Computational Study of the Self-Initiation Mechanism in Thermal Polymerization of Methyl Acrylate

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This computational study deals with the mechanism of spontaneous initiation in thermal polymerization of alkyl acrylates (e.g., methyl, ethyl, and n-butyl acrylate). The mechanism is presently still unknown. Density-functional theory (DFT) and Moller–Plesset (MP2) calculations are used to explore the Flory and Mayo mechanisms of self-initiation in methyl acrylate. On the singlet surface, a low-barrier, concerted \( [4 + 2] \) Diels–Alder mechanism for the formation of a dihydropyran adduct (DA) and a high-barrier nonconcerted \( [2 + 2] \) diradical (\( \text{M}_2^* \)) mechanism for the formation of dimethyl cyclobutane-1,2-dicarboxylate (DCD) were found using B3LYP/6-31G*. Several levels of theory were used to validate the transition states, and the pathways for the DA and DCD formations on the singlet surface were determined using intrinsic reaction coordinate (IRC) calculations. On the triplet surface, a triplet diradical intermediate (\( \text{M}_2^t \)) was identified that is structurally similar to \( \text{M}_2^* \) but lower in energy. The spin–orbit coupling constant for crossover of the diradical from singlet to triplet surface was calculated. Monoradical generation from the two intermediates, DA and \( \text{M}_2^t \) via hydrogen transfer to or from a third methyl acrylate was studied. It was found that generation of two monoradical species was possible from \( \text{M}_2^t \) and is proposed as a likely explanation for experimentally observed spontaneous-initiation.

1. Introduction

Acrylic resins are widely used as primary binders in coatings formulations for the automobile industry.1 Due to stringent environment regulations to reduce volatile organic content (VOC), resins with lower solvent content, lower average molecular weight, and higher functionality have replaced previous formulations. A resin with higher functionality has more dead-polymer chains that are capable of undergoing further reactions. High-temperature (above 373 K) polymerization of acrylates had to be used to produce low-average-molecular-weight resins in place of traditional low-temperature polymerization.3–5 Although trace quantities of initiators have been reported by Chiefari et al. to be sufficient to initiate polymerization,6 thermal initiators are fairly expensive, and residual initiators are known to cause undesirable coloration in resins.9 While claims have been made that spontaneous thermal polymerization in alkyl acrylates was not possible,7 Grady et al.8 reported sustained, reproducible, spontaneous, thermal polymerization of alkyl acrylates in the absence of any known extrinsic initiators at temperatures above 373 K. It has been speculated that trace quantities of inherent hydroperoxide impurities in the monomers may be initiating polymerization, but electrospray ionization-Fourier transform mass spectrometry (ESI-FTMS) profiles indicated the lack of such end group structures.9 Rantow et al.10 probed the initiation step using nuclear magnetic resonance spectroscopy (NMR) and macroscopic mechanic modeling, but the results were inconclusive.

Due to the large size of the system of interest, density-functional-theory (DFT)-based methods are attractive alternatives to wave-function-based quantum chemical methods12 to predict the initiating species and mechanism of initiation. Although DFT-based methods are not nearly as accurate in predicting barriers13 as the highest-level quantum chemical techniques are, the efficiency of DFT permits analysis of complex multiatom systems like the acrylate dimers studied here. The use of modern hybrid exchange-correlation and decent basis sets has been shown to yield reasonable agreement with experimental values for reactions (i.e., initiation, propagation, chain transfer) occurring in free radical polymerization.12,14 In addition, once potential energy surfaces are explored approximately with DFT, higher-level approaches are valuable for local analysis of important molecular structures.

