

MODELLING THE COMPETING PATHWAYS IN THE FREE RADICAL
POLYMERIZATION OF ACRYLATES

by

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To my mum and dad
The most valuable persons in my life

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ABSTRACT

MODELLING THE COMPETING PATHWAYS IN THE FREE RADICAL POLYMERIZATION OF ACRYLATES

The size of the α -substituent is expected to play a role in the propagation reaction in free radical polymerization. The possibility of the approach of the propagating radical to the monomer can be reduced due to the presence of a bulky group attached to the α carbon atom. It is expected that when the propagating radical is stabilized by some factors, the attack of this radical to the monomer is less favourable compared to the less stable radical. Stability of the radical also affects the termination reactions as well.

The presence of an electron donor and an electron withdrawing group causes captodative (cd) effect in radical polymerization. Cd substitution brings about a push-pull resonance stabilization, due to a geminal substitution with both electron-withdrawing and electron-donating groups on the same atom. α -substituted acrylate monomers have been modeled by using the quantum mechanical methods in order to understand the structure reactivity relationship on the propagation and the dispropagation reactions. The propagation and termination rate constants for α -substituted acrylate monomers have been calculated with the B3LYP/6-31+G* methodology. The polymerization kinetics has been considered in order to understand whether correlations between theoretical and experimental findings can be established.

The other task of this study is to use the Density Functional Theory (DFT) descriptors in order to understand the cyclopolymerizability of diallylic monomers. Density Functional Theory (DFT) descriptors have been used in order to predict the site selectivity in cyclic polymerization.

ÖZET

AKRİLATLARIN SERBEST RADİKAL POLİMERİZASYONLARINDA BİRBİRİNİ TAKİP EDEN REAKSİYONLARIN MODELLENMESİ

Akrilatların α karbonlarında bulunan sübstitüentlerin büyüklüklerinin serbest radikal polimerizasyon tepkimelerinin yayılma reaksiyonlarında önemli rol oynadıkları düşünülmektedir. Yayılma reaksiyonunda bulunan radikalın monomere yaklaşma ihtimali α pozisyonunda bulunan grubun büyüklüğü nedeni ile azalabilir. Yayılma reaksiyonlarına çift bağa katılan radikalın kararlılığı arttıkça monomere saldırma isteği kararlılığı daha az olan radikale oranla düşeceği beklenir. Radikalın kararlılığı yayılma tepkimelerinde olduğu gibi, sonlanma tepkimelerinde de etkilidir.

Aynı karbon atomu üzerinde bulunan elektron veren ve elektron çeken gruplar “capto-dative” adı verilen bir etki yaratırlar. Aynı atomun üstünde bulunan elektron iten ve electron çeken gruplar akrilat monomerlerinde rezonans yolu ile kararlılığı sağlarlar. Bu çalışmada α karbonlarında sübstitüent olan akrilatların yayılma ve sonlanma tepkimeleri modellenerek reaktiviteleri ile yapıları arasındaki ilişki araştırılmıştır. Yayılma ve bitirme reaksiyon hızları B3LYP/6-31+G* metodolojisi kullanılarak hesaplanmıştır. Polimerizasyon kinetiği deneysel ve hesapsal sonuçlar arasında bağlantı kurulması açısından incelenmiştir.

Çalışmanın diğer bir amacı da DFT tanımlayıcıları kullanarak dialilik monomerlerin siklopolimerizasyonunu anlamaktır. DFT tanımlayıcıları siklopolimerizasyon reaksiyonlarında oluşan halkanın 5 veya 6 üyeli oluşunu belirlemek amacıyla kullanılmıştır.

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LIST OF SYMBOLS/ABBREVIATIONS

E_c^{VWN}	Vosko-Wilk-Nusair Correlation Functional
$E_c[p]$	Correlation Energy
E_{gas}	Energy of the gaseous phase
$E_x[p]$	Exchange Energy
E_x^{exact}	Exact Exchange Energy
ΔE_0	Relative Electronic Energy at 0 K
ΔE_x^{B88}	Becke's Gradient Correction
$f(r)$	Fukui Function
ΔG_{298}	Relative Gibbs Free Energy at 298 K
ΔH_{298}	Relative Enthalpy at 298 K
$J[p]$	Coulomb Energy
$p(r)$	Electron Density
$s(r)$	Local Softness
S	Global Softness
ΔS	Relative Entropy
$T[p]$	Kinetic Energy of Interacting Electron
$T_s[p]$	Kinetic Energy of Non-interacting Electron
U_x^{p}	Exchange Energy Density
$V_{\text{ee}}[p]$	Interelectronic Interaction Energy
$V(r)$	External Potential
ψ_i	Kohn-Sham Orbitals
B3LYP	Becke-3-Parameter Lee-Yang-Parr Functional
B88	Becke 88 Exchange Functional
DFT	Density Functional Theory

