Theoretical Insights Into Thermal Self-Initiation Reactions of Acrylates

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4.1 Introduction

Acrylic resins are made from alkyl acrylates and methacrylates as homo- and co-polymers, sometimes combined with other thermoplastic monomers. Their chief application in coatings is as primary binders with end applications in the architectural and automotive markets. Environment regulations to reduce volatile organic contents (VOCs) have led to the introduction of resin formulations with lower solvent contents, lower average molecular weights, and higher functionality [1,2]. To produce low average−molecular weight resins, high-temperature (above 373 K) polymerization of acrylates has been used in place of traditional low-temperature polymerization. Peroxide or nitrile initiators have been widely used to initiate high-temperature polymerization. Low concentrations of thermal initiators are typically used in free-radical polymerization. However, thermal initiators are relatively expensive, and residual (unreacted) initiators in final resin products cause undesirable coloration [3].

Experimental studies [4−7] reported spontaneous thermal polymerization in alkyl acrylates at temperatures above 373 K. However, electrospray ionization−Fourier transform mass spectrometry (ESI-FTMS) of polymer samples from spontaneous polymerization did not show any initiator end-group structures that point to chain initiation by trace quantities of impurities in the monomers [4,5,7]. The initiation step was probed using nuclear magnetic resonance spectroscopy (NMR) and macroscopic scale mechanistic modeling, but the results were inconclusive [6,8]. High rates of spontaneous thermal polymerization of alkyl acrylates accompanied by significant contributions of chain-transfer reactions in solvents of varying polarity, such as benzene, xylene, ethyl acetate, methyl amyl ketone, and isopropyl alcohol, were reported [9].

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Experimental studies of spontaneous thermal polymerization of methyl methacrylate (MMA) at high temperatures (100–130°C) showed low conversion of the monomer to high average–molecular weight polymers and high conversion of the monomer to oligomers (such as dimers and trimers) and 1,1,2,2-tetrasubstituted cyclobutanes [10–14]. Evidence of the formation of diradicals and of the initiation mechanism were derived from the formation of a significant amount of a linear unsaturated dimer, dimethyl 1-hexene 2,5 carboxylate [10–12]. Low rates of polymerization of MMA were reported in nonpolar solvents [15], and high rates in halogenated solvents and polar protic solvents, such as thiophenol.

The inability of experimental studies to explain how polymer chains are initiated or to identify the species that initiates the chains in spontaneous thermal free-radical polymerization, has motivated efforts to investigate spontaneous thermal polymerization theoretically using computational quantum chemistry [16–19]. These efforts, with experimental evidences and macroscopic-scale mechanistic modeling, have shown that alkyl acrylates and methacrylates themselves initiate polymer chains at high temperatures [10–13,20–23].

The organization of the rest of this chapter is as follows: The Flory and Mayo self-initiation mechanisms are reviewed in Section 4.2. Sections 4.3 and 4.4 put into perspective advances made in understanding the thermal self-initiation of alkyl acrylates and methacrylates, respectively. Section 4.5 reviews studies on thermal solvent-monomer co-initiation of free-radical polymerization. Finally, the chapter ends with concluding remarks.

4.2 Flory and Mayo Self-Initiation Mechanisms

Self-initiation mechanisms proposed by Flory [24] and Mayo [25] (Fig. 4.1) have served as important model mechanisms for the past several decades. Mayo proposed that two styrene molecules undergo a [4 + 2] cycloaddition reaction, forming a Diels-Alder adduct (DAA) intermediate, which loses a hydrogen to a third monomer, producing two monoradicals that initiate polymerization. Many experimental studies have validated Mayo's mechanism by reporting the presence of the DAA intermediate in the thermal polymerization of styrene [25]. Density functional theory (DFT) calculations using B3LYP/6-31G* and BPW91/6-31G* levels of theory revealed that the DAA intermediate is the key intermediate in styrene polymerization, and two monoradicals are generated via hydrogen transfer from the DAA intermediate to a third monomer [26]. It became evident that the self-initiation behavior of styrene is different from those of acrylates and methacrylates. Stickler and Meyerhoff [10] indicated that spontaneous thermal polymerization of MMA is not possible via Mayo's mechanism, because the DAA intermediate of MMA is not able to undergo homolysis to generate monoradicals.

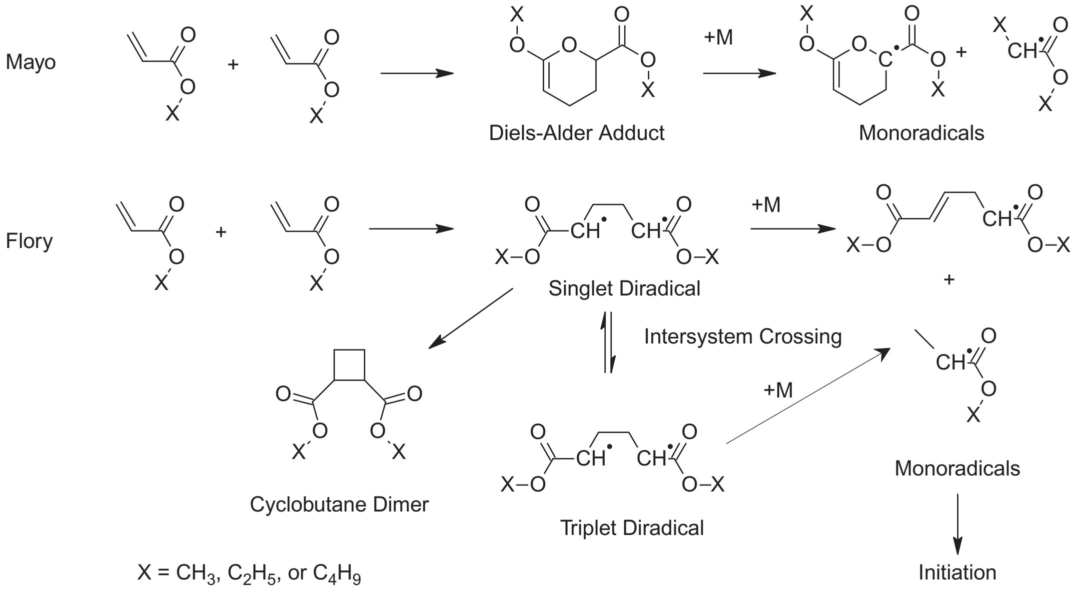

Figure 4.1

Flory and Mayo mechanisms for self-initiation of MA, EA, and *n*BA. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Computational study of the self-initiation mechanism in thermal polymerization of methyl acrylate, J. Phys. Chem. A 113 (2009) 10787–10794. Copyright 2009 American Chemical Society.*

According to Flory's mechanism (Fig. 4.1), two monomer molecules react and form a 1,4 singlet (ground state) diradical ($\bullet M_{2s}\bullet$). The singlet diradical can undergo ring closure to form cyclobutane derivatives, but can also undergo intersystem crossing to form a longer-lived triplet diradical ($\bullet M_{2t}\bullet$), which can abstract a hydrogen from or transfer a hydrogen to a third monomer molecule, forming two monoradicals that can initiate polymer chains. Note that Fig. 4.1 shows only a hydrogen transfer to monomer reaction. Pryor and Lasswell [23] postulated that the 1,4-diradical can initiate polymerization only in its triplet (excited) state. They proposed that various monomers other than styrene, e.g., MMA, can generate monoradicals via Flory's mechanism. Stickler and Meyerhoff [10] reported that for MMA, the activation energies of monoradical generation and dimer formation via a Flory-type diradical are comparable. This provided the initial understanding that diradicals are probably involved in chain initiation, but no solid evidence of whether their singlet or triplet state is involved, was reported. Khuong et al. [26] reported that the self-initiation might be via both Flory's and Mayo's mechanisms. They suggested a stepwise diradical mechanism, instead of a concerted pathway, for the formation of the DAA intermediate, which can then transfer a hydrogen atom and form monoradicals.

4.3 Alkyl Acrylate Thermal Self-Initiation

4.3.1 Prior Experimental Knowledge

Experimental studies [6,8,27] reported spontaneous thermal polymerization in alkyl acrylates at temperatures above 373 K. Higher conversions and lower average molecular weights were also achieved in spontaneous polymerization of alkyl acrylates than in that of MMA [6,9,11,13]. No cyclobutane derivatives or linear dimers were reported in spontaneous polymerization of alkyl acrylates. The differences in polymer morphology and kinetics of individual reactions were attributed to structural differences between acrylate and methacrylate monomers. NMR spectroscopy and ESI-FTMS of polymer samples from spontaneous polymerization did not reveal any initiator end-group structures, pointing to chain initiation by trace quantities of impurities in the monomers [6]. High rates of thermal spontaneous polymerization of alkyl acrylates accompanied by significant chain-transfer reactions were reported in solvents of varying polarity, such as benzene, xylene, isopropyl alcohol, methyl *n*-amyl ketone, and ethyl acetate [8]. These suggested that chain transfer and initiation reactions occur appreciably, irrespective of the solvent type.

Quan et al. [6] showed that at high temperatures, polymerization of alkyl acrylates occurs in the absence of any known added thermal initiators. Studies [4–7] revealed that acrylic resins with a low polydispersity index (1.4–1.6) can be produced in prolonged spontaneous polymerization of alkyl acrylates (~24 hours). While these results pointed to a strong contribution of β-scission reactions to the polymerization, they did not reveal the identity of the actual initiating species in the spontaneous polymerization. Furthermore, initiation rate constants estimated from polymer sample measurements [27] did not provide any information on the nature of the intermediates formed by the chain initiation reaction steps, since the reaction mechanism used in the macroscopic-mechanistic model did not explicitly account for the chain initiation reaction steps. Prior to the computational quantum chemistry studies presented in the next section, there was no evidence to confirm or reject conclusively that (1) triplet diradicals are formed, (2) intersystem crossing occurs, or (3) triplet state of the diradicals are involved in the chain initiation. In addition, very little was known about the generation of monoradicals from the triplet diradicals.

4.3.2 Knowledge Gained Using Quantum Chemical Calculations

Srinivasan et al. [16,17] computationally studied thermal self-initiation of methyl acrylate (MA), ethyl acrylate (EA), and *n*-butyl acrylate (*n*BA). Matrix-assisted laser desorption ionization (MALDI) mass spectrometry analysis of polyalkyl acrylates produced by spontaneous thermal polymerization provided complementary laboratory evidence that indicated chain initiation by initiating species created via postulated and computationally confirmed mechanisms. This section puts into perspective the advances that were made computationally by studying thermal self-initiation of MA, EA, and *n*BA.

Srinivasan et al. [16,17] conducted DFT calculations on the singlet and triplet surfaces by means of restricted open-shell and unrestricted wave functions, respectively. In particular, they used B3LYP34,35/6-31G*. They optimized molecular geometries of reactants, transition states, and products on the triplet and singlet surfaces; carried out Hessian calculations to characterize reactants and transition states; and performed intrinsic reaction coordinate calculations in the forward and reverse directions to determine minimum-energy pathways. They used MP2/6-31G* to perform validations studies; the multiconfigurational self-consistent field (MCSCF)/6-31G* to carry out spin-orbit coupling calculations; the rigid rotor harmonic oscillator (RRHO) approximation to predict energy barriers; scaling factors from the National Institute of Standards and Technology (NIST) scientific and technical database [28] to calculate temperature corrections, activation entropies, and zero point vibrational energies; transition state theory to predict rate constants; the Wigner tunneling correction; [29] and GAMESS [30] in the gas phase to perform all of the calculations.