The self-initiation of styrene has been extensively studied, and the mechanisms proposed by Flory15 and Mayo16 serve as important prototypes. Mayo16 proposed that two molecules of styrene undergo a \( [4 + 2] \) cycloaddition reaction to form a Diels–Alder intermediate which is often denoted as AH because it can lose a hydrogen to a third monomer to produce a pair of monoradicals that initiate polymerization. According to the Flory15 mechanism, two monomers undergo \( [2 + 2] \) cycloaddition reaction to form a cyclobutane dimer (CBD), and this ring can open to form a diradical (\( \text{M}_2^t \)), which can abstract a hydrogen atom from a third monomer to form monoradicals that initiate polymerization. Khuong et al.17 pointed out that self-initiation could possess aspects of both the Flory and Mayo mechanisms. They proposed a stepwise diradical mechanism in place of a concerted pathway for formation of \( \text{AH} \), which can then undergo hydrogen transfer to initiate polymerization. Numerous experimental studies18–20 have validated Mayo’s
mechanism by detecting the presence of a Diels–Alder (AH) intermediate in thermal polymerization of styrene. DFT calculations using B3LYP/6-31G* and BPW91/6-31G* levels of theory confirmed AH to be the key intermediate in styrene polymerization and hydrogen transfer from AH as the nonradical generating reaction.17

Pryor and Lasswell21 suggested that Flory’s mechanism can be extended to various monomers, e.g., methyl methacrylate (MMA), with a (M3q) triplet diradical species initiating polymerization for monomers other than styrene. It has become clear that the insights from styrene do not necessarily apply to acrylates or methacrylates. Stickler and Meyerhoff22 agreed, suggesting that Mayo’s mechanism does not lead to spontaneous polymerization of MMA, because the AH intermediate is incapable of undergoing homolysis and generating nonradicals. They also reported that the activation energy for dimer formation via a Flory-type M3q (146 kJ mol⁻¹) was comparable with that of the initiation step. This supported the conclusion that diradicals probably initiate polymerization, but no concrete evidence of whether it was in the singlet or triplet state was reported.

Salem and Rowland23 proposed that the bifunctional behavior of diradicals allows free mixing of closely lying singlet and triplet states, which under favorable conditions can produce radiationless crossover from singlet to triplet (S1 → T1). This process is known as intersystem crossing (ISC), and the most common mechanism through which it can occur is known as spin-orbit coupling (SOC). Previous studies24 on hydrocarbon diradicals and oxygen-containing radicals have shown that SOC effectively describes the mixing of singlet and triplet states, so SOC is the main mechanism that governs intersystem crossing. Significant intersystem crossing can be facilitated by a dense continuum of vibrational states, as found in relatively large molecules such as benzene.25–26 Smaller diradicals can undergo intersystem crossing via collision with solvent or inert gases.27,28 The singlet–triplet energy difference in homosymmetric diradicals such as ethylene has been shown to be generally small (35.6 kJ mol⁻¹) in comparison to heterosymmetric diradicals such as linear methylene (129.7 kJ mol⁻¹).29,30

Solution-phase free radical polymerization can be affected by solvent molecules in various ways that can lead to a significant effect in the calculated and experimental rate constants.31 Due to its high dielectric constant, a polar solvent can stabilize transition state structures and reduce reaction barriers. Solvents can affect reactions, viz., propagation, chain transfer specific interactions such as hydrogen bonding or complex formation and via bulk diffusion effects. In addition, the solvent affects the calculated entropy of activation and consequently rate constants of bimolecular reactions. The effect of polar interactions can be treated with continuum models.32 However, these models fail to account for entropy differences or the effect of direct solvent interactions. Quantum modeling of solutes and solvent molecules has been reported to be computationally infeasible in polymerization systems.33 No simplified model currently exists to reduce the difference between gas and solution phase rate constants. Calculations using a continuum model to study solvent effects on propagation in free radical polymerization of acrylonitrile have shown that introduction of the toluene solvent field into the calculations had little effect on the activation energy and transition state structures estimated via gas-phase simulations.34 Furthermore, experiments using xylene and other inert solvents show no effect on the initiation reaction in spontaneous thermal polymerization of methyl acrylate (MA).8 Therefore, in this study, gas-phase calculations are performed, and the rigid rotor harmonic oscillator approximation (RRHO) is used to calculate the thermodynamics and kinetics of the reactions.

