establish at what chain length the propagation step converges to its long chain limit. For this reason, we do not include an initiator fragment in the chain, and we consider all chain lengths (i.e., n = 0.5, 1, 1.5, ...). Calculations were performed for the model reactions displayed in Scheme Fig. 1, and also for corresponding "heavy" versions of the propagating radical. In earlier
work, Heuts et al. [24,25] argued that beyond the propyl radical stage (in ethylene polymerization), the predominant effect of the remaining chain on the barrier height is merely a mass effect that can be modeled reasonably well using a “heavy hydrogen” on the terminal carbon (opposite to the active chain end), anti to the rest of the polymer chain. The heavy hydrogen is assigned a mass of 9999 amu but has identical electronic properties to those of a normal hydrogen atom. Calculations performed with the heavy hydrogen atom are denoted with a prime to distinguish them from the corresponding normal calculations. For instance the rate coefficient $k_p^\prime$, denotes the propagation rate coefficient of the dimer radical, substituted with a heavy hydrogen atom.

2.2. Electronic-structure calculations

Standard ab initio molecular orbital theory and density functional theory calculations were carried out using GAUSSIAN 03 [57] and MOLPRO 2000.6 [58]. All DFT calculations on radicals were performed with an unrestricted wavefunction, while all ab initio calculations on radicals were performed with restricted open-shell wavefunctions.

Our benchmark level of theory was chosen on the basis of earlier assessment studies for radical addition to C=C double bonds [59,60]. The geometries of the reactants, products and transition structures were optimized at the B3-LYP/6-31G(d) [61] level of theory, and frequencies were also calculated at this level and scaled by the appropriate scale factors [62]. For each species considered, care was taken to ensure that the optimized structure was the global (rather than merely local) minimum energy structure by first performing extensive conformational searches at this level. The conformational searches involved optimization of all possible unique conformations obtained by rotating about each bond in the molecule. In the case of the largest systems (i.e., $n = 2.5$ and $n = 3$) this was not feasible. For these systems, the conformations were based on the conformationally screened dimers, and only the nine conformations (corresponding to rotations about the last two relevant bonds of the molecule) were examined. We also checked a small number of all-gauche structures in case an anchimeric effect between the radical center and the CN group of the ante-penultimate unit was operating. Using the B3-LYP/6-31G(d) optimized structures, improved energies were then obtained at the G3(MP2)-RAD level of theory [14]. This high-level composite procedure aims to approximate restricted-open-shell coupled cluster theory calculations [URCCSD(T)] with a large triple zeta basis set as the sum of URCCSD(T)/6-31G(d) calculations and a basis set correction term, calculated at the

![Scheme 1](image-url)
ROMP2 level of theory. The method has been demonstrated to provide “chemical accuracy” (≈1 kcal mol⁻¹) when assessed against large test sets of thermochemical data [14].

As part of this work, we also examined whether lower-cost computational procedures might be substituted for the high-level composite methods on larger systems. Earlier assessments for radical addition to C=C double bonds [59,60] (and indeed other radical reactions, including abstraction [63], addition to C≡S bonds [18], and bond dissociation energies [22,64,65]), have demonstrated that high levels of theory are unfortunately required for the accurate treatment of these radical reactions. However, it was noted in these earlier studies that the ROMP2/6-311+G(3df,2p) method could generally yield reliable relative values of the barrier heights and enthalpies, and we recently suggested in the context of our studies on RAFT polymerization that ROMP2/6-311+G(3df,2p) may be suitable for approximating G3(MP2)-RAD values via an ONIOM-based procedure [41,42].

In ONIOM [52], one first defines a “core” section of the molecule/transition structure that includes the reaction center and principal substituents. For instance, in the oligomeric propagation reaction, \( \text{CH} \cdot \text{CHXCH}_{2} \cdot \text{CHXCH}_{2} \cdot \text{CHX} \cdot \text{CH}_{2} = \text{CHX} \) (see scheme 2), the core could be modeled as \( \text{CH}_{2} \cdot \text{X} + \text{CH}_{2} = \text{CHX} \) (see Scheme 2). One then calculates the core system at both the high (in this case G3(MP2)-RAD) and lower (in this case ROMP2/6-311+G(3df,2p)) levels of theory, and the full system at just the lower level. The G3(MP2)-RAD barriers and enthalpies for the core system are then corrected for the substituent effect (of the rest of the molecule), as calculated at the ROMP2/6-311+G(3df,2p) level. In the present work, we calculate the ONIOM values for core systems of varying sizes (core = 0.5, 1 and 1.5), and compare these with the corresponding standard G3(MP2)-RAD values, in order to determine the minimum sized “core” system that will reliably yield accurate results.