4.3.2.1 Mayo mechanism

4.3.2.1.1 Diels-Alder reaction

To identify the most likely reaction mechanisms of MA, EA, and *n*BA self-initiation using computational quantum chemistry, the Mayo mechanism was first postulated and examined. Figs. 4.2, 4.3 and 4.4 show the molecular structures of reactants, intermediates, and products of MA, EA, and *n*BA [4 + 2] cycloaddition reactions. Diels-Alder dimers of MA, EA, and *n*BA were found to form on the singlet surface via Mayo's concerted pathway. In the thermal cycloaddition [4 + 2] reaction of the conjugated diene of a monomer molecule and the dienophile of a second monomer molecule, concerted reaction pathways were found, which agrees with orbital symmetry rules [16]. Endo- and exo-transition states were found, and for MA the energy of the exo transition state was calculated to be $\sim 2.1\ \mathrm{kJ\ mol^{-1}}$ higher than that of the endo transition state. Because this energy difference

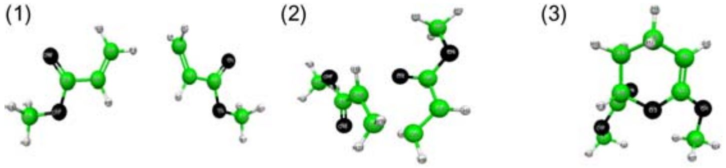

Figure 4.2

Molecular structures of reactants (1), intermediate (2), and product (3) of the MA [4 + 2] cycloaddition reaction. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Computational study of the self-initiation mechanism in thermal polymerization of methyl acrylate, J. Phys. Chem. A 113 (2009) 10787–10794. Copyright 2009 American Chemical Society.*

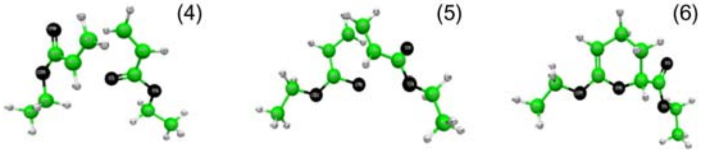

Figure 4.3
Molecular structures of the reactants (4), intermediate (5), and product (6) of the EA [4 + 2] cycloaddition reaction. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Self-initiation mechanism in spontaneous thermal polymerization of ethyl and n-butyl acrylate: a theoretical study, J. Phys. Chem. A 114 (2010) 7975–7983. Copyright 2010 American Chemical Society.*

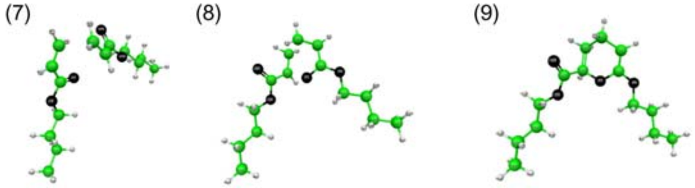

Figure 4.4
Molecular structures of reactants (7), intermediate (8), and product (9) of the *n*BA [4 + 2] cycloaddition reaction. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Self-initiation mechanism in spontaneous thermal polymerization of ethyl and n-butyl acrylate: a theoretical study, J. Phys. Chem. A 114 (2010) 7975–7983. Copyright 2010 American Chemical Society.*

is very small, the two products can be formed simultaneously. However, steric interactions and electrostatic repulsions between parts of the DAA may favor the formation of one product over the other. The final products were found to be meta orientation DAA dimers, whose energies are different from those of para orientation DAA dimmers by less than 1 kJ mol^{-1} [16,17,31]. This implied that the relative formation of the products depends on the initial orientation of the reactants. The energy barrier of the exo product formation is 117.1 kJ mol^{-1} (zero point energy corrected), which is 2.1 times higher than that of the endo product. However, the energy of the endo product is higher than that of the exo by ~2.9 kJ mol^{-1}. Therefore, the exo product is thermodynamically favorable, while the endo product is kinetically favorable. A kinetic product is favored more at low temperatures, but a thermodynamic product at high temperatures.

In spontaneous thermal polymerization of MA, the formation of a significant amount of the exo product was reported [16]. Table 4.1 presents significantly different transition state geometries and energy barriers that were obtained for MA, EA, and *n*BA by conducting intrinsic reaction coordinate (IRC) calculations from the transition state in the forward and reverse directions using B3LYP and MP2 [16–18]. Because of the fast equilibration of the

Table 4.1: Energy Barrier (E_0), Enthalpy ($\Delta H^{\ddagger}_{298}$) in kJ mol^{-1}; Frequency Factor (A); and Rate Constant (k) (M^{-1} s^{-1}) for Diels-Alder Adduct Formation [16,17]. Reported Barriers are Zero-Point Vibrational Energy Corrected. Rate Constants Were Computed Using Transition-State Theory.

Monomer Type	Level of Theory	E_0	$\Delta H^{\ddagger}_{298}$	Log$_e$ A	k
MA	B3LYP/6-31G*	122.3	118.4	8.67	1.41×10^{-18}
EA		139.8	136.2	9.93	3.78×10^{-21}
*n*BA		139.9	139.9	6.22	2.10×10^{-23}
MA	MP2/6-31G*	93.9	89.0	7.07	4.07×10^{-14}
EA		112.5	109.1	10.60	4.12×10^{-16}
*n*BA		88.4	82.3	6.60	3.82×10^{-13}

system, the reactions can reverse, forming monomers from the Diels-Alder adducts. The absence of m/z peaks corresponding to the DAAs in the ESI-FTMS spectra [31] of polymer samples obtained from spontaneous solution-phase polymerization of EA and *n*BA supports this theoretical finding. These results suggest that DAAs of MA, EA, and *n*BA do not play an appreciable role in chain initiation in spontaneous thermal homopolymerization of MA, EA, and *n*BA.

4.3.2.2 *Flory mechanism*

4.3.2.2.1 [2 + 2] Thermal cycloaddition reaction

The theoretical finding that the rate of the first reaction of the Mayo mechanism ([4 + 2] cycloaddition reaction) is very low, indicated that alkyl acrylates are not likely to self-initiate via the Mayo mechanism. The Flory mechanism was then postulated and evaluated using computational quantum chemistry. It was found that a nonconcerted [2 + 2] thermal cycloaddition reaction occurs between two monomer molecules on the singlet surface [16,17]. The [2 + 2] cycloaddition reaction forms dimethyl cyclobutane 1,2 dicarboxylate (DMCD), diethylcyclobutane 1,2 dicarboxylate (DECD), and dibutylcyclobutane 1,2 dicarboxylate (DBCD) via a singlet-diradical transition state, in the cases of MA, EA, and *n*BA, respectively. Figs. 4.5, 4.6 and 4.7 show molecular structures of the reactants, intermediates, and products of the MA, EA, and *n*BA [2 + 2] cycloaddition reactions, respectively. The reaction of the monomers forming the singlet diradical was found to be greatly stereospecific (cis-monomers forming cis-dimer, and trans-monomers forming trans-dimer) [16,17], which agrees well with the Woodward-Hoffmann rules for electrocyclic reactions. A cis diradical formed stereospecifically can be twisted via internal rotation, forming a trans diradical. Trans and cis diradicals produce trans and cis dimers, respectively. Accordingly, stereorandomness, cis monomers forming a trans dimer and vice versa, is present in the system.

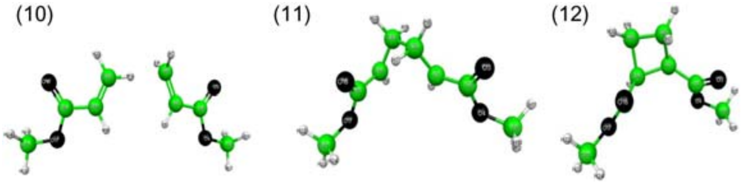

Figure 4.5
Molecular structures of the reactants (10), intermediate (11), and product (12) of the [2 + 2] thermal cycloaddition of MA. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Computational study of the self-initiation mechanism in thermal polymerization of methyl acrylate, J. Phys. Chem. A 113 (2009) 10787–10794. Copyright 2009 American Chemical Society.*

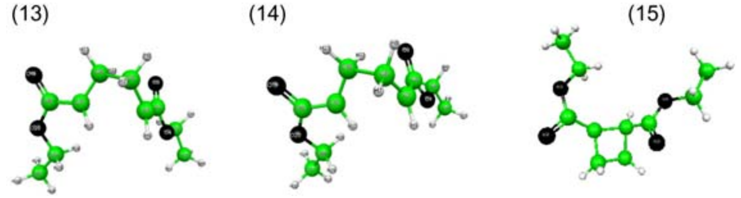

Figure 4.6
Molecular structures of the reactants (13), intermediate (14), and product (15) of the [2 + 2] thermal cycloaddition of EA. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Self-initiation mechanism in spontaneous thermal polymerization of ethyl and n-butyl acrylate: a theoretical study, J. Phys. Chem. A 114 (2010) 7975–7983. Copyright 2010 American Chemical Society.*

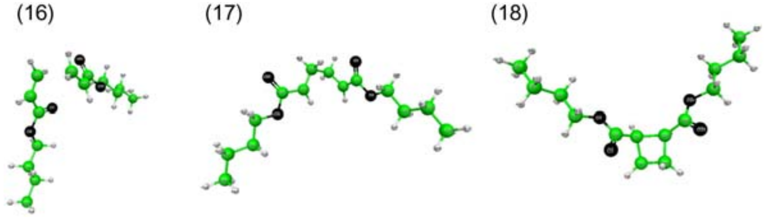

Figure 4.7
Molecular structures of the reactants (16), intermediate (17), and product of the [2 + 2] thermal cycloaddition of *n*BA (18). *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Self-initiation mechanism in spontaneous thermal polymerization of ethyl and n-butyl acrylate: a theoretical study, J. Phys. Chem. A 114 (2010) 7975–7983. Copyright 2010 American Chemical Society.*

Experiments have not shown any dimer formation in spontaneous thermal polymerization of MA, EA, and *n*BA. High conversions ($>$ 80%) of these monomers have been to polymers rather than dimers. Despite the lack of any reported experimental evidence, these monomers

Table 4.2: Energy Barrier (E_0), Enthalpy ($\Delta H^{\ddagger}_{298}$) in kJ mol^{-1}, Frequency Factor (A); and Rate Constant (k) (M^{-1} s^{-1}) for the Cyclobutane Dimer Formation. Reported Barriers are Zero-Point Vibrational Energy Corrected. Rate Constants Were Computed Using Transition-State Theory.

Monomer Type	Level of Theory	E_0	$\Delta H^{\ddagger}_{298}$	ln A	k
MA	B3LYP/6-31G*	189.1	186.2	9.72	5.37×10^{-30}
EA		189.0	184.9	9.75	9.35×10^{-30}
*n*BA		197.4	199.0	20.20	1.04×10^{-27}
MA	MP2/6-31G*	145.2	140.3	9.97	5.86×10^{-22}
EA		153.4	149.7	11.20	6.01×10^{-23}
*n*BA		170.8	167.5	9.70	9.77×10^{-27}

may form a trace amount of dimers in their spontaneous polymerization. Table 4.2 compares the energy barriers of the DECD, DMCD, and DBCD formation reactions calculated using two different levels of theory: B3LYP/6-31G* and MP2/6-31G*. The energy barriers for the formation of the MA, EA, and *n*BA dimers were found to be similar, indicating that the end-substituent group has a small effect on the barrier. MP2 yielded lower barriers but similar bond lengths for the predicted geometries, compared to B3LYP.

A singlet transition state was found for the formation of each of the cyclobutane 1,2 dicarboxylates (DBCD, DECD, and DMCD). Each of these follows the one-step stereorandom mechanism previously proposed in this chapter. The formation of the singlet diradicals of *n*BA, EA, and MA reactions were found to be exothermic, favoring the formation of the cyclobutane dimers. For example, the standard enthalpy changes for the formation of the singlet diradicals of *n*BA and EA were predicted to be −45 and −60 kJ mol^{-1}, respectively. However, these dimers have not been identified via mass spectrometry, pointing to the following possible reaction paths: (1) each cyclobutane dimer may undergo ring-opening to form a diradical, which then reacts with a third monomer molecule and exchanges a hydrogen to form two monoradicals that initiate polymerization; (2) before undergoing ring closure the singlet diradical reacts with a third monomer molecule and exchanges a hydrogen; and (3) the singlet diradical undergoes intersystem crossing, forming a triplet diradical, which reacts with a third monomer molecule to generate monoradicals. The ring-opening reaction is very unlikely to occur at an appreciable rate due to its very high energy barrier. It has been postulated that for MMA self-initiation the reaction path 3 is more likely than the reaction path 2 [10−13]. In the case of MA, EA, and *n*BA, the triplet diradical is a key intermediate in their self-initiation [9,16,17,31].