Treatment of internal rotation in small and large molecules has been extensively studied in the last 60 years.35,36 Pitzer35 used the one-dimensional rigid rotor model to describe anharmonic motions associated with low-frequency vibrational modes in equilibrium and transition state geometries. In recent years, the one-dimensional hindered rotor model36 has been used to compute the vibrational partition function for free-radical polymerization of ethylene, vinyl chloride, acrylonitrile, and acrylate monomers, and it has shown good agreement between calculated and experimental propagation rate constants. The predicted enthalpies and activation energies have been shown to be insensitive to the choice of rotor model. While the harmonic oscillator approximation tends to overestimate frequency factors and rate constants, it is computationally less demanding, and it has been found to be highly accurate in comparison to the hindered rotor model in a few large molecules. Rate constants comparable to experiment were predicted in self-initiation in thermal polymerization of styrene37 using B3LYP/6-31G*, without applying the hindered rotor model. In the present study, no internal rotation treatment has been applied. The calculated rate constants may be overestimated somewhat due to neglect of internal rotation, but this effect is not likely to be significant, and the reported barriers and activation energies are expected to be adequately accurate.

In this paper, DFT11 is used to explore the Flory and Mayo mechanisms of self-initiation for methyl acrylate (Figure 1). The formation of key intermediates on the singlet and triplet surfaces is studied. An energy map of the singlet surface is constructed to describe the pathways for the formation of the DA and DCD using B3LYP/6-31G*.37,38 Validation of the transition states is performed with different levels of theory. The triplet energy surface is calculated. Spin-orbit coupling constants39 for singlet—triplet crossover are estimated using MCSCF/6-31G*. Monoradical generation via hydrogen transfer from DA and triplet diradical is studied. Energy barriers for the dimer and nonradical formation are calculated. The paper is organized as follows. Section 2 describes computational methods used in the study. Section 3 presents and discusses the computational results. Finally, concluding remarks are given in section 4.

2. Computational Methods

All theoretical calculations in this work were performed using GAMESS.40 DFT calculations on the singlet and triplet surfaces were performed using restricted open-shell and unrestricted wave functions, respectively. B3LYP/6-31G* was chosen as the level of theory to construct the potential energy surface profiles and estimate transition states due to its successful use in the study of free radical polymerization of alkenes and self-initiation of styrene.12,14,17 No DFT study has been conducted for self-initiation in MMA or any alkyl acrylate previously. The molecular geometries of reactants, products, and transition states were optimized on the singlet and triplet surfaces. Vibrational frequency calculations were performed to characterize reactants and transition states. Intrinsic reaction coordinate calculations were performed in the forward and reverse directions to determine minimum-energy pathways. Assessment of the transition states and energy barriers was performed with various basis sets and with DFT and MP2: B3LYP/6-31G**, B3LYP/6-311G*, B3LYP/6-31G(2df,p), MP2/6-31G**, MP2/6-31G*, and MP2/6-311G*. Spin–orbit coupling calculations were carried out using MCSCF/6-31G*. Reported energies (relative to the energy of the reactant) were calculated using a rigid rotor
3. Results and Discussion

3.1. Singlet Energy Surface. The singlet potential energy surface profile was constructed by constraining two internuclear distances, 1.45 Å ≤ r(C6–C13) ≤ 2.4 Å and 1.6 Å ≤ r(C1–C14) ≤ 3.4 Å, as shown in Figure 2. The numbers inserted in the plot point to the potential energies of some of the key chemical structures drawn below the plot. Multiple peaks and valleys representing saddle points and minima on the surface profile was constructed by constraining two internuclear