Our previous assessment studies have revealed that popular hybrid DFT methods, such as B3-LYP [61], are not suitable for studying radical addition reactions [18,60]. However, since these methods are much less computationally intensive than G3(MP2)-RAD, there has been a growing trend in the polymer field to adopt these methods in studies of the radical polymerization reactions. It is therefore worth examining the magnitude of the error that might be introduced through this practice. For each reaction, barriers and enthalpies were thus calculated using the methods KMLYP [53], MPW1B95 [54], BB1K [55] and MPWB1K [54] in conjunction with the 6-311+G(3df,2p) basis set.

2.3. Rate calculations

Propagation rate coefficients \( k_p(T) \) were calculated at 273.15, 298.15, 313.15 and 348.15 K via standard transition state theory, using the standard textbook formulae [11]:

\[
k_p(T) = \frac{k_b T}{h} (\epsilon^0)^{1-m} e^{-\Delta G^\ddagger/RT} = \frac{k_b T}{h} (\epsilon^0)^{1-m} \frac{Q_1}{Q_{\text{reactants}}} e^{-\Delta E^\ddagger/RT} = k_0 e^{-E_a/RT},
\]

where \( k_0 \) is the tunneling correction factor (which can be assumed to be unity for radical addition reactions), \( T \) is the temperature (273.15, 298.15, 313.15 and 348.15 K), \( k_b \) is Boltzmann’s constant (1.380658 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1} ), h is Planck’s constant (6.6260755 \times 10^{-34} \text{ J s} ), \( m \) is the molecularity of the reaction, \( \epsilon^0 \) is the standard unit of concentration (mol L⁻¹), \( R \) is the universal gas constant (8.3142 J mol⁻¹ K⁻¹), \( Q_1 \) and \( Q_i \) are the molecular partition functions of the transition structure and reactant \( i \) respectively, \( \Delta G^\ddagger \) is the Gibb’s free energy of activation, and \( \Delta E^\ddagger \) is the zero-point energy corrected energy barrier for the reaction. The value of \( \epsilon^0 \) depends on the standard-state concentration assumed in calculating the thermodynamic quantities (and translational partition function). In the present work, these quantities were calculated for 1 mole of an ideal gas at 1 atm and 273.15, 298.15, 313.15 and 348.15 K and, hence \( \epsilon^0 = 0.04462, 0.04087, 0.03892, \) and 0.03500 mol L⁻¹ respectively. The Arrhenius frequency factor \( (A) \) and activation energy \( (E_a) \) are related to the enthalpy and entropy of activation as follows [66]:

\[
A = (\epsilon^0)^{1-m} \frac{k_b T}{h} e^{-(\Delta S^\ddagger/RT)} \quad \text{and} \quad E_a = \Delta H^\ddagger + mRT.
\]
than frozen) scans were used. The contribution of these modes to the total entropy and enthalpy were then calculated via standard methods, as follows. For all modes, the rotational potentials $V(\theta)$ were fitted with a Fourier series of up to 18 terms, and the corresponding energy levels were found by numerically solving the one-dimensional Schrödinger equation (3) for a rigid rotor, using a Fortran program described previously [24,25,68]:

$$\frac{\hbar^2}{8\pi^2 I} \frac{\partial^2 \Psi}{\partial \theta^2} + V(\theta) \Psi = \epsilon \Psi.$$  \hspace{1cm} (3)

The reduced moment of inertia ($I_r$) was calculated using the equation for $I^2$, as defined by East et al. [69]. The resulting energy levels $\epsilon_i$ were then summed to obtain the partition function at the specified temperature, as follows:

$$Q_{\text{rot}} = \frac{1}{\sigma_{\text{int}}} \sum_i \exp \left( - \frac{\epsilon_i}{k_B T} \right),$$  \hspace{1cm} (4)

where $\sigma_{\text{int}}$ is the symmetry number associated with that rotation.

It should be noted that, in this method, the low frequency torsional modes have been approximated as one-dimensional rigid rotors, while in practice these modes can be coupled with another. However, as noted in Section 1, recent studies of coupled internal rotations in radical addition, and also in the heats of formation of the $n$-alkanes, indicated that the errors incurred in using a one-dimensional treatment are relatively minor, particularly when compared with the errors incurred under the harmonic oscillator approximation [49,50].