The energy barriers of the [2 + 2] cycloaddition reaction of MA predicted by B3LYP and various basis sets (6-31G*, 6-31G**, and 6-311G*) were found to be about 45 kJ mol^{-1} higher than those obtained with MP2 and the same basis sets (191.1, 191.1, and 199.1 kJ mol^{-1} estimated by B3LYP versus 145.3, 148.4, and 146.0 kJ mol^{-1} obtained with

MP2) [16]. Such a large difference in the energy barriers predicted by DFT and the wave function-based methods may be indicative of the complexity of the electronic structures of the diradicals involved in the self-initiation reactions. In addition, the reaction of two singlet monomers that produces a triplet diradical is a spin-forbidden reaction that involves a change of spin-state [32–34]. Classical transition state theory cannot be applied directly to the spin-forbidden reaction [35], as it assumes that the reaction occurs on a single potential energy surface (PES) with spin-conservation. However, non-adiabatic transition state theory (NA-TST) [36], which fully considers non-adiabatic effects, singlet-triplet surfaces, and inter-system crossing, is an attractive alternative [19]. Accordingly, the [2 + 2] cycloaddition reactions of MA, MMA, and *n*BA that involve diradicals require special attention to reliably predict energy barriers.

Table 4.3 shows values of the energy barrier of the [2 + 2] cycloaddition reaction of MA, calculated using G4(MP2)-6X and various density functionals with the 6-31G* basis set. It indicates that density functionals, such as B3LYP [37–39], BMK [40], wB97x-D [41], and M06-2X [42] that have been used widely in computational quantum chemistry study of polymerization reactions overestimate the barrier significantly. Moreover, the functionals TPSSh [43], TPSS [44], and PBE0 [45] are suitable for studying the [2 + 2] cycloaddition reaction. Table 4.4 presents values of the crossing coefficient, the spin-orbit coupling constant (SOC), E_c, and the adiabatic and non-adiabatic rate constants of MA at various temperatures obtained with PBE0/6-31G*, TPSSh/6-31G*, and TPSS/6-31G*. Evidently, the energetics of the minimum-energy crossing point (MECP), the point with the lowest energy at the crossing hypersurface, relative to the reactants calculated using the three functionals are within 5 kJ mol^{-1}. This is in agreement with energy barriers calculated for the [2 + 2] cycloaddition reaction of MA in a benchmark study with TPSSh, TPSS, and PBE0 [16]. The small value of SOC indicates weak spin-orbital coupling at the crossing point. A study of the spin-forbidden transition in the polymerization of MA, EA, *n*BA, and MMA using PBE0/6-31G* showed that the overall nonadiabatic rate coefficients are of the same order for MA, EA, and *n*BA (Table 4.5) [16–18]. This implies that the size of the end-substituent alkyl group does not appreciably affect the crossing probability and the energy of the

Table 4.3: Energy Barrier (E_0) in kJ mol^{-1} for [2 + 2] Cycloaddition Reaction of MA and Percent Deviation (PD) Relative to G4(MP2)-6X for Various Density Functionals (DFs) with 6-31G* Basis set [19].

DF	G4(MP2)-6X	B3LYP	PBE0	BMK	TPSS	TPSSh
E_0	156	187	163	196	148	162
PD	0.0%	19.9%	4.5%	25.6%	5.1%	3.8%
DF	**revTPSS**	**M06-L**	**M06**	**M06-2X**	**wB87x-D**	
E_0	139	143	165	201	195	
PD	10.9%	8.3%	5.8%	28.8%	25.0%	

Table 4.4: Spin-Orbit Coupling Constant (SOC) in cm^{-1}, Crossing Energy (E_c) in kJ mol^{-1}, Crossing Coefficient $\Gamma(T)$, and Adiabatic Rate Constant $k^{A}(T)$ Without Crossing Correction and Nonadiabatic Rate Constant $k^{NA}(T)$ in M^{-1} s^{-1} Obtained with PBE0/6-31G*, TPSS/6-31G*, and TPSSh/6-31G* at T(K) for MA [19].

	PBE0/6-31G*		TPSSh/6-31G*		TPSS/6-31G*	
SOC	0.94		1.33		1.26	
E_c	127.5		130.5		124.6	
T	393	413	393	413	393	413
$\Gamma(T)$	2.20E-5	1.91E-5	4.44E-5	3.99E-5	4.09E-5	3.80E-5
$k^{A}(T)$	8.22E-11	5.75E-10	2.06E-11	1.50E-10	1.84E-10	1.23E-9
$k^{NA}(T)$	1.80E-15	1.10E-14	9.14E-16	5.99E-15	7.52E-15	4.68E-14

Table 4.5: Spin-Orbit Coupling Constant (SOC) in cm^{-1}, Crossing Energy (E_c) in kJ mol^{-1}, Crossing Coefficient $\Gamma(T)$, and Adiabatic Rate Constant $k^{A}(T)$ Without Crossing Correction and Nonadiabatic Rate Constant $k^{NA}(T)$ in M^{-1} s^{-1} Obtained with PBE0/6-31G* at T (K) for MA, EA, *n*BA, and MMA [19].

	MA		EA		*n*BA		MMA	
SOC	0.94		0.78		0.83		1.35	
E_c	127.5		127.4		128.4		98.7	
T	393	413	393	413	393	413	393	413
$\Gamma(T)$	2.20E-5	1.91E-5	1.51E-5	1.31E-5	1.70E-5	1.48E-5	4.52E-5	4.23E-5
$k^{A}(T)$	8.22E-11	5.75E-10	2.79E-11	1.97E-10	9.95E-11	7.03E-10	9.19E-8	4.13E-7
$k^{NA}(T)$	1.80E-15	1.10E-14	4.21E-16	2.58E-15	1.69E-15	1.04E-14	4.16E-12	1.75E-11

MECP. The hopping probability of MMA is close to those of acrylates, but the barrier between MMA and the MECP of MMA is higher than those of the acrylates, which may be due to the stabilization effect of the methyl group attached to the alpha carbon of MMA [19]. The rate coefficient of the triplet diradical formation reaction of MMA was found to be 3−4 orders higher than those of MA, EA, and *n*BA. The higher rate coefficient of MMA points to the possibility of exploiting spin chemistry to accomplish faster monomer self-initiation via stabilizing the diradical, leading to a lower MECP energy.

4.3.2.2.2 Triplet diradical formation

Quantum chemistry calculations revealed that the singlet diradicals of MA, EA, and *n*BA very likely undergo intersystem crossing and form triplet diradicals, which can exchange a hydrogen with a monomer molecule, generating monoradicals capable of initiating polymerization [16,17]. The calculations showed that the singlet gauche diradical transition state and the triplet diradical intermediate of MA, EA, and *n*BA are structurally very similar. The energies of the triplet diradicals of MA, EA, and *n*BA relative to the reactants were found to be 113, 128, and 110 kJ mol^{-1}, respectively. Liu et al. [19] studied singlet-triplet spin crossover of diradicals in self-initiation of MA, EA, MMA, and *n*BA, by accounting for the nonadiabatic effect due to the intersystem crossing. They identified MECPs for MA, EA, MMA and *n*BA self-initiation reactions using GAMESS [46], and calculated spin-orbital coupling constants at the MECPs using complete active space multiconfiguration self-consistent field (CASSCF) wave functions. They found that the size of the end-substituent alkyl group does not affect the crossing probability and the energy of the MECP appreciably.

Using MCSCF(6,6)/6-31G*, spin-orbit coupling constants for the singlet-to-triplet diradical crossovers of MA, EA, and *n*BA were calculated to be 1.94, 15.1, and 5.2 cm^{-1}, respectively. The transition probability, which can be calculated using the Landau-Zener model [47,48], is directly related to the spin-orbit energy interaction matrix and consequently the spin-orbit coupling constant. A low spin-orbit coupling constant is indicative of a low crossing probability. Accordingly, diradicals of MA, EA, and *n*BA cannot rapidly crossover from the singlet state to the triplet. The lack of spontaneous initiation in MA, EA, and *n*BA at low temperatures ($<$120°C) may be due to low collision rates, which reduces the vibrational density of accessible states and therefore the crossover probability. These imply that, for self-initiation of MA, EA, and *n*BA to occur, a high monomer concentration and a high temperature are needed.

The work by Liu et al. [19] showed that the singlet-triplet spin crossover of the diradicals is the rate-limiting step in the self-initiation of MA, EA, and *n*BA, and that MMA has a higher self-initiation rate constant than these acrylates, which is due to the lower energy barrier between MMA reactants and the MMA singlet-triplet minimum-energy crossing point. It also showed that PBE0, TPSS and TPSSh are cost-effective functionals for exploring monomer self-initiation reactions of acrylates.

4.3.2.2.3 Monoradical formation

It has been reported that in styrene, the DAA intermediate formed after hydrogen cleavage aromatizes to stabilize the monoradical [49], but DFT studies showed that this does not occur for the MA, EA, and *n*BA DAA intermediates (MA data in Table 4.6). Because a molecule of these monomers has two oxygen heteroatoms, abstraction of an hydrogen from a monomer molecule by an oxygen atom of a second monomer molecule was first investigated; [16,17,31] the study showed that such hydrogen abstraction is very unlikely to occur. Therefore, hydrogen transfer from an alkyl acrylate DAA is not a viable pathway for monoradical generation, which is in agreement with the results reported by Stickler and Meyerhoff [13] for thermal polymerization of MMA.

Reactions in which the singlet and triplet diradicals donate (transfer) and accept (abstract) a hydrogen from a third monomer molecule were studied [16,17]. All three MA, EA, and *n*BA

Table 4.6: Energy Barrier (E_0), Enthalpy ($\Delta H^{\ddagger}_{298}$), and in kJ mol^{-1}, Frequency Factor (A); and Rate Constant (k) (M^{-1} s^{-1}) for Monoradical Formation [17,50]. Reported Barriers are Zero-Point Vibrational Energy Corrected.

Temperature (K)	Reaction	E_a	$\Delta H^{\ddagger}_{298}$	ln A	Wigner Tunneling Coefficient	k
			Methyl Acrylate			
298	Hydrogen transfer from • M_{2t} • to MA	81.1	76.2	16.6	4.8	4.7×10^{-7}
373		83.7	77.5	17.5	3.4	2.6×10^{-4}
413		85.2	78.3	17.9	3.0	3.2×10^{-3}
298	Hydrogen abstraction from • M_{2t} • to MA	96.9	92.0	15.6	2.7	1.7×10^{-10}
373		99.4	93.2	16.5	2.1	3.8×10^{-7}
413		100.8	93.6	16.9	1.9	7.7×10^{-6}
			Ethyl Acrylate			
298	Hydrogen transfer from • M_{2t} • to EA	91.3	99.5	18.2	4.8	8.1×10^{-10}
373		91.3	97.7	19.3	3.4	2.3×10^{-6}
413		91.3	98.8	19.8	3.0	5.2×10^{-5}
298	Hydrogen abstraction from • M_{2t} • to EA	99.7	102.5	16.4	2.7	4.9×10^{-12}
373		99.7	102.6	17.3	2.1	3.9×10^{-8}
413		99.7	104.2	17.7	1.9	8.1×10^{-7}
			***n*-Butyl Acrylate**			
298	Hydrogen transfer from • M_{2t} • to *n*BA	78.1	79.3	13.3	4.8	5.4×10^{-9}
373		78.1	80.5	14.3	3.4	3.9×10^{-6}
413		78.1	81.1	14.6	3.0	4.8×10^{-5}
298	Hydrogen abstraction from • M_{2t} • to *n*BA	94.4	99.0	19.0	2.7	2.9×10^{-10}
373		94.4	101.0	20.2	2.1	1.2×10^{-6}
413		94.4	102.1	20.7	1.9	3.1×10^{-5}

singlet diradicals were found to undergo ring closure before hydrogen transfer, suggesting that such diradicals are unable to generate a monoradical. However, MA, EA, and *n*BA triplet diradicals were found able to transfer or abstract a hydrogen [16,17]. For each of the monomers, the hydrogen transfer from the triplet diradicals to the monomer molecules was found to have a lower energy barrier than hydrogen abstraction by the triplet diradicals from the monomer molecules [16,17]. A comparison of the reaction rates of hydrogen transfer from MA, EA, and *n*BA triplet diradicals did not show a correlation between the energy barrier and rate coefficient of the reaction and the size of the end substituent group for the monomers. Figs. 4.8, 4.9 and 4.10 show transition-state geometries for the monoradical generation reactions in homopolymerization of MA, EA, and *n*BA, respectively.