EA	Electron Affinity
HF	Hartree-Fock Theory
IE	Ionization Energy
LDA	Local Density Approximation
LYP	Lee-Yang-Parr Correlation
MPW1K	Modified Perdew-Wang 1 Parameter Method for Kinetics
TST	Transition State Theory
VKS	Kohn-Sham Potential
ZPE	Zero Point Vibrational Energy

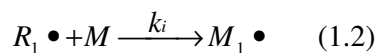
1. INTRODUCTION

1.1. Free Radical Polymerization

Free radical polymerization proceeds via a chain mechanism, which mainly consists of 3 types of reactions involving free radicals. [1]

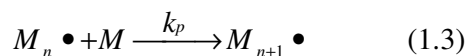
- (1) Initiation ; radical generation from a non-radical species
- (2) Propagation ; radical addition to a substituted alkene
- (3) Termination ; atom transfer, atom abstraction or radical radical recombination

The initiators which are generated by thermal or photochemical homolytic cleavage of covalent bonds initiate polymerization. 2,2'-azobisisobutyronitrile (AIBN) and 1,1'-azobiscyclohexane-1carbonitrile (ACN) are examples of commercially available initiators. The primary radicals add to the carbon-carbon double bonds of the monomers yielding primary propagating radicals that propagate further. Initiation of radical polymerization is a two step mechanism. The first step which is usually the rate determining step which involves homolysis of an initiator and gives a pair of radicals. The second step is addition of these radicals to the monomer forming a propagating radical. [2]



k_d is the catalyst dissociation constant and k_i is the rate constant for the initiation step. M represents the monomer. The rate of initiation is determined by the rate of decomposition of the initiator. The nature of the initiator influences the rate of polymerization, the molecular weight of the polymer formed, the polymer structure and the polymer properties. The rate of decomposition increases with increasing delocalization of the unpaired electron of the radical that is formed. Steric factors also influence the rate of decomposition and suppress further the reaction of the primary propagating radical. [3, 4]

Primary radicals which are generated by the decomposition of the initiator add to the monomer to form primary propagating radicals. This process goes on by rapid propagation steps to form radical centers. Each addition forms a new radical which resembles the previous one, but is larger by one monomer unit. In order to have high molecular weight polymers, the propagation step must occur at high rate compared to the other elementary reactions. The general representation for the propagation reaction is

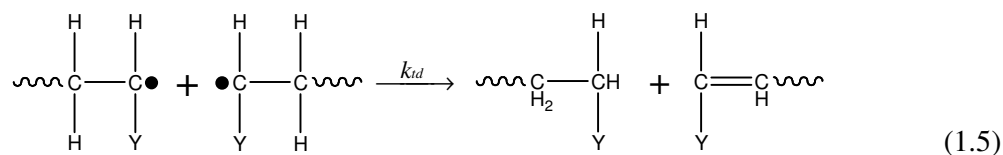
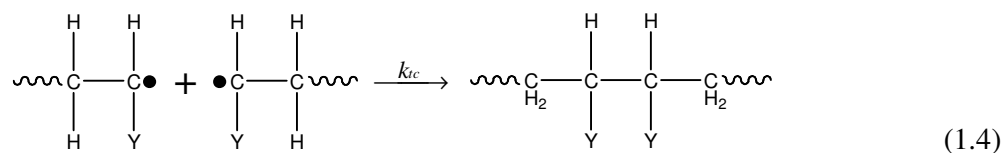


where k_p is the rate of propagation. [5, 6]

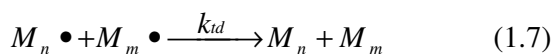
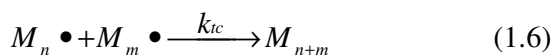
The propagating radicals must not be too stable in order for addition to monomer to proceed at a high rate. The rate of addition of propagating radicals to monomers is affected by polarity, resonance and steric factors. In general, the rate constants for propagation reaction decrease with increasing chain length and branching. Bond formation is not energetically suppressed, but the possibility that the radical and the monomer approach each other such that bond formation can occur is reduced. The

magnitude of the propagation rate constant is determined by the reactivity of both the monomer and the polymer radical. [7, 8, 9]

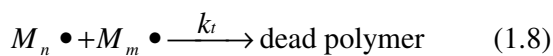
The propagating polymer chain stops growing by termination. Termination is a bimolecular reaction of the propagating radicals that ends by combination or disproportionation. Termination reaction leads to the deactivation of the propagating radical chain ends. The end group of the polymer chain is either saturated via coupling (1.4) or unsaturated via termination (1.5) .