2.4. Solvent effects

The influence of the solvent on the propagation rate was estimated using the ab initio conductor-like solvation model (COSMO), a widely used self-consistent reaction field approach [70]. Continuum models place solute molecules in a cavity surrounded by a polarizable continuum whose reaction field modifies the energy and the properties of the solute. In the ab initio COSMO approach the solvent reaction field is created by simulating a solvent with a given dielectric constant, such that the polarization charges distributed on the cavity surface are included in the solute Hamiltonian. Hence, it is possible to perform iterative procedures leading to the self-consistence between the solute wavefunctions and the solvent polarization. Although these pure electrostatic solute–solvent interactions are very important (e.g., in molecular complexes or transition states that are stabilized by charge transfer), non-electrostatic contributions, such as dispersion, repulsion and cavitation, cannot be neglected and are also present in COSMO. Since these non-electrostatic interactions are included in a rather simple form, errors for molecules with specific molecular interactions (e.g., hydrogen bonding) may be large. However, in the present reactions we do not expect these specific molecular interactions to be significant.

In the COSMO method, the molecular cavities have been optimized by means of the united atom for Hartree–Fock procedure in order to obtain the best fit to the experimental free energies of solvation. Since the size of the cavities is parameterized for Hartree–Fock wavefunctions, the free energies of solvation in this study were estimated at HF/6-311+G(d,p), so as to avoid non-canceling errors. The calculations yield a free energy of solvation ($\Delta G_{\text{aq}}$) for each species, which was used to correct the gas-phase free energy ($G_g$), and thus yield the total free energy in solution ($G_{\text{solv}}$) as follows:

$$G_{\text{aq}} = G_g + \Delta G_{\text{solv}}.$$  

The geometry relaxation induced by the solvent on the solute molecules cannot often be neglected. Therefore, the geometries of monomers, radicals and TSs were re-optimized using COSMO in conjunction with B3LYP/6-31G(d). The solvent effects on the reaction rates were modeled for three solvents, toluene, tetrahydrofuran (THF) and dimethyl formamide (DMF). The dielectric constants of these solvents span a range of solvent polarities from 2.38 for toluene, through 7.58 for THF to 38.25 for DMF [71]. Moreover, toluene and THF are widely used in the free-radical polymerization of VC, whereas DMF is suitable in the polymerization of AN, and also makes a good model for bulk AN ($\varepsilon = 33.0$). In addition to these general calculations, the propagation rate coefficient of VC in benzene (i.e., $\varepsilon = 2.28$) at 298.15 K and the propagation rate coefficient of AN in bulk AN monomer (i.e., $\varepsilon = 33.0$) at 348.15 K were calculated so as to allow for direct comparison with experiment.

3. Results and discussion

Barriers and enthalpies (0 K) for the propagation of acrylonitrile (AN) and vinyl chloride (VC) are shown as a function of model size and level of theory in Table 1. The corresponding propagation rate coefficients and associated Arrhenius parameters at 298.15 K, as calculated at the highest level of theory under the hindered rotor and harmonic oscillator approximations, are provided in Table 2. Rate coefficients at the other temperatures (273.15, 313.15 and 348.15 K) are provided in the Supporting Information. The B3-LYP/6-31G(d) optimized geometries of the reactants, products and transition structures for the acrylonitrile and vinyl chloride propagation reactions are shown in Figs. 1 and 2 respectively; complete geometries (in the form of Gaussian archive entries), together with the rotational potentials used in the calculation of the hindered rotor partition functions, are provided in the Supporting Information. Table 3 shows the calculated free energies of solvation in the presence of the various solvents, and the corresponding corrected rate coefficients. In what follows we use these data to establish and benchmark a reliable methodological approach for studying radical propagation reactions. We first examine the effect of the level of theory on the accuracy of the results; we then examine the effect...
The propagation step of free-radical polymerization of acrylonitrile (AN) and vinyl chloride (VC) was studied using various density functional theory methods. The reaction barriers and activation energies were calculated using ONIOM (core = 1.5) and the ROMP2/6-311+G(3df,2p) reaction barriers. The propagation rate coefficients and activation energies are presented in Table 1 for AN and VC. Table 2 shows the propagation rate coefficients $k_p(T)$ (L mol$^{-1}$ s$^{-1}$), the Arrhenius frequency factors $A(T)$, and activation energies $E_a$ (kJ mol$^{-1}$) for the propagation step of free-radical polymerization of acrylonitrile (AN) and vinyl chloride (VC).
of chain length and the effect of the solvent on the calculated propagation rate coefficients. We conclude with an assessment of the accuracy of the calculations, and discuss some of the outstanding issues in applying computational chemistry to the prediction of rate coefficients in radical polymerization.