In summary, theoretical studies indicated that the generation of monoradicals in the spontaneous thermal polymerization of MA, EA, and *n*BA occurs preferably via hydrogen transfer from triplet radicals to monomer molecules, rather than through hydrogen abstraction by triplet diradicals from monomer molecules. These results showed

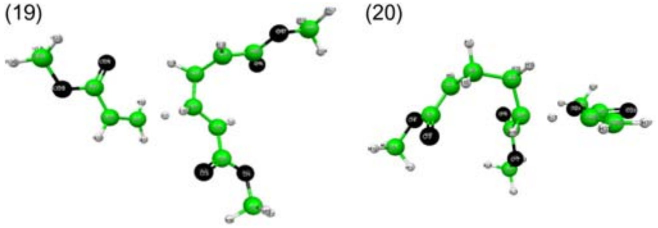

Figure 4.8
Transition-state geometries for the monoradical generation reactions in MA polymerization: (19) hydrogen abstraction by a triplet diradical from an MA molecule, and (20) hydrogen transfer from a triplet diradical to an MA molecule. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Computational study of the self-initiation mechanism in thermal polymerization of methyl acrylate, J. Phys. Chem. A 113 (2009) 10787–10794. Copyright 2009 American Chemical Society.*

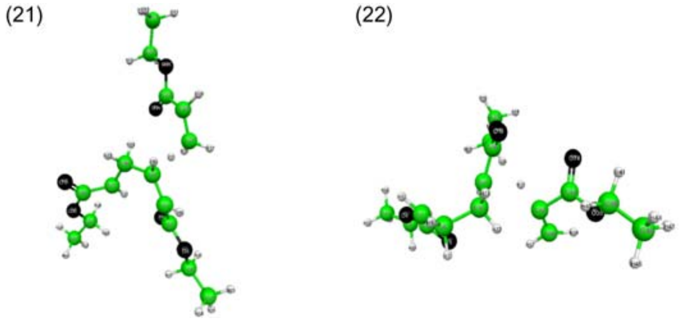

Figure 4.9
Transition-state geometries for the monoradical generation reactions in EA polymerization: (21) hydrogen abstraction by a triplet diradical from an EA molecule, and (22) hydrogen transfer from a triplet diradical to an EA molecule. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Self-initiation mechanism in spontaneous thermal polymerization of ethyl and n-butyl acrylate: a theoretical study, J. Phys. Chem. A 114 (2010) 7975–7983. Copyright 2010 American Chemical Society.*

conclusively that triplet diradicals are main intermediates in the production of initiating species in spontaneous thermal polymerization of alkyl acrylates.

4.3.3 Alkyl Acrylate Summary

Computational quantum chemistry studies of MA, EA, and *n*BA singlet and triplet potential-energy surfaces have shown that there are two dimers on the singlet surface for both Mayo and Flory mechanisms. A DAA is formed via a concerted pathway. Cyclobutane species are formed via a nonconcerted diradical pathway for MA, EA, and *n*BA. The

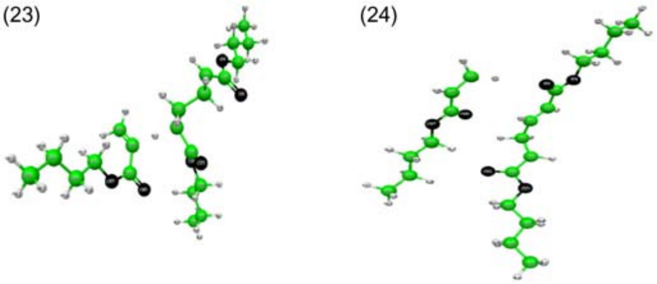

Figure 4.10
Transition-state geometries for the monoradical generation reactions in *n*BA polymerization: (23) hydrogen abstraction by a triplet diradical from an *n*BA molecule, and (24) hydrogen transfer from a triplet diradical to an *n*BA molecule. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Self-initiation mechanism in spontaneous thermal polymerization of ethyl and n-butyl acrylate: a theoretical study, J. Phys. Chem. A 114 (2010) 7975–7983. Copyright 2010 American Chemical Society.*

reactions that generate singlet diradicals from two MA, EA, and *n*BA molecules have similar energy barriers, indicating that the end substituent groups of the monomers have little effect on the diradical formation. Triplet diradical intermediates play a central role in the self-initiation of MA, EA, and *n*BA. Monoradical generation in MA, EA, and *n*BA systems primarily occurs via hydrogen transfer from triplet diradicals to monomer molecules. These findings are supported by spectroscopic polymer characterization results. Masses of the MA, EA, and *n*BA monoradical structures predicted by computational quantum chemistry are in agreement with the masses of chain initiating groups of the dominant peaks in ESI/FTMS spectra of spontaneously polymerized poly(MA), poly(EA), and poly(*n*BA), respectively. For these monomers, the rate-limiting reaction in their self-initiation reaction path is the intersystem crossing (singlet-to-triplet diradical) reaction.

4.3.4 Comparison With Estimates Obtained From Laboratory Experiments

Reaction kinetic parameters can also be estimated from polymer property measurements using a macroscopic-scale mechanistic polymerization reactor model. Table 4.7 compares values of the MA apparent self-initiation reaction rate coefficient at six temperatures predicted by computational quantum chemistry, with those estimated from measurements of MA conversion in batch reactors in which spontaneous thermal polymerization of MA occurred [21]. These results show that the experimentally estimated and the first principles–predicted MA apparent self-initiation reaction rate coefficient values agree well. A similar study carried out for *n*BA [20] showed that the apparent self-initiation reaction kinetic parameter estimates obtained from conversion measurements also agree well with values predicted via purely theoretical quantum chemical calculations (Table 4.8).

Table 4.7: Experimentally Estimated and Theoretically Predicted Values of MA Apparent-Self-Initiation-Reaction Rate Coefficient ($L.mol^{-1}.s^{-1}$).

Temperature (K)	413.2	433.2	453.2	473.2	493.2
Experimentally estimated [21]	1.07×10^{-13}	1.15×10^{-12}	1.00×10^{-11}	7.25×10^{-11}	4.47×10^{-10}
Theoretically predicted [19]	4.61×10^{-14}	2.30×10^{-13}	9.95×10^{-13}	3.80×10^{-12}	1.30×10^{-11}

Table 4.8: Experimentally Estimated and Theoretical Predicted Values of the *n*BA Apparent-Self-Initiation Reaction Rate Coefficient ($L.mol^{-1}.s^{-1}$).

Temperature (K)	Experimental [20]	Theoretical [9]	Theoretical [19]
413.2	3.30×10^{-15}	2.81×10^{-18}	1.04×10^{-14}
433.2	2.20×10^{-14}	2.86×10^{-17}	4.72×10^{-14}
453.2	4.00×10^{-13}	2.37×10^{-16}	1.95×10^{-13}
473.2	1.50×10^{-12}	1.64×10^{-15}	7.11×10^{-13}
493.2	6.80×10^{-12}	9.74×10^{-15}	2.34×10^{-12}

4.4 Methacrylate Thermal Self-Initiation

4.4.1 Prior Experimental Knowledge

Experimental studies of the spontaneous thermal polymerization of MMA at high temperatures (100–130°C) showed the production of high average molecular–weight polymers, low conversion of monomer to polymer, and the formation of a significant amount of oligomers (such as dimers and trimers) after 75 hours of batch operation [10–14,23]. Experimental observation of the formation of a significant amount of linear unsaturated dimer, dimethyl 1-hexene 2, 5 carboxylate [10–12] motivated the postulations that MMA self-initiation occurs, MMA diradical species are formed, and MMA triplet diradicals generate species that initiate polymerization of MMA [51].

Unlike the DAA of styrene, that of MMA was reported as unable to generate monoradicals via the molecular-assisted homolysis mechanism [14,52]. The absence of evidence to support the presence of the monoradicals in solution [13] was the basis for suggesting that MMA does not self-initiate via the Mayo mechanism. The isolation of *cis*- and *trans*-dimethyl 1,2-dimethyl-cyclobutane-1,2-dicarboxylates (DDCDs) in solution [11] pointed to the occurrence of diradical-based mechanisms in spontaneous thermal polymerization of MMA. This was supported by: (1) a high concentration of the linear dimer, dimethyl 2-methyl-5-methylidene-hexanedioate (DMMH), which is generated via the diradical intermediate route [10–14]; and (2) the formation of dimethyl 2,5-dimethylhexanedioate (DDH), which is produced via double hydrogen transfer from protic solvents to the 1, 4-diradical [53–55]. In addition, lower conversions (~5%), higher molecular–weight polymers, and higher concentrations of dimers were reported in spontaneous polymerization of MMA than in that of styrene [23,56], and the rate of spontaneous polymerization of MMA in nonpolar solvents was found to be significantly lower than that of styrene [6,10−13,23]. Higher MMA conversions in halogenated solvents and thiophenol were reported [10], supporting the argument that heavy atoms in halogenated solvents and inert gases can aid singlet-to-triplet crossover (intersystem crossing) via collisions [54,57,58]. Further evidence of the positive effect of heavy atoms on monomer self-initiation was provided by the high rate of spontaneous polymerization of chlorinated ethyl methacrylates [55]. The rate of spontaneous thermal polymerization of MMA was reported to be comparable to the rate of photo-initiated polymerization of naphthalene, in which intersystem crossing of diradicals was previously known [55]. On the basis of these similarities, it was concluded that intersystem crossing may occur in spontaneous polymerization of MMA. Also, a lower monomer conversion to polymer and higher polymer average molecular weights were reported in spontaneous polymerization of MMA than in that of alkyl acrylates [6,9,11,13]. No cyclobutane derivatives or linear dimers were observed in spontaneous polymerization of acrylates. It was hypothesized that acrylate and methacrylate monomers have different polymer morphology and reaction kinetics due to their different molecular structures [18].

Macroscopic-scale mechanistic polymerization reactor mathematical models were also used to determine whether the initiating species are triplet diradicals [54]. However, this approach was not able to determine the true nature of the intermediates that are formed, because these models did not account for the formation or decomposition of these intermediates [54].

Before the theoretical studies reviewed in this chapter, there was no evidence to deny or support conclusively that (1) singlet-to-triplet intersystem crossing occurs, (2) MMA triplet diradicals are formed, or (3) the triplet diradicals contribute to MMA self-initiation. Furthermore, it was not certain that MMA triplet diradicals can produce monoradicals.