dimensions. The single imaginary frequency calculated for the exo transition state, is 117.1 kJ mol⁻¹ (zero point energy corrected) above that of the reactant, which is 2.1 kJ mol⁻¹ higher than that of the endo product. In the reaction, one of these products (B or C) will be preferred as a thermodynamic product and the other as a kinetic product. The lowest energy product is the thermodynamic product, which is found by comparing the molecular energies of the exo and endo products, respectively. The energy of the endo DA, C, is higher than the exo DA, B, by ≈2.9 kJ mol⁻¹. Therefore, the exo product is the thermodynamic product. The kinetic product is identified by comparing energies of the endo and exo DA transition states; the endo transition state has a lower energy and is the kinetic product. The kinetic product is favored when the temperature of the reaction is insufficient to overcome the energy barrier and the thermodynamic product is favored at high enough temperatures when sufficient energy is available to overcome the barrier. In spontaneous high-temperature polymerization of methyl acrylate, the formation of exo DA, B, is predicted to be significant. Results from intrinsic reaction coordinate (IRC) calculations from the transition state, A, in the forward and reverse directions are shown in Figure 3. In each direction, 250 points were calculated.

We modeled the exo transition state, A, with different basis sets and with DFT and MP2, as shown in Table 1. Calculations show that B3LYP and MP2 yield transition state geometries and energy barriers that are significantly different, as given in Table 1. B3LYP/6-31G (2df, p), was selected because it has been shown to be a reliable level of theory in G346,47 and G448 to calculate geometries and transition states. In order to obtain an accurate thermochemical estimate for the reactions under study, calculations were performed using G4 theory. We encountered computational difficulties while using higher levels of theory, e.g., coupled cluster or MP4 methods with a large
basis set, due to the large size of the methyl acrylate system. In view of these, we believe that the true value of activation energy, enthalpy, frequency factor, and rate constant for DA formation lies within the range of values shown in Table 1, and these values serve as a reasonable *a priori* prediction for experimental verification.
3.1.2. Dimethyl Cyclobutane-1,2-dicarboxylate (DCD) Formation. We found a nonconcerted [2 + 2] thermal cycloaddition reaction to occur between C1==C6 and C13==C14 atoms to form DCD. Figure 2 shows that the formation of DCD is via a singlet gauche conformation diradical transition state (6). The extensive flat region on the singlet surface (7) suggests that the system (diradical) may be induced to spend a longer time exploring the surface before ring closure. The geometry of the calculated diradical transition state (6) is \( r(C6-C13) = 1.597 \, \text{Å}, \ r(C1-C14) = 2.788 \, \text{Å}, \ \text{and} \ \phi(C1-C6-C13-C14) = 57.6^\circ. \)

Figure 3 depicts the reaction pathway for the formation of DCD, 8, from 6. The flat region on the singlet surface can act like an intermediate, as reported by Hoffmann et al., for the tetramethylene diradical who termed this geometry a “twixty”. It is fundamentally similar to the stereorandom one-step diradical decay process proposed by Dervar et al., for the diazene-derived tetramethylene, but it is different from the two independent stereorandom steps model of Doubleday Jr., for cyclobutane-derived tetramethylene. We found that the transformation from the methyl acrylate reactants to DCD is highly stereospecific, which is in good agreement with the Woodward–Hoffmann rules for electrocyclic reactions. DCD, 8, is of cis orientation, and is produced from 6, with the same stereochemistry (Scheme 1). Furthermore, the trans diradical that is required to produce trans DCD, can be produced by internal rotation of 6 (Scheme 1). The diradical, 6, is formed stereospecifically and then is scrambled via internal rotation to form the trans diradical. The scrambling stops with the formation of trans DCD, and the stereochemistry from the trans diradical is transferred intact to the product. This suggests that the stereorandomness in methyl acrylate is built after formation of a diradical via internal rotation. The diradical, 6, in one step decays to yield DCD (Scheme 1), which agrees with the model of Dervar et al. The two-step stereorandom model involves shared transition states, and stereorandomness is built into the formation and decay of the diradical. The absence of this model in our calculations can be attributed to the generalized notion that the stereochemistry of the forming diradical is dependent on the precursor (methyl acrylate) and as dynamical treatment is required to predict the two-step model. Experiments have not shown DCD formation in spontaneous thermal polymerization of methyl acrylate. High monomer conversion (≥80%) indicates the preference to form polymers in comparison to dimers. It may be possible that trace concentrations of DCD do form as in spontaneous polymerization of MMA but have been unmeasured. It is highly probable that the singlet diradical undergoes intersystem crossing to form a triplet diradical, which can act as an intermediate for generating initiating monoradical species. The transition state and energy barriers obtained from the B3LYP/6-31G* were compared with those calculated using other levels of theory, as given in Table 2. We found MP2 to show lower barriers and no significant difference in the bond lengths of the predicted geometries in comparison to B3LYP.