3.1. Accuracy of the rate calculations

There are two main components that can affect the accuracy of the calculated rate coefficients: the accuracy of the electronic-structure calculations, and the models and approximations used in calculating the partition functions and reaction rates. If we consider first the electronic-structure calculations, we note that previous assessment studies have already established that the G3(MP2)-RAD//B3-LYP/6-31G(d) procedure can yield “chemically accurate” results, both for the specific case of radical addition to C=C double bonds [59,60] and also for a range of other radical reactions (including abstraction [63], addition to C=S bonds [18], and bond dissociation energies [22,64,65]). The purpose of the present assessment is merely to establish whether any lower cost computational methods can provide a reasonable substitute for this computationally intensive method. To this end, Table 1 compares the performance of a number of low-cost DFT, MP2 and ONIOM-based procedures against our benchmark level of theory.

If we consider first the DFT methods, we note that B-LYP, B3-LYP and BB1K have mean absolute deviations (MADs) of 10 kJ mol\(^{-1}\) or more in the barrier heights and, in the case of B-LYP and B3-LYP, errors of over 20 kJ mol\(^{-1}\) in the reaction enthalpies. These methods are clearly not suitable for studying these reactions. The other DFT methods fare much better, having MADs in the range of 2–7 kJ mol\(^{-1}\). However, the errors are variable, and errors of as much as 10 kJ mol\(^{-1}\) occur in a number of instances. This presence of non-systematic errors in DFT methods has been demonstrated previously for the related case of radical addition to C=O double bonds, and also for bond dissociation energies in simple closed-shell systems [64,65], and can be a concern if one uses the calculated results to study substituent effects. For these reasons, DFT
procedures should be used only cautiously for radical reactions. Of the procedures considered, KMLYP shows the smallest errors, and might be considered if the computational cost of higher-level methods is prohibitive. However, even in this case, the method shows significant errors in the reaction enthalpies, and, moreover, its results are very dependent on an empirical correction term, which is difficult to define for systems containing \( \pi \)-conjugated systems or transition states with breaking \( \pi \)-bonds. In general, it appears that none of the current DFT functionals are suitable for studying the energetics of the propagation reaction.

Consistent with previous studies of radical reactions [18,22,59,60,63–65], ROMP2/6-311+G(3df,2p) again shows excellent performance. The MAD in the barrier heights is just 2.9 kJ mol\(^{-1}\); the MAD in the enthalpies is larger (13.4 kJ mol\(^{-1}\)), however, unlike the DFT methods, the error is relatively constant (varying by less than 2 kJ mol\(^{-1}\) over all monomers and all chain lengths). As a result, ROMP2/6-311+G(3df,2p) appears to be suitable for measuring substituent effects, and hence for use in the ONIOM method. As explained above, in the ONIOM method we treat the inner core of the molecular systems at the higher level of theory, G3(MP2)-RAD, while the energy contribution of the rest of the molecular system is calculated at ROMP2/6-311+G(3df,2p). The ONIOM procedure was used for estimating the propagation barriers and enthalpies of free-radical polymerization for different inner core model sizes (\( n = 0.5, 1 \) and 1.5). With the smallest core (\( n = 0.5 \)), the MAD is just 1.8 kJ mol\(^{-1}\) and the maximum error just 2.7 kJ mol\(^{-1}\). Not surprisingly, this error decreases even further as the core size increases (to 0.6 kJ mol\(^{-1}\) for \( n = 1 \) and 0.1 kJ mol\(^{-1}\) for \( n = 1.5 \)). Clearly one should use the largest core size possible; however, it would appear that (even with a core size of \( n = 0.5 \)), the ONIOM-based method offers an excellent cost-effective
approach to studying propagation processes in radical polymerization.