4.4.2 Knowledge Gained Using Quantum Chemical Calculations

4.4.2.1 Mayo mechanism

4.4.2.1.1 Diels-Alder reaction

To identify the most likely reaction mechanisms of MMA self-initiation using computational quantum chemistry, the Mayo mechanism was first postulated (Fig. 4.11). Density functional theory studies showed that MMA favors the formation of a meta-like DAA [18]. Fig. 4.12 shows molecular structures of the reactants (25), intermediate (26), and product (27) of the MMA-DAA formation reaction. Table 4.9 presents the energy barrier and rate constant of the formation of the DAA, calculated using different levels of theory. The calculated DAA-formation barriers for MMA (106.3 and 82.7 kJ mol^{-1})

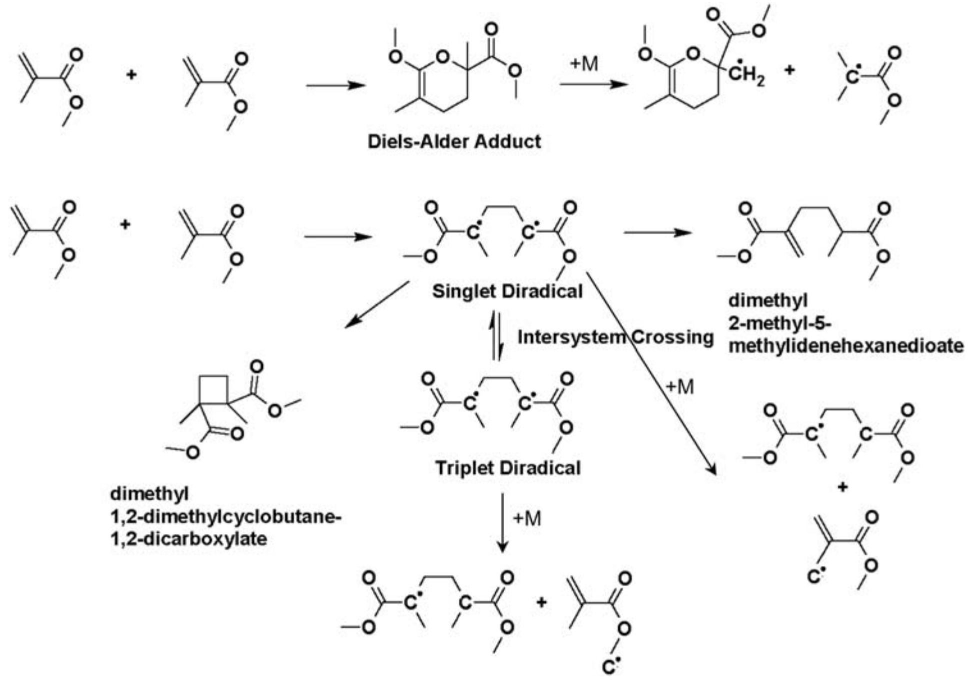

Figure 4.11

Flory and Mayo mechanisms of self-initiation for MMA. Note that this figure shows only two hydrogen-transfer-from-monomer reactions. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Computational evidence for self-initiation in spontaneous high-temperature polymerization of methyl methacrylate, J. Phys. Chem. A 115 (2011) 1125–1132. Copyright 2011 American Chemical Society.*

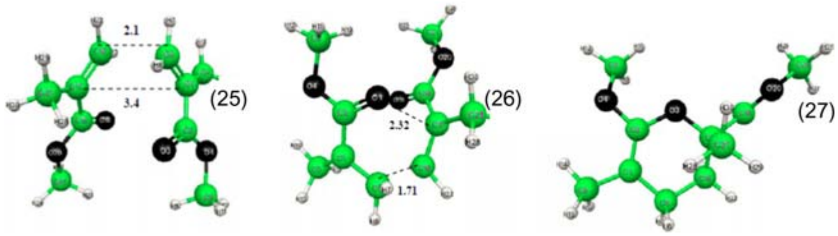

Figure 4.12

Molecular structures of the reactants (25), intermediate (26), and product (27) of MMA-DAA formation reaction. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Computational evidence for self-initiation in spontaneous high-temperature polymerization of methyl methacrylate, J. Phys. Chem. A 115 (2011) 1125–1132. Copyright 2011 American Chemical Society.*

are both lower than that of the DAA formation for styrene (148 kJ mol^{-1}) [59] and MA (122 kJ mol^{-1}) [60]. Nevertheless, no DAA species, even at low concentrations ($\sim 10^{-3}$ M), has been reported in spontaneous polymerization of MMA [25].

Table 4.9: Energy barrier (E_0), enthalpy ($\Delta H^{\ddagger}{}_{298}$) in kJ mol^{-1}, Frequency Factor (A); and Rate Constant (k) (M^{-1} s^{-1}) for DAA Intermediate Formation in MMA [18]. Reported Barriers are Zero-Point Vibrational Energy Corrected.

Monomer Type	Level of Theory	E_0	$\Delta H^{\ddagger}{}_{298}$	k
MMA	B3LYP/6-31G*	106.3	101.3	3.1×10^{-15}
MMA	MP2/6-31G*	82.7	77.6	1.4×10^{-10}

Furthermore, the enthalpy of the DAA formation reaction is nearly zero (the forward and backward reactions have little or no overall thermodynamic driving force). These indicate that the reverse Diels-Alder reaction appreciably occurs at high temperatures. Thus, the DAA is formed, but it does not play a central role in initiating MMA thermal polymerization. The transition-state geometries were validated using MP2/6-31G* level of theory [18].

4.4.2.2 Flory mechanism

4.4.2.2.1 Dimethyl 1,2-dimethylcyclobutane 1,2 dicarboxylate formation

Quantum chemistry calculations using B3LYP/6-31G* identified a nonconcerted, single transition state and a flat potential energy surface with no energy minimum for the singlet diradical, eventually leading to the production of *cis*- and *trans*-isomers of the DDCD [18]. Figs. 4.13 and 4.14 show the molecular structures of the reactants, intermediates, and products of the MMA cis- and trans-DDCD reactions. The predicted energy barriers, enthalpies, and rate coefficients for the DDCD formation reactions calculated using B3LYP/6-31G* and MP2/6-31G* are given in Table 4.10. The activation energies predicted using MP2/6-31G* (123.2 and 146.2 kJ mol^{-1}) are close to 126 and 141 kJ mol^{-1}, which have been obtained experimentally for *trans*-DDCD and *cis*-DDCD, respectively. Intrinsic reaction coordinate calculations performed using B3LYP/6-31G* in the forward and reverse directions from the transition states of *cis*-DDCD and *trans*-DDCD determined a stereorandom one-step diradical mechanism for the formation of these dimers, which agrees with the mechanisms found for spontaneous polymerization of pentafluorostyrene [61] and alkyl acrylates [16,17]. However, the ring closure and the DDCD formation are faster in MA, EA, and *n*BA than in MMA [18].

4.4.2.2.2 DMMH intermediate formation

The formation of dimethyl 2-methyl-5-methylidene-hexanedioate (DMMH), a linear dimer, was found to occur via intramolecular hydrogen transfer; that is, transfer of an hydrogen from the methyl group attached to the alpha carbon atom of the first monomer to the alpha carbon atom of the second monomer [18] (Fig. 4.15). The energy barrier for the DMMH formation was calculated to be 116.8 kJ mol^{-1} using B3LYP/6-31G* and 96 kJ mol^{-1} using MP2/6-31G* (Table 4.11). The predicted enthalpies and rate constants were found to agree

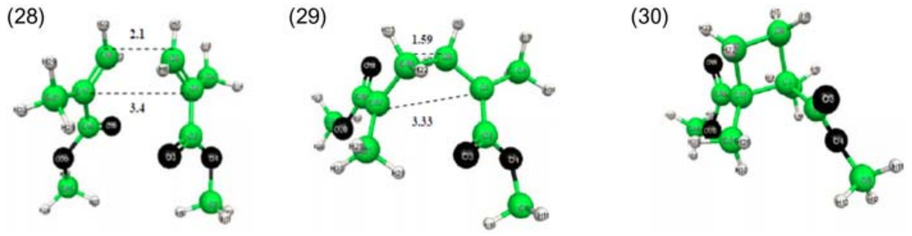

Figure 4.13

Molecular structures of the reactants (28), intermediate (29), and product (30) of the MMA *cis*-DDCD reaction. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Computational evidence for self-initiation in spontaneous high-temperature polymerization of methyl methacrylate, J. Phys. Chem. A 115 (2011) 1125–1132. Copyright 2011 American Chemical Society.*

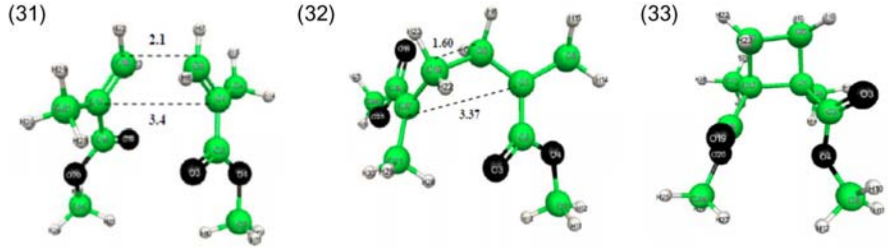

Figure 4.14

Molecular structures of the reactants (31), intermediate (32), and product (33) of the MMA *trans*-DDCD reaction. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Computational evidence for self-initiation in spontaneous high-temperature polymerization of methyl methacrylate, J. Phys. Chem. A 115 (2011) 1125–1132. Copyright 2011 American Chemical Society.*

Table 4.10: Energy Barrier (E_0), Enthalpy ($\Delta H^{\ddagger}{}_{298}$) in kJ mol^{-1}, and Rate Constant (k_{DDCD}) (M^{-1} s^{-1}) for the DDCD Formation in MMA at 298 K Using two Levels of Theory [18]. The Reported Energies are Zero-Point Vibrational Energy (ZPVE) Corrected.

Level of Theory	Isomer	E_0	$\Delta H^{\ddagger}{}_{298}$	k_{DDCD}
B3LYP/6-31G*	*trans*	188.2	183.3	1.8×10^{-29}
B3LYP/6-31G*	*cis*	226.3	221.4	3.8×10^{-36}
MP2/6-31G*	*trans*	123.2	118.3	1.9×10^{-17}
MP2/6-31G*	*cis*	146.2	141.3	1.8×10^{-21}

well with experimental values [10,12]. The DMMH formation is kinetically favored over that of DDCD and its energy barrier is lower than that of DDCD. This is in agreement with previous experimental studies reporting a higher concentration of DMMH than DDCD in

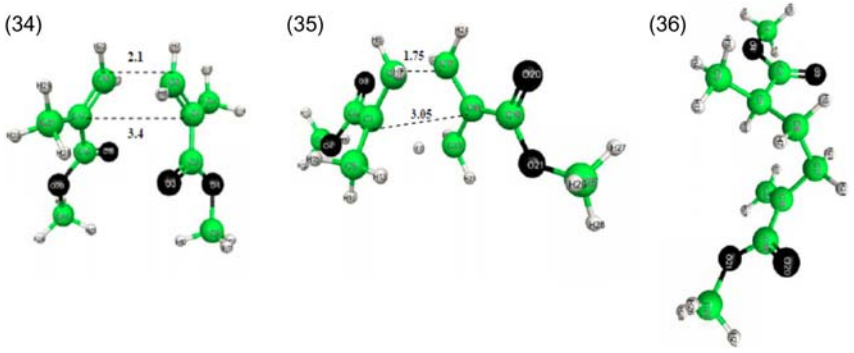

Figure 4.15

Molecular structures of the reactants (34), intermediate (35), and product (36) of the MMA DMMH-formation reaction. *Adapted from: reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Computational evidence for self-initiation in spontaneous high-temperature polymerization of methyl methacrylate, J. Phys. Chem. A 115 (2011) 1125–1132. Copyright 2011 American Chemical Society.*

Table 4.11: Energy Barrier (E_0), Enthalpy ($\Delta H^{\ddagger}_{298}$) in kJ mol^{-1}, Frequency Factor (A); and Rate Constant (k) (M^{-1} s^{-1}) for DMMH Formation in MMA. Reported Barriers are Zero-Point Vibrational Energy Corrected.