3.2. Triplet Energy Surface and Spin-Orbit Coupling. The energy contour map of the triplet surface is shown in Figure 4. The triplet and singlet surfaces are dramatically different. We found a diradical intermediate (9) with a bond length between C6 and C13 \( r(C6-C13) = 1.552 \, \text{Å}, \) no real bond between C1 and C14 \( r(C1-C14) = 3.021 \, \text{Å}, \) and a dihedral angle \( \phi(C1-C6-C13-C14) = 62.2^\circ, \) as shown in Figure 4. All frequencies were positive, confirming that this structure is a local minimum. The energy of the triplet diradical intermediate is 113 kJ/mol above that of the reactant (zero point energy corrected).

We found that there is a strong structural similarity between the singlet gauche diradical transition state, 6 \( r(C6-C13) = 1.597 \, \text{Å}, \) \( \phi(C1-C6-C13-C14) = 57.6^\circ, \) and the triplet diradical intermediate, 9 \( r(C6-C13) = 1.552 \, \text{Å}, \) \( \phi(C1-C6-C13-C14) = 62.2^\circ. \) The differences in bond lengths and angles are \( \approx 0.045 \, \text{Å} \) and \( \pm 5^\circ, \) respectively. We estimated the spin–orbit coupling constant using MCSCF (6/6-31G*) for the singlet–triplet crossover to be \( A = 1.94 \, \text{cm}^{-1}. \) The energy difference between the ground-state singlet diradical and the lowest-energy triplet level \( \Delta E_{S-T} \) is 78 kJ mol\(^{-1}, \) which is comparable to \( \Delta E_{S-T} = 70 \, \text{kJ mol}^{-1} \) predicted using B3LYP/6-31G*. According to Salem and Rowland, even if a vibronic degeneracy exists between the singlet and triplet diradical, a large density of states in the reaction manifold is required for intersystem crossing. Methyl acrylate is a fairly large molecule, and the diradical has ionic character in the singlet state. The presence of halogenated solvents at high temperatures has been shown to occur in spontaneous thermal polymerization of MMA with halogenated solvents at high temperatures. It is speculated that the high temperatures (above ca. 120 °C) at which spontaneous thermal initiation in methyl acrylate polymerization has been reported may induce sufficient collisions between the diradical and solvent to ensure the occurrence of the intersystem crossing.

3.3. Monoradical Generation. Monoradical formation in thermal polymerization of styrene has been proposed to occur through the molecular-assisted homolysis mechanism, which involves hydrogen transfer from the Diels–Alder intermediate to a third monomer to generate two monoradicals. We tested this mechanism by performing a hydrogen transfer reaction from...
TABLE 1: Bond Length, Activation Energy (Ea), Enthalpy (ΔH298), and Free Energy (ΔG298) in kJ mol⁻¹, Frequency Factor (A) and Rate Constant for exo DA Formation (kDA) in M⁻¹ s⁻¹ at 298 K Using Different Levels of Theorya

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<th>level of theory</th>
<th>r(C14–O3), Å</th>
<th>r(C6–C13), Å</th>
<th>Ea</th>
<th>ΔH298</th>
<th>ΔG298</th>
<th>log_10 A</th>
<th>kDA</th>
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<td>167.28</td>
<td>7.25</td>
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a The reported energies are zero point vibrational energy (ZPVE) corrected.