The other main factors affecting the accuracy of the rate coefficients (as they correspond to a model reaction in the gas phase) are the models and approximations used in calculating the partition functions and rate coefficients. In the present work, the rate coefficients were calculated using standard transition state theory, and the partition functions were based on the statistical thermodynamics of an ideal gas under the rigid rotor/harmonic oscillator approximation. However, the accuracy was improved by treating low frequency (<300 cm\(^{-1}\)) torsional modes as one-dimensional hindered rotors. This hindered rotor (HR) model adds considerably to the cost of the calculations as it entails that full rotational potentials are obtained for each low frequency torsional mode. It is therefore, useful to examine whether the harmonic oscillator (HO) approximation yields reasonable results. The rate coefficients for the various systems are calculated under both models and are shown in Table 2. It can be seen that, in contrast to our results for the RAFT polymerization process \([39,42]\), the HO approximation behaves surprisingly well for polymer systems studied here. The results differ from those obtained under the HR model by a factor of 0.8–2.3 for the rate coefficients and 0.9–3.3 for the frequency factors. Hence it would appear that the HO approximation is suitable for reasonable order-of-magnitude estimates of the rate coefficients for propagation rate coefficients.

Thus far we have considered simple transition state theory in conjunction with the one-dimensional hindered rotor approximation as our benchmark level of theory. However, there are of course more sophisticated models that might have been chosen. We have used standard (rather than variational) transition state theory because we have shown previously that this simplification does not significantly affect the accuracy of the calculated rate coefficients for radical addition to C=S double bonds \([42]\). In this related system, the addition barriers are much lower and variational effects should (if anything) be greater than in the propagation reactions of the present work. Another simplification adopted in the present work is to calculate a single rate coefficient for the global minimum energy conformation of the propagating radical, rather than calculate rate coefficients for all possible conformations, and then average the results according their populations (i.e., based on a Boltzmann analysis). This simplification is necessary because the calculation of full rotational potentials and G3(MP2)-RAD energies for all conformations would be impractical. Although in principle our approach yields rate coefficients that are likely to be upper bounds to the true Boltzmann-averaged propagation rates, it seems unlikely that this source of error will be significant in the present reactions. For, conformations that are similar in energy to the global minimum are likely to differ in only 1 or 2 remote rotations, and are thus likely to have similar propagation rates. Thus, although they would contribute to the overall propagation rate, they would not affect the average value. Conversely, conformations that are much higher in energy (and would be expected to have different propagation rates) are not likely to be significantly populated, and thus do not make a significant contribution to the overall rate.

Another potential error relates to the fact that we have used a one-dimensional hindered rotor model for calculating the partition functions because the calculation of even two-dimensional rotational potentials would be computationally prohibitive for these large systems. As noted above, previous studies on related systems have indicated that the one-dimensional approach yields reasonably accurate results \([49,50]\). Moreover, in the present work, the assignment of the frequencies to the various low-frequency torsional modes was relatively straightforward and the modes did not qualitatively appear (when animated) to be significantly coupled with one another. However, in our on-going studies of more complicated polymer systems (such as the acrylates and methacrylates) we have noticed that, as the chain size increases, the modes tend to couple with one another and it becomes increasingly difficult to define pure rotations. As a result, the one-dimensional hindered rotor approximation may produce a larger error by replacing mixed rotations with pure rotational potentials. Further investigation of the accuracy of the one-dimensional hindered rotor approximation in these systems, and the development of some cost-effective means for decoupling these modes, would thus be desirable. Nonetheless, it would appear on the basis of the present work that a simple solution to this problem, provided one could accept a level of error of the order of a factor of 3, would be to adopt the harmonic oscillator approximation.
3.2. Chain length effects

In order to determine the minimum-sized chemical system that could reliably model the propagation of a polymeric propagating radical, we calculated the propagation rate coefficient (using our benchmark level of theory) for systematically longer chain lengths. We also compared rate coefficients that were calculated with and without the use of a “heavy hydrogen” to simulate the effect of mass on the chain. The rate coefficients, frequency factors and reaction barriers (under harmonic oscillator model) are plotted as a function of chain length in Fig. 3; the corresponding values under both this model and the hindered rotor model are provided in Table 2.

From Table 2, it is clear that the barriers show no change at all beyond the dimer stage (i.e., the barriers for \( n = 2.5 \) are the same as those for \( n = 3 \) to within 0.1 kJ mol\(^{-1}\)) and hence, from an enthalpic viewpoint, we may consider the \( n = 3 \) system as our long chain limit. We note that the barriers have converged to within 1 kJ mol\(^{-1}\) of this limit once the penultimate unit of the polymer radical has been included (i.e., \( n = 2 \)), with reasonable results being achievable when the primary substituent of this unit is included (i.e., for \( n = 1.5 \)). However, it is also clear that the use of shorter chains than this can incur large errors, and this adds further support to the notion that penultimate unit effects are important in free-radical copolymerization [10]. Although there is some minor fluctuation, the frequency factors also appear to have converged (to within a factor of 1.2 of one another) at the trimer radical stage, and appear largely to have converged (to within a factor of 1.5 of this limit) for the \( n = 1.5 \) model system.