Level of Theory	E_0	$\Delta H^{\ddagger}_{298}$	k
B3LYP/6-31G*	117.3	112.3	2.7×10^{-16}
MP2/6-31G*	97.2	92.3	3.3×10^{-12}

MMA self-initiated polymerization [10]. As this fast DMMH formation reaction competes with (occurs in parallel with) the reactions that lead to the formation of monoradicals, less monoradicals are generated in spontaneous polymerization of MMA; slower rates of spontaneous polymerization of MMA in inert solvents, such as benzene and toluene, have been reported [10]. These findings point to the differences made by the methyl group attached to the alpha carbon of MMM. The absence of this methyl group in MA, EA, and *n*BA prevents the formation of a linear dimer on the singlet potential energy surfaces of MA, EA, and *n*BA, and makes self-initiation of MA, EA, and *n*BA faster.

4.4.2.2.3 Triplet diradical formation

Exploring the triplet energy surface using B3LYP/6-31G*, it was found that the energy difference between the singlet diradical transition state and the triplet diradical intermediate ($\Delta E_{\text{S-T}}$) is 80 kJ mol^{-1}, about 2 kJ mol^{-1} more than that of MA [60]. The MECP from singlet to triplet was first identified using B3LYP/6-31G* and then optimized using MCSCF/6-31G*. On the basis of molecular orbitals provided by MCSCF and through including the full Breit-Pauli operator [62], the spin-orbit coupling constant was calculated to be 2.5 cm^{-1}. According to the Landau-Zener model [47,48], such a low value of the spin-orbit coupling constant points to a low probability of the singlet-to-triplet diradical transition. Interaction of MMA with heavy atoms and inert gases has been found to help the crossover [15,51]; higher rates of MMA polymerization in halogenated solvents bubbled with nitrogen or argon have been reported [54,55].

4.4.2.2.4 Monoradical formation

B3LYP/6-31G* was used to study how monoradicals are formed in spontaneous thermal polymerization of MMA. Hydrogen transfer from an MMA DAA to an MMA molecule via the molecular assisted homolysis mechanism was studied [18]. The DAA was found unable to donate a hydrogen to an MMA molecule, which agrees with previous results [11,14,16,17].

Transfer of an hydrogen from the singlet and triplet diradicals to an MMA molecule, and abstraction of a hydrogen by the singlet and triplet diradicals from an MMA molecule were also studied. Stable transition states for hydrogen abstraction by the singlet and triplet diradicals from monomer molecules and hydrogen transfer from the triplet diradical to a monomer moelcule were found. However, no transition state was determined for hydrogen transfer from a singlet diradical to a monomer molecule, supporting the unlikeliness of molecular-assisted homolysis in MMA. Transition-state geometries for the three likely MMA monoradical generation reactions are shown in Fig. 4.16. It was found that the energy barrier for hydrogen abstraction by the singlet and triplet diradicals from an MMA molecule is much lower than that of hydrogen transfer from the triplet diradical to an MMA molecule [18] (Table 4.12), which is different from the mechanisms of monoradical generation in MA, EA, and *n*BA. This indicates that in MMA, both singlet and triplet diradicals participate in the generation of monoradicals. Accordingly, in MMA, monoradical formation is most likely to occur via (1) hydrogen abstraction by a singlet diradical from the methyl group attached to the alpha carbon of an MMA molecule, and (2) hydrogen abstraction by a triplet diradical from the methyl group that is attached to an oxygen atom of an MMA molecule. It is worth noting that intramolecular hydrogen transfer from the methyl group attached to an alpha carbon atom of a monomer unit to the alpha carbon atom of the other monomer unit of a singlet diradical leads to the formation of the dimer DMMH (dead polymer chain), but intermolecular hydrogen abstraction by the singlet diradical from the methyl group attached to the alpha carbon of an MMA molecule generates monoradicals. Calculated rate coefficients of these parallel (competing) reactions indicate that these reactions are equally likely to occur. This may explain the low monomer conversion and the formation of high molecular weight polymer reported for MMA self-initiated polymerization. It also points to the strong impact of the methyl group attached to the alpha carbon atom of MMA on the self-initiation mechanism of MMA.

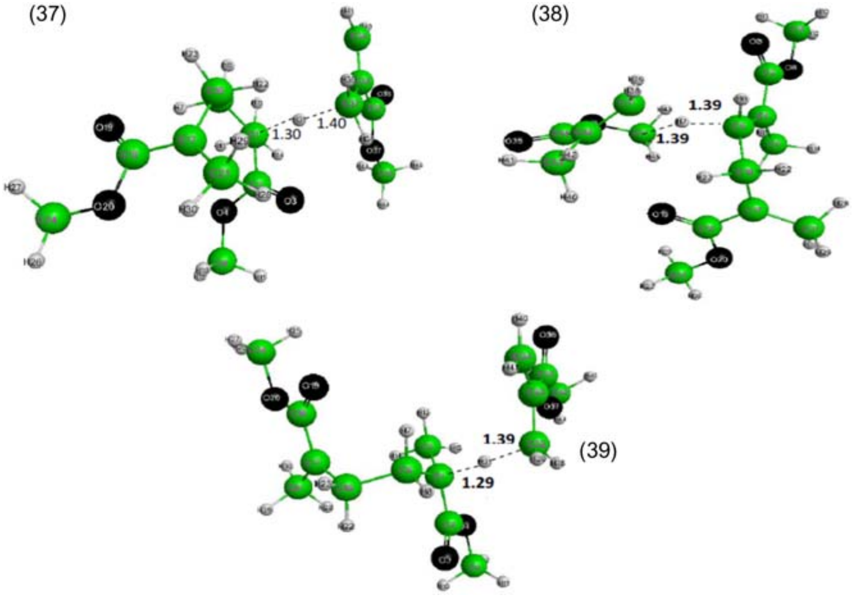

Figure 4.16

Transition state geometries of MMA monoradical generation reactions. 37: Abstraction of a hydrogen by a singlet diradical from an MMA molecule. 38: Transfer of a hydrogen to a triplet diradical from an MMA molecule. 39: Abstraction of a hydrogen by a triplet diradical from an MMA molecule. *Adapted from reprinted with permission from S. Srinivasan, M.W. Lee, M.C. Grady, M. Soroush, A.M. Rappe, Computational evidence for self-initiation in spontaneous high-temperature polymerization of methyl methacrylate, J. Phys. Chem. A 115 (2011) 1125–1132. Copyright 2011 American Chemical Society.*

Table 4.12: Energy Barrier (E_0) and Enthalpy ($\Delta H^{\ddagger}_{298}$) in kJ mol^{-1}; and Rate Constant (k) (M^{-1} s^{-1}) for Monoradical Formation in MMA. Reported Barriers are Zero Point Vibrational Energy Corrected.

Reaction	Level of Theory	E_0	$\Delta H^{\ddagger}_{298}$	k
Hydrogen abstraction by $\bullet M_{2s}\bullet$	B3LYP/6-31G*	98.1	93.2	3.8×10^{-10}
Hydrogen transfer from $\bullet M_{2t}\bullet$		175.5	170.1	6.4×10^{-23}
Hydrogen abstraction by $\bullet M_{2t}\bullet$		102.1	97.2	7.7×10^{-11}

4.4.3 Methacrylate Summary

Computational quantum chemistry allowed for a thorough investigation of chain initiation in self-initiated thermal polymerization of MMA. It showed that DAA, DMMH, and DDCD bimolecular intermediates of MMA are formed on the singlet surface. It revealed that DAA and DMMH of MMA are formed via a concerted pathway, but DDCD via a nonconcerted pathway. The energy barriers for the formation of DDCD and DMMH are larger than that of DAA and comparable to energy barrier values obtained experimentally. The existence of the low-energy diradical intermediate on the triplet surface supports the hypothesis made by Pryor and Laswell [23]. In alkyl acrylates, monoradical formation most likely occurs via hydrogen transfer from triplet diradicals to monomer molecules. However, in methacrylates, monoradical formation most likely occurs via hydrogen abstraction by both singlet and triplet diradicals from methyl groups of MMA molecules. These theoretical findings are in agreement with the previous experimental results. Computational quantum chemistry provided new proof for the diradical mechanism of self-initiation of MMA and new insights into hydrogen abstraction by diradicals in self-imitated thermal polymerization of MMA.

4.5 Monomer-Solvent Coinitiation

4.5.1 Prior Experimental Knowledge

Previous experimental studies [63–66] showed that a solvent can affect chain initiation in polymerization of methacrylates and acrylates. Ouchi et al. [67] reported that some aldehydes can initiate MA polymerization. Kaim [63,64] later found that cyclohexanone (CHo) helps initiation of MMA, *n*BA, and acrylamide free-radical polymerization. Kaim [64] proposed an initiation mechanism involving the formation of a CHo-monomer complex, which then dissociates and produces monoradicals. Xu et al. [66] reported that atom transfer radical polymerization of MMA with $CuCl_2$/*N,N,N',N',N''*-pentamethyldiethylenetriamine in CHo achieves high conversion without using any initiators.

An experimental study of spontaneous thermal polymerization of *n*BA and MA [65] revealed that *n*BA and MA polymerize much more in CHo than in xylene and dimethyl sulfoxide, and polymers formed in CHo have lower average molecular weights than those in xylene and dimethyl sulfoxide. It was known that in CHo without any added initiators, while MMA polymerizes at low temperatures ($<100^{o}C$), MA polymerizes at high temperatures ($>100^{o}C$). It was also found that MMA polymerizes slowly in nonpolar solvents [15] but fast in halogenated and polar protic solvents. The higher polymerization rates in halogenated solvents and thiophenol (polar protic) were attributed to rapid chain transfer, and fast crossover of diradicals from the singlet to triplet state, via collisions with the heavy halogen or sulfur atoms [15,51,58]. However, the heavy atom effect was found to be weaker in thiophenol than in halogenated solvents.

In summary, the experimental studies led to the postulation of a reaction path that involved cyclohexanone and generated monoradicals at a rate higher than that of monomer self-initiation. However, they did not result in conclusively determining initiation mechanisms or initiating species that justify the solvent effects.

4.5.2 Knowledge Gained Using Quantum Chemical Calculations

Electronic-level modeling has been used to explore postulated mechanisms of solvent-assisted free-radical chain initiation. To identify initiation mechanisms and initiating species in spontaneous thermal homopolymerization of MA and MMA in CHo, Liu et al. [68] investigated the following four different mechanisms using DFT and second-order Møller-Plesset perturbation theory (MP2): (1) Kaim [64], (2) Flory [69], (3) Cyclohexanone α-hydrogen transfer, and (4) Mayo [70], shown in Fig. 4.17. Transition-state geometries for each mechanism were determined using B3LYP/6-31G* and assessed with MP2/6-31G*, and rate coefficients and activation energies were determined using the transition-state theory. The harmonic oscillator approximation and tunneling corrections were also applied.

4.5.2.1 Kaim mechanism

According to Kaim's mechanism [63,64], Scheme I(a) in Fig. 4.17, the CHo-monomer complex is formed via simultaneous interactions between two types of atom pairs; the carbonyl oxygen of a monomer molecule interacts with an α-hydrogen of a CHo molecule, and the carbonyl group of the CHo molecule interacts with the β-carbon of the monomer molecule. Kaim postulated that this weakly associated complex decomposes and generate monoradicals that initiate polymerization.

Using computational quantum chemistry, Liu et al. [68] determined that the formation of the monomer-CHo intermediate has a high energy barrier: 256 kJ mol^{-1} for MA and 215 kJ mol^{-1} for MMA. Furthermore, the formation of the radicals proposed by Kaim requires breaking an O—C covalent bond of the monomer unit in the intermediate, the energy barrier of which is more than 300 kJ mol^{-1}. Accordingly, the formation of monoradicals via the dissociation of the monomer-CHo intermediate is not energetically favorable, implying that Kaim's mechanism is very unlikely to occur. Scheme I(b) in Fig. 4.17 shows a modified Kaim mechanism. In summary, Liu et al. [68] found that the Kaim mechanism [Fig. 4.17(I)] is very unlikely to be the mechanism of the observed initiation, as the activation energy of the complex formation reaction is very high and the complex is unable to decompose to generate monoradicals.