TABLE 2: Bond Length, Activation Energy (Ea), Enthalpy (ΔH298), and Free Energy (ΔG298) in kJ mol⁻¹, Frequency Factor (A), and Rate Constant for DCD Formation (kDCD) in M⁻¹ s⁻¹ at 298 K Using Different Levels of Theorya

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<th>level of theory</th>
<th>r(C1–C14), Å</th>
<th>r(C6–C13), Å</th>
<th>Ea</th>
<th>ΔH298</th>
<th>ΔG298</th>
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<td>3.73 × 10⁻¹²</td>
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a The reported energies are zero point vibrational energy (ZPVE) corrected.

SCHEME 1: Stereorandom One-Step Diradical Mechanism

4. Concluding Remarks

The self-initiating mechanisms of Flory and Mayo were extensively examined to understand spontaneous thermal initia-
tion in high-temperature polymerization of methyl acrylate using B3LYP/6-31G*. Pathways for endo and exo DA were found. The transition state for the endo DA was observed to be slightly lower (≈2.1 kJ mol$^{-1}$) than that of the exo DA. The nonconcerted singlet diradical pathway for formation of DCD was found with an energy barrier 70 kJ mol$^{-1}$ higher than that of the endo DA. Validation of the transition states and energy barriers was carried out using several levels of theory. MP2 was found to predict similar transition geometries but lower energy barriers than B3LYP. A key intermediate, the triplet diradical, which forms via intersystem crossing from the singlet diradical was found. The spin orbit coupling constant for this crossover has been predicted to be a low value, $A = 1.94$ cm$^{-1}$.

The monoradical generation was found not to occur by hydrogen transfer from DA. Hydrogen transfer from triplet diradical to monomer was found to cause monoradical generation. In summary, the evidence points to the mechanism of spontaneous thermal initiation of methyl acrylate being via diradicals that are in the triplet state (as shown in Figure 6). Therefore, this study supports the claim of Pryor and Lasswell$^{17}$ that the Flory diradical mechanism can explain spontaneous polymerization of other molecules beyond styrene.

**Figure 4.** Contour map of the triplet potential energy surface, $r$(C1–C14) vs $r$(C6–C13). All energies are relative to the singlet reactant in kJ mol$^{-1}$. All bond lengths in Å. Color nomenclature (highest to lowest energy): red, green, blue, magenta, cyan, yellow. 9: triplet diradical intermediate.

**SCHEME 2: Hydrogen Abstraction and Transfer Reactions via Triplet Diradical**

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<tr>
<th>$T$, K</th>
<th>$E_a$, kJ mol$^{-1}$</th>
<th>$\Delta H^0$, kJ mol$^{-1}$</th>
<th>$\Delta G^0$, kJ mol$^{-1}$</th>
<th>$\text{log}_e A$, s$^{-1}$</th>
<th>$k^*$ without tunneling, Wigner</th>
<th>$k^*$ with tunneling</th>
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<tr>
<td>298</td>
<td>81.14</td>
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- $k^*$ The reported barriers are zero point vibrational energy (ZPVE) corrected.
- $\text{log}_e A$ Wigner tunneling correction.$^{44}$
- Rate constant from transition state theory.$^{45}$

**Figure 6.** Proposed mechanism of self-initiation in thermal polymerization of methyl acrylate.
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Supporting Information Available: Cartesian coordinates and total energies of the stationary points and total energies of the geometries at fixed grid points of singlet and triplet potential energy surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(2) VOC’s Directive, EU Committee of the American Chamber of Commerce in Belgium, ASBL/VZW, Brussels, July 8, 1996.
(8) Grady, M. C.; Quan, C.; Sorouh, M. Patent Application Number 60/448,393, filed on July 2, 2003, status: pending.
(40) http://cccbdb.nist.gov.