On the basis of these results, it would appear that the minimum-sized chemical model that can reliably mimic the polymerization system is the \( n = 1.5 \) system. This model produces excellent relative values of the barriers and frequency factors, and produces absolute values of the rate coefficients that agree to within a factor of 1.6 of their corresponding long chain values.

It is worth comparing these results with the earlier theoretical study of ethylene propagation and the relevant experimental literature. As explained in Section 1, in their earlier study of ethylene propagation, Heuts et al. [24,25] concluded that the rate coefficient for ethylene propagation had largely converged by hexyl radical stage (i.e., \( n = 3 \), and that convergence to the long chain limit could be induced at the propyl radical stage (i.e., \( n = 1.5 \)) if a gamma-hydrogen were to be replaced with a “heavy hydrogen”, having a mass of 9999 amu. Our (higher-level) results for AN and VC are largely consistent with these conclusions, with the exception that the heavy hydrogen does not appear to be necessary for these (heavier) monomers. From an experimental perspective, the chain length dependence of acrylonitrile propagation has been studied for the first 10 propagation steps using the nitroxide trapping technique [51]. Since 2,2′-azobisisobutyronitrile (AIBN) was used as an initiator, the first unit of the propagating radical (\( \text{C(HCH}_3)\text{CN} \)) instead of \( \text{CH(CH}_3)\text{CN} \) differs slightly from ours, though its chemical influence should be expected to diminish with the subsequent propagation steps. They found that, over the entire 10 steps, the rate coefficients for each step varied by less than a factor of 3. While exact convergence was only obtained at the pentamer stage; convergence to within a factor of 2 was obtained at the dimer stage, which is again consistent with our conclusions. Moreover, as will be discussed below, the absolute values of the rate coefficients from these studies agree with our calculated values to within less than a factor of 2.

More generally, the question of whether the propagation rate coefficient is chain length dependent has been a matter of some debate in the polymer literature. It is generally agreed that, depending on the system, strong chain length effects may occur for the first few steps. For instance Deady et al. [72] used nitroxide trapping experiments to show that the first propagation step in styrene polymerization (which, in their system was actually the AIBN-derived \( \text{C(HCH}_3)\text{CN} \) radical adding to styrene monomer) was an order of magnitude faster than the addition of polystyryl radical to styrene. This is hardly surprising, given that one might expect strong polar stabilization of the transition structure in the former, but not the latter cases. However, whether chain length effects extend beyond the oligomer stage is a matter of some controversy. For example, Olaj et al. [73] have reported on the basis of careful pulsed laser polymerization (PLP) experiments that chain length effects (of the order of 40–60%) extend well beyond the \( n = 100 \) stage. However, others have argued that this extended chain length effect is an artefact of band broadening in the size-exclusion chromatography analysis of the PLP polymers, and the
effect disappears when mass spectrometry is used instead [51]. Moreover, the direct measurement of the early propagation steps via nitroxide trapping experiments [51,72] supports the idea that the chain length effects do converge after the first few steps. Whilst minor fluctuations in the frequency factors cannot yet be ruled out, our theoretical results also support the notion that convergence is fast, and hence small model systems are appropriate for studying the polymeric propagation rate coefficients.

3.3. Solvent effects

Thus far we have been considering propagation rate coefficients for gas-phase reactions; most polymerization processes are carried out in the solution phase. To investigate the magnitude of the solvent effect, the free energies of solvation were calculated for the propagation steps of the dimer species for both vinyl chloride and acrylonitrile (Table 3). It can be seen that, regardless of the polarity of the solvent, the reaction barriers for the propagation step either increase or decrease by 2.4 kJ mol$^{-1}$ at most. When this solvent effect is translated into an effect on the reaction rate at 298.15 K, the corrections span the range of 1.1–2.4 (including factors increasing and decreasing $k_p$). These numbers indicate that the solvent effects are not very significant and that gas-phase calculations are probably sufficient for these reactions. This is not actually surprising, the transition state is relatively early, and one might expect its solvation energy to be very similar to that of the reactants. Moreover, in these homopropagation reactions, the polar stabilization of the transition state would be relatively small, and would thus be relatively unaffected by the solvent dielectric constant. However, in other systems (particularly cross-propagation reactions) solvent effects may be expected to be more significant and, in those cases, a more sophisticated treatment may be necessary.