4.5.2.2 Flory mechanism

Liu et al. [68] then studied the two types of cycloaddition reactions shown in Figure 4.17 (II), which involve the C = O bond of CHo and the C = C bond of MA and MMA.

4.5.2.2.1 Methyl acrylate

For the 2,2,3-cycloaddition, Liu et al. [68] located a nonconcerted transition state and found that the energy barriers estimated using B3LYP and MP2/6-31G* to be much larger than that of the [2 + 2] cycloaddition in MA self-initiation [16]. Liu et al. [68] did not find an

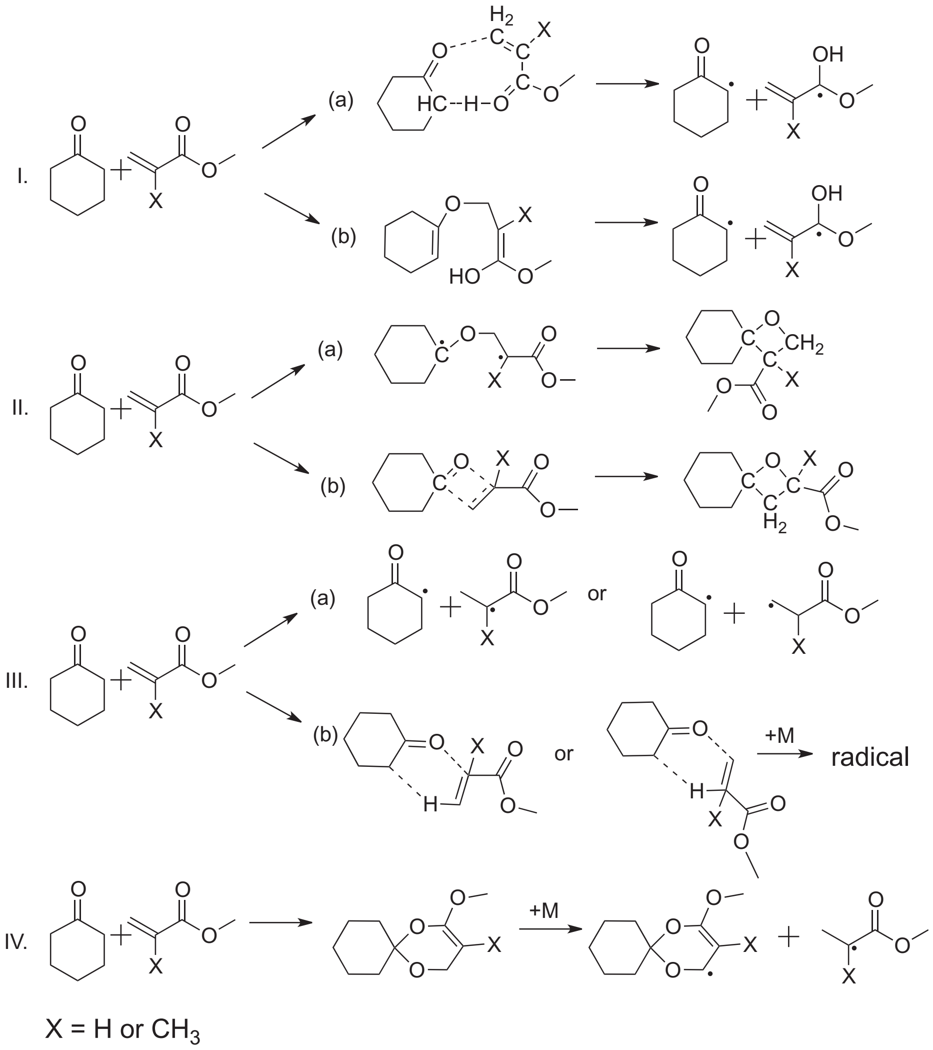

Figure 4.17

Cylcohexanone-monomer co-initiation mechanisms. I: (a) Mechanism proposed by Kaim, and (b) Modified Kaim mechanism based on first-principles calculations; II: Flory's mechanism (a) 2,2,3-cycloaddition (2,2,3,3-cycloaddition), and (b) 2,2,4-cycloaddition (2,2,4,4-cycloaddition); III: Two cyclohexanone α-hydrogen transfer mechanisms, (a) direct hydrogen transfer reaction, and (b) complexation-involved hydrogen transfer reaction; and IV: Mayo's mechanism. *Adapted from reprinted with permission from S. Liu, S. Srinivasan, M.C. Grady, M. Soroush, A.M. Rappe, Computational study of cyclohexanone-monomer co-initiation mechanism in thermal homo-polymerization of methyl acrylate and methyl methacrylate, J. Phys. Chem. A 116 (2012) 5337–5348. Copyright 2012 American Chemical Society.*

energy-minimum singlet diradical intermediate, which disputes previous results indicating that nonconcerted cycloaddition can occur via a stepwise biradical mechanism [16,71]. A triplet diradical with a structure similar to that of the nonconcerted transition state was identified; its energy was calculated to be higher than that of the singlet transition state by 18.9 kJ mol^{-1} given that the singlet transition state has lower energy, the intersystem crossing cannot be energetically favored. Based on these, it was concluded that the occurrence of intersystem crossing of the singlet diradical transition state to an active triplet diradical is less likely than the production of inactive 2,3-substituted oxetane.

For the 2,2,4-cycloaddition reaction, Liu et al. [68] found no nonconcerted transition state. However, they identified a concerted transition state and reported that the activation energy of this concerted 2,2,4-cycloaddition, calculated using B3LYP, to be greater than that of nonconcerted 2,2,3-cycloaddition. This shows that the concerted pathway is less favored, which agrees with Woodward and Hoffmann rules for [2 + 2] cycloaddition; that is, the formation of a concerted transition state is thermally forbidden. IRC calculations showed that the ring closure happens earlier in the reaction coordinate in the concerted pathway than in the nonconcerted pathway [68]. A stable triplet diradical intermediate, whose geometry is similar to the geometry of the concerted singlet transition state, was identified. Its energy is 51 kJ mol^{-1} less than that of the concerted transition state. The energy of the MECP structure identified using B3LYP/6-31G* was found to be 264 kJ mol^{-1} more than that of the reactants.

4.5.2.2.2 Methyl methacrylate

For the 2,2,3,3-cycloaddition reaction, Liu et al. [68] found a nonconcerted transition state but no stable singlet diradical intermediate. Because the energy of the triplet diradical of MMA-CHo is more than that of the singlet diradical transition state, singlet-to-triplet diradical crossover is not likely in the nonconcerted 2,2,3,3-cycloaddition, which agrees with the MA-CHo 2,2,3-cycloaddition mechanism.

Using B3LYP, Liu et al. [68] found that the energy barrier of the 2,2,4,4-cycloaddition is 30 kJ mol^{-1} higher than that of the 2,2,3,3-cycloaddition, which indicates that the latter is energetically preferred. There is a triplet diradical, the energy of which is 44.6 kJ mol^{-1} less than the singlet transition state. The MECP structure was found to have 241 kJ mol^{-1} more energy than the reactants.

In summary, Liu et al. [68] found that the CHo-involved Flory mechanism is not a likely mechanism that initiates polymerization of MA and MMA in CHo for the following reasons: (1) the energy barrier of the 2,2,4-cycloaddition (2,2,4,4-cycloaddition) reaction is significantly larger than that of the 2,2,3-cycloaddition (2,2,3,3-cycloaddition) reaction; and (2) the singlet diradical transition state in the 2,2,3-cycloaddition (2,2,3,3-cycloaddition) should receive energy to undergo intersystem crossing to generate monoradicals.

4.5.2.3 Cyclohexanone α-hydrogen transfer mechanism

In this mechanism, an α-hydrogen of CHo is transferred to the C = C bond of MA or MMA, as shown in Fig. 4.17(III). Liu et al. [68] explored two CHo α-hydrogen transfer mechanisms: (1) a direct hydrogen transfer mechanism (scheme III(a) in Fig. 4.17), and (2) complexation-involved hydrogen transfer mechanism (scheme III(b) in Fig. 4.17). In the direct hydrogen transfer mechanism, an α-hydrogen of CHo is transferred to the β-carbon atom of a monomer molecule, forming two monoradicals. In the complexation-involved hydrogen transfer mechanism, a monomer-CHo complex is formed via interactions between the oxygen atom of CHo and an unsaturated carbon atom of a monomer molecule. Simultaneously, an α-hydrogen of CHo is transferred to the other unsaturated carbon atom of the monomer molecule, leading to the formation of a monomer-CHo intermediate. An α-hydrogen of CHo can be transferred to the β-carbon or α-carbon atom of a monomer molecule; the former hydrogen transfer is called a Markovnikov addition, and the latter an anti-Markovnikov addition. Fig. 4.18 shows a monomer-CHo intermediate formed by the Markovnikov addition. Liu et al. [68] also studied hydrogen abstraction by a monomer molecule from the monomer-CHo intermediate to form monoradicals.

A computational investigation of the direct transfer mechanism for MA showed that the energy barrier of the forward reaction (reverse radical disproportionation) is more than 350 kJ mol^{-1}, while the reverse reaction, monoradicals forming CHo and MA (radical disproportionation), is barrierless. This agrees with previous reports [72] that radical disproportionation is usually barrierless.

Thermal dissociation of the monomer-CHo intermediate to form monoradicals was found to be unlikely [68]. However, a monomer molecule can abstract a hydrogen from the CHo β-carbon that is attached to an unsaturated carbon of the monomer-CHo intermediate to form monoradicals. Fig. 4.18 shows this reaction for a monomer-CHo intermediate formed

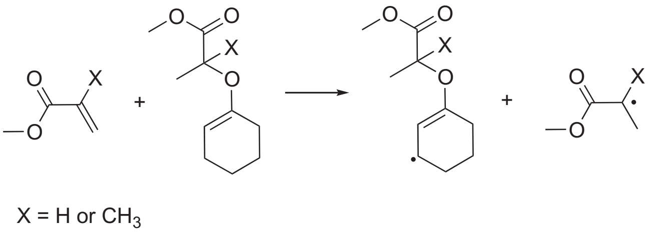

Figure 4.18

Monoradical generation from a monomer-CHo intermediate formed by the Markovnikov addition. *Adapted from reprinted with permission from S. Liu, S. Srinivasan, M.C. Grady, M. Soroush, A.M. Rappe, Computational study of cyclohexanone-monomer co-initiation mechanism in thermal homo-polymerization of methyl acrylate and methyl methacrylate, J. Phys. Chem. A 116 (2012) 5337–5348. Copyright 2012 American Chemical Society.*

by the Markovnikov addition. The activation energy of the reaction shown in Fig. 4.18 was found to be 132.2 kJ mol^{-1} for MA and 160.8 kJ mol^{-1} for MMA (calculated using B3LYP/6-31G*), suggesting that the α-hydrogen transfer is a likely initiation mechanism in thermal polymerization of MA and MMA in CHo.

4.5.2.4 Mayo mechanism

Liu et al. [68] computationally studied the Mayo mechanism shown in Fig. 4.17(IV), which involves a thermal cycloaddition [4 + 2] reaction. The cycloaddition reaction leads to the formation of the DAA intermediate, which can subsequently donate an hydrogen to a monomer molecule, forming two monoradicals (Fig. 4.19). Liu et al. [68] found concerted transition states for the formation of the DAA in MA and MMA. Their calculated activation energies for the formation of MA-CHo DAA (135 kJ mol^{-1}) and MMA-CHo DAA (144 kJ mol^{-1}) are similar to that of DAA formation in styrene self-initiation (110.4 kJ mol^{-1} with B3LYP/6-31G* using UHF wave functions) [71]. The activation energies for the formation of these MA-CHo and MMA-CHo DDAs are comparable with those for MA-CHo and MMA-CHo intermediates formed by the Markovnikov additions.

Liu et al. [68] studied the monoradical generation reaction (Fig. 4.18) using B3LYP/6-31G* and calculated energy barriers of 118.9 kJ mol^{-1} and 128.0 kJ mol^{-1} for monoradical generation from MA-CHo DAA and MMA-CHo DAA, respectively. These energy barriers (for the monoradical generation reaction from the DAAs) are −25 kJ mol^{-1} less than those of monoradical generation reactions for MA-CHo and MMA-CHo intermediates formed by the Markovnikov additions. This monoradical generation mechanism is similar to the molecular-assisted homolysis mechanism proposed for self-initiation in styrene [71].

4.5.3 Monomer-Solvent Coinitiation Summary

Results from theoretical studies of the four different mechanisms of CHo-monomer coinitiation in the thermal polymerization of MA and MMA (summarized in Fig. 4.20) showed that the modified Kaim mechanism is unlikely to produce the level of monoradicals

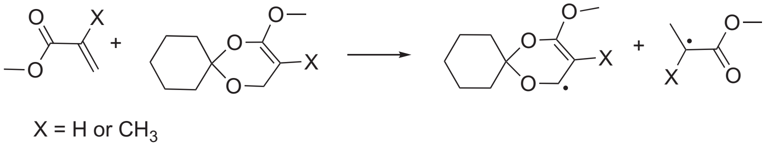

Figure 4.19

Hydrogen transfer from the DAA to a second monomer molecule. *Adapted from reprinted with permission from S. Liu, S. Srinivasan, M.C. Grady, M. Soroush, A.M. Rappe, Computational study of cyclohexanone-monomer co-initiation mechanism in thermal homo-polymerization of methyl acrylate and methyl methacrylate, J. Phys. Chem. A 116 (2012) 5337–5348. Copyright 2012 American Chemical Society.*

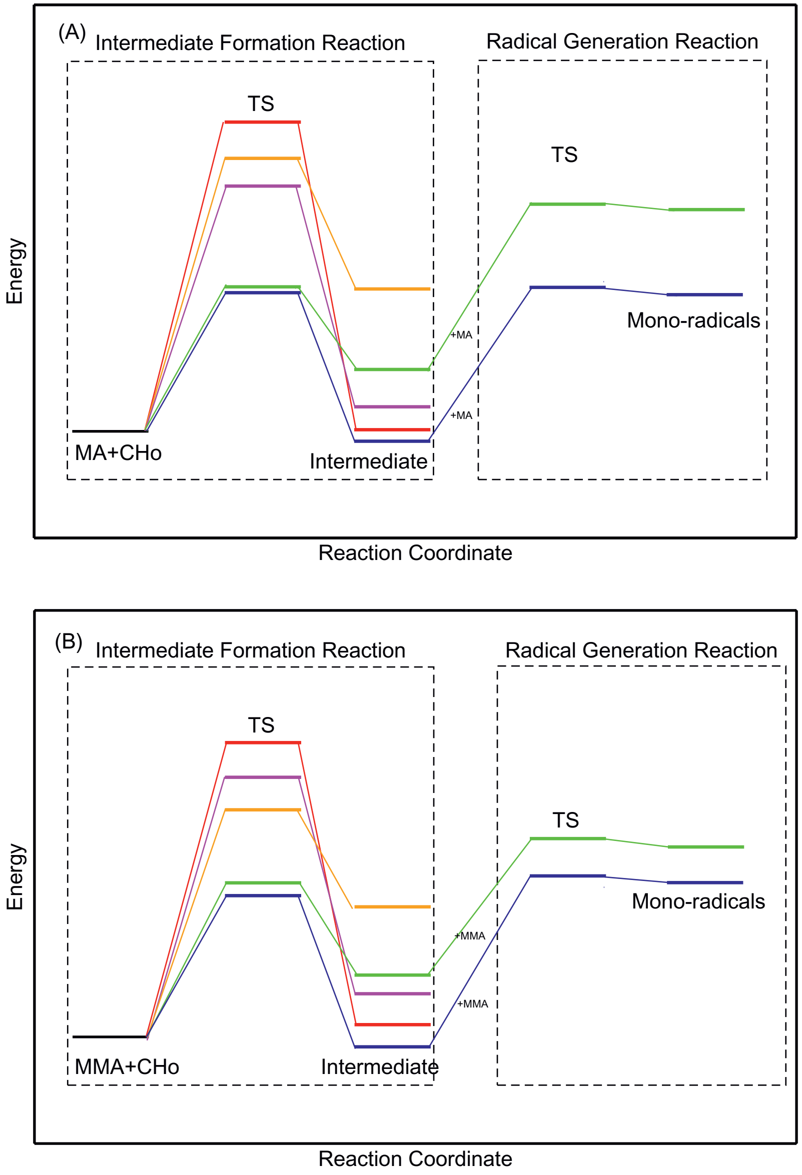

Figure 4.20

Comparison of the four mechanisms: (A) reaction of MA and CHo; (B) reaction of MMA and CHo. Orange: Modified Kaim mechanism. Magenta: 2,2,3-cycloaddition (2,2,3,3-cycloaddition). Red: 2,2,4-cycloaddition (2,2,4,4-cycloaddition). Blue: Complexation-involved hydrogen transfer reaction. Green: Mayo mechanism. *Adapted from reprinted with permission from S. Liu, S. Srinivasan, M. C. Grady, M. Soroush, A.M. Rappe, Computational study of cyclohexanone-monomer co-initiation mechanism in thermal homo-polymerization of methyl acrylate and methyl methacrylate, J. Phys. Chem. A 116 (2012) 5337–5348. Copyright 2012 American Chemical Society.*

needed to attain the experimentally observed high polymerization rate. This is due to the higher activation energy for the complex formation reaction and the inability of the complex to decompose and release monoradicals for initiation. The Flory mechanism is also incapable of generating monoradicals due to (1) the inability of the singlet diradical species to undergo intersystem crossing and (2) the significantly higher activation energies of the 2,2,4-cycloaddition (2,2,4,4-cycloaddition) route. However, the complexation-involved hydrogen transfer reaction is likely to initiate polymerization, because the intermediate is capable of donating a hydrogen and thus forming monoradicals. The Mayo mechanism is also likely to initiate polymerization by forming the DAA intermediate, which can subsequently donate an hydrogen to a monomer molecule, producing monoradicals. In summary, the Mayo and complexation-involved hydrogen transfer mechanisms are both capable of generating monoradicals in thermal homopolymerization of MA and MMA in cyclohexanone. The computational quantum chemistry studies indicated that the presence of a cyclic compound, such as cyclohexanone, in the reaction mixture favors the occurrence of Mayo's rather than Flory's mechanism, which agrees with previous studies [14,23–25].

4.6 Conclusion

DFT calculations showed that alkyl acrylates such as *n*BA, MA, and EA generate monoradicals (that are suitable for polymer chain initiation) at high temperatures by themselves via the three elementary reaction steps in series: [16,17]

$$\mathrm{M} + \mathrm{M} \rightarrow \bullet\mathrm{MM}\bullet_s \tag{4.1}$$

$$\bullet\mathrm{MM}\bullet_s \rightarrow \bullet\mathrm{MM}\bullet_t \tag{4.2}$$

$$\bullet\mathrm{MM}\bullet_t + \mathrm{M} \rightarrow \mathrm{MM}\bullet\ + \mathrm{M}\bullet \tag{4.3}$$

In the first reaction, two monomer molecules (M) react and form a singlet diradical (with two α-carbon radicals). In the second reaction, the singlet diradical undergoes intersystem crossing to form a triplet diradical. Finally, in the third reaction, the triplet diradical transfers a hydrogen to a third monomer molecule to form two monoradicals (a one-monomer unit monoradical with an α-carbon radical and a two-monomer unit monoradical with a carbon-carbon double bond and an α-carbon radical). The computational quantum chemistry studies showed that the second step is the slowest reaction, which governs the overall rate of the monomer self-initiation. The overall (apparent) self-initiation reaction, in which three monomer molecules react to form the two monoradicals, is:

$$3\mathrm{M} \xrightarrow{k_{i,m}} \mathrm{MM}\bullet_{.} + \mathrm{M}\bullet \tag{4.4}$$

which is second order.

DFT calculations revealed that, at high temperatures, methacrylates such as MMA by themselves undergo the following most-likely reactions: [18]

$$\mathrm{M} + \mathrm{M} \rightarrow \bullet\mathrm{MM}\bullet_{\mathrm{s}} \tag{4.5}$$

$$\bullet\mathrm{MM}\bullet_{\mathrm{s}} \rightarrow \bullet\mathrm{MM}\bullet_{\mathrm{t}} \tag{4.6}$$

$$\bullet\mathrm{MM}\bullet_{\mathrm{t}} + \mathrm{M} \rightarrow \mathrm{MM}\bullet_{.} + \mathrm{M}\bullet \tag{4.7}$$

$$\bullet\mathrm{MM}\bullet_{\mathrm{s}} + \mathrm{M} \rightarrow \mathrm{MM}\bullet_{.} + \mathrm{M}\bullet \tag{4.8}$$

$$\bullet\mathrm{MM}\bullet_{\mathrm{s}} \rightarrow \mathrm{MM} \tag{4.9}$$

The first two reactions, (4.5) and (4.6), are the same as those for alkyl acrylates [i.e., (4.1) and (4.2)]. However, in the reaction (4.7), the triplet diradical abstracts a hydrogen from the methyl group attached to the ester oxygen of a methacrylate monomer molecule (M) to form two monoradicals (a one-monomer unit monoradical with a primary-carbon radical and a two-monomer unit monoradical with an α-carbon radical). In the reaction (4.8), a singlet methacrylate diradical abstracts a hydrogen from the methyl group attached to the α-carbon of a methacrylate molecule to form the two monoradicals. The last reaction, (4.9), forms unreactive dimmers from the singlet diradicals. The theoretical studies showed the following relative rates of the reactions: (4.6) < (4.5) < (4.7); (4.5) < (4.8); (4.7) < (4.8). Accordingly, for methacrylates the overall (apparent) self-initiation reactions:

$$3\mathrm{M} \xrightarrow{k_{i,m,t}} \mathrm{MM}\bullet_{.} + \mathrm{M}\bullet \tag{4.10}$$

$$3\mathrm{M} \xrightarrow{k_{i,m,s}} \mathrm{MM}\bullet_{.} + \mathrm{M}\bullet \tag{4.11}$$

are both second order. The rate coefficients of the MMA apparent self-initiation reactions were found to be 3–4 orders higher than that of MA [19]. The higher rate constant for MMA suggested that a potential route for utilizing spin-chemistry to achieve faster self-initiation via lowering the energy of MECP by stabilizing the diradical [19]. PBE0, TPSS, and TPSSh were found to be cost-effective functionals for exploring self-initiation reactions of acrylates.

DFT confirmed that alkyl acrylates and methacrylates generate monoradicals (that are suitable for polymer chain initiation) at high temperatures in the presence of cyclohexanone (S) also via the two elementary reaction steps in series: [68]

$$\mathrm{M} + \mathrm{S} \rightarrow \mathrm{MS} \tag{4.12}$$

$$\mathrm{MS} + \mathrm{M} \rightarrow \mathrm{MS}\bullet + \mathrm{M}\bullet \tag{4.13}$$

In the first reaction, (4.12), a monomer molecule and a solvent molecule react and form a monomer-solvent intermediate. In the second reaction, (4.13), the monomer-solvent intermediate reacts with a second monomer molecule to form two monoradicals. The theoretical studies showed that the first reaction, which is first order with respect to M and S, is slower than the second one; the first reaction governs the rate of the overall (apparent) co-initiation reaction:

$$2\mathrm{M} + \mathrm{S} \xrightarrow{k_{i,m,s}} \mathrm{MS}\bullet + \mathrm{M}\bullet \tag{4.14}$$

in which one solvent and two monomer molecules react to form two monoradicals. This reaction is first order with respect to both M and S.

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