It should be noted that, although the COSMO model includes contributions from the electrostatic solute–solvent interactions and non-electrostatic components (such as dispersion, repulsion and cavitation), these are dealt with in a semi-empirical manner. As noted above, this approach can fail if there are specific solute–solvent interactions (such as complex formation). Moreover, the free energies of solvation were parameterized without taking into account the loss of rotational and translational degree of freedom that the solute experiences in the solution. Although this is a common approach for accounting for solvent effects, it has been noted that this procedure may overestimate entropic factors [74]. A more thorough examination of the effect of the solvent, using more sophisticated models would be desirable. Nonetheless, as will be shown below, the present calculations do reproduce the experimental solution-phase values, which would suggest that this simple approach to estimating the effect of the solvent is justified for these reactions.

3.4. Comparison with experiment

Having examined systematically the effect of the level of theory, chain length and solvent on the calculated rate coefficients, we are now in a position to compare our “best” theoretical values against experiment (see Table 4). In the case of acrylonitrile, there do not appear to be studies of the polymeric system. However, the first eight propagation steps at 75 °C in bulk have been studied using a nitroxide trapping technique [51]. As noted above, the values for the early propagation steps might be expected to differ slightly to our values because in the experimental study AIBN was used as an initiator, though the effect of this fragment will become progressively smaller as the chain lengthens. From Table 4, it is seen that the experimental ($n = 2$) value is within a factor of 2 of both the gas-phase and the solution-phase values. The theoretical solution-phase rate constant almost reproduces (within a factor of 1.1) the experimental $k_p$ of AN at the long chain limit (i.e., with $n = 8$). In the case of vinyl chloride, pulsed laser polymerization experiments do not appear to have been performed as yet; however, measurements of the propagation rate at 25 °C in THF and benzene, have been performed by electron spin resonance (ESR) spectroscopy [75] and rotating sector (RS) [76] experiments respectively. From Table 4, we note that both experimental values are within a factor of 1.3 of the solution-phase values, and within a factor of

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**Table 4**

Comparison of theoretical and experimental propagation rate coefficients (L mol$^{-1}$ s$^{-1}$) for acrylonitrile (AN) and vinyl chloride (VC)$^a$

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$T$ (°C)</th>
<th>Technique</th>
<th>Solvent</th>
<th>Experiment (L mol$^{-1}$ s$^{-1}$)</th>
<th>Ref.</th>
<th>Theory (L mol$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN ($n = 2$)</td>
<td>75</td>
<td>Nitroxides</td>
<td>Bulk</td>
<td>2400</td>
<td>[51]</td>
<td>3210</td>
</tr>
<tr>
<td>AN ($n = 8$)</td>
<td>75</td>
<td>Nitroxides</td>
<td>Bulk</td>
<td>4600</td>
<td>[51]</td>
<td>1360</td>
</tr>
<tr>
<td>VC</td>
<td>25</td>
<td>ESR$^c$</td>
<td>Benzene</td>
<td>5400 ± 1500</td>
<td>[75]</td>
<td>7150</td>
</tr>
<tr>
<td>VC</td>
<td>25</td>
<td>RS$^d$</td>
<td>THF</td>
<td>3130</td>
<td>[76]</td>
<td>3530</td>
</tr>
</tbody>
</table>

$^a$ Theoretical values were calculated at the G3(MP2)-RAD/B3-LYP/6-31G(d) level of theory in conjunction with the hindered rotor approximation for the $n = 2$ model.

$^b$ Solution values were calculated as follows: $k_{obs}$ (AN) was calculated at 348.15 K with $\varepsilon = 33.0$ that represents the AN bulk solvent ($\Delta G_{obs} = -0.7$ kJ mol$^{-1}$); $k_{obs}$ (VC) in benzene was calculated at 298.15 K with $\varepsilon = 2.28$ ($\Delta G_{obs} = -2.3$ kJ mol$^{-1}$); $k_{obs}$ (VC) in THF was calculated at 298.15 K with $\varepsilon = 2.38$ ($\Delta G_{obs} = -0.5$ kJ mol$^{-1}$).

$^c$ Electron spin resonance spectroscopy.

$^d$ Rotating sector.
2 of the gas-phase values. Moreover, the calculated solution-phase values accurately reproduce the differing effects of the THF and benzene solvents on the propagation rate, which adds further confidence to the accuracy of the solvent model used in the present work. In summary, the calculations for both monomers show excellent agreement with the corresponding experimental values.

3.5. Outstanding issues

In this work we have demonstrated that the accurate prediction of propagation rate coefficients in free-radical polymerization is now possible. Moreover, we have shown that this accuracy may be achieved using relatively small models of the propagating radicals (e.g., \( n = 1.5 \)), and that accurate G3(MP2)-RAD barriers may be approximated via a relatively cost-effective ONIOM-based approach. With these simplifications, and aided by on-going increases in computer power, this accurate methodology is now feasible for normal olefinic monomers, such as styrene or methyl methacrylate. It is of course necessary to test this methodology on these larger monomers (particularly those for which IUPAC benchmark values of \( kp \) are available), and a more sophisticated examination of the treatment of solvent effects and coupled internal rotations would also be desirable. Nonetheless, through the use of high-level composite procedures and a systematic examination of chain length effects, we have gone a long way toward demonstrating that the accuracy of our rate constants is not the result of a fortuitous cancellation of errors, and that the methodology yields the “right answer for the right reason”.

Despite this success, some outstanding problems remain. In particular, although the ONIOM-based approach allows us to calculate the reaction barriers on these large systems, other computational bottlenecks are now emerging. One such bottleneck is the need to identify minimum energy conformations for the oligomeric species. We currently identify these via a complete conformational search; that is, we optimize geometries for every (non-unique) conformation about every bond (or forming bond) in the molecule or transition structure. For example, in the AN dimer radical, \( \text{CH(CN)}-\text{CH}_2-\text{CH(CN)}\text{CH}_3 \), we need to consider nine conformations, corresponding to all combinations of the three non-unique conformations about the two C–C bonds shown. Although this is possible for the AN dimer radical, the conformational space grows exponentially with the size of the system, and for larger molecules a full search will rapidly become impossible. For instance with nine connected C–C bonds, up to \( 3^9 \) (nearly 20000) conformations would need to be considered in absence of symmetry. In the present work, the minimum conformations that were identified on the basis of these searches were simple syndiotactic all-trans structures that could have been predicted using simple stereo-electronic arguments. However, this cannot be assumed to be generally the case. In more complicated systems (such methyl acrylate or vinyl acetate), and particularly for longer chains, the possibility of unexpected anchimeric effects cannot be ruled out, and it is important to screen possible conformations thoroughly. We are currently evaluating accurate cost-effective alternatives for dealing with this problem, such as ONIOM-based approaches, stochastic approaches (such as simulated annealing), genetic algorithms and a new systematic algorithm that we have developed for efficiently exploring conformational space.

A related computational bottleneck is the requirement that we map full rotational potentials for every low frequency torsional mode. In the absence of symmetry, this entails 36 separate geometry optimizations for each mode. Although feasible for the present systems, this too can rapidly become computationally impractical. Moreover, if it becomes necessary to treat low frequency modes as multidimensional coupled rotations, the computational cost will compound further. More efficient methods for treating these low frequency torsional modes would thus be desirable. One obvious solution is to adopt the harmonic oscillator approximation. Our present results suggest that the error associated with this simplification is only of the order of a factor of 2–3. However, this is unlikely to provide a general solution for other radical polymerization reactions. For example, we have demonstrated elsewhere that the error in the harmonic oscillator approximation for studying \( \beta \)-scission in the RAFT process is over an order of magnitude \([39,42]\). We are currently examining other possibilities, such as the use of frozen (rather than relaxed) scans, and the use of “standard rotational potentials” of certain functional groups, as calculated for smaller polymer chains.

Despite these problems, it is clear that accurate quantum-chemical calculations of the individual rate coefficients in free-radical polymerization are now feasible, and that computational chemistry now offers a viable alternative to experiment in situations in which the model-free experimental determination of rate coefficients is difficult or impossible.

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Appendix A. Supplementary data

B3-LYP/6-31G(d) optimized geometries in the form of GAUSSIAN archive entries (Table S1); rotational potentials and assigned low-mode vibrational frequencies (Table S2); propagation rate coefficients \( kp(T) \) (L mol\(^{-1}\) s\(^{-1}\)), frequency factors \( A(T) \), free energies of reaction \( \Delta G^\circ(T) \) (kJ mol\(^{-1}\)) and activation energies \( E_a \) (kJ mol\(^{-1}\)) at
$T = 273.15, 298.15, 313.15$ and 348.15 K (Table S3 and S4). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemphys.2005.09.042.

References