These two reactions can be expressed in general terms



where k_{tc} and k_{td} are the rate constants for termination by coupling and disproportionation respectively. The termination step can be depicted as



where $k_t = k_{tc} + k_{td}$. (1.9)

Termination is very important since it affects the molecular weight distribution of the polymer formed and some of its properties. Termination also affects the overall polymerization rate.

1.2. General Properties and Applications of Acrylates

Acrylate monomers are esters that contain vinyl groups, directly attached to the carbonyl carbon. [10]

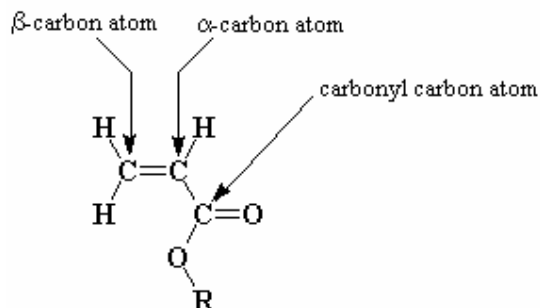


Figure 1.1. General representations for acrylates

The acrylate monomers are very reactive and they polymerize easily. The acrylate polymers which are generated are flexible and weatherable. They have adhesion, internal plasticization and resistance to abrasion properties.

Acrylate polymers and co-polymers are frequently used in construction adhesives and pressure sensitive adhesives. They are widely used as molecular building blocks, or

intermediates due to chemical structures and useful chemical functionalities. Acrylates are also used as monomers in the production of copolymers in textile and adhesive resins as well as surface coatings. They are widely used in water-based coatings. Some are used in paints, leather finishing and paper coatings. Acrylic copolymers are used as film coatings and leather finishes, particularly nubuck and suede. A balance of properties including molecular mobility, resin viscosity, solubility, hydrophobicity, thermal stability and low toxicity are critical for selecting a material for use as a plasticizer. Some acrylates are used as monomers to make flocculants for water treatment.

1.3. Free Radical Polymerization Kinetics

In order to have radical chain reactions successfully in the synthesis of high molecular weight polymers used for several applications, one needs some information concerning the kinetics of radical reactions.

When the reaction kinetics are considered, the rate of generation of radicals that are capable of initiating the polymerization process, can be described with the following first order rate law;

$$v_i = -2f \frac{d[I]}{dt} = 2fk_d[I] \quad (1.10)$$

where k_d corresponds to the rate coefficient of the initiator decomposition and f is the initiator efficiency. Not all generated primary free radicals initiate polymer growth. After decomposition, the free radicals are very close to each other and recombination may occur. An efficiency of zero means no initiation takes place, whereas $f=1$ corresponds to the case where the generated primary radical initiates polymerization.

The rate expression for termination v_t can be written as follows since the process is a bimolecular one

$$v_t = 2k_t[M^\bullet]^2 \quad (1.11)$$

where k_t is the termination rate constant and $M^\bullet$ is radical concentration. The rate constant $2k_t$ is actually $(k_{tc} + k_{td})$.

In order to have a final expression for overall polymerization process, a stationary state approach is defined. According to the stationary state approach, free radical concentration is constant during the whole process. In this case, the assumption is that the rate of initiation of radicals (generation of active radicals) is equal to the rate of termination of radicals (removal of active radicals yielding dead polymers).

$$\frac{d[R^\bullet]}{dt} = 2fk_d[I] - v_i = 0 \quad (1.12)$$

where v_i is the rate of disappearance of the Radical $[R^\bullet]$ and represented with the following expression

$$v_i = k_i[R^\bullet][M] \quad (1.13)$$

Rate of formation of new chain radical can be expressed as follows

$$\frac{d[M^\bullet]}{dt} = v_i - 2k_t[M^\bullet]^2 = 2fk_d[I] - 2k_t[M^\bullet]^2 = 0 \quad (1.14)$$

$$[M^\bullet] = \left(\frac{fk_d[I]}{k_t} \right)^{1/2} \quad (1.15)$$

The rate expression for propagation can be written as follows ;

$$v_p = k_p[M][M^\bullet] = k_p[M] \left(\frac{fk_d[I]}{k_t} \right)^{1/2} \quad (1.16)$$

where k_p is the rate constant for the propagation. $[M^\bullet]$ is replaced with the equation (1.15) and the final expression for the rate of polymerization, R_p is;

$$R_p = -\frac{d[M]}{dt} = k_p \left(f \frac{k_d}{k_t} \right)^{1/2} [M][I]^{1/2} \quad (1.17)$$

where k_p stands for the propagation rate constant. In the derivation of polymerization rate, the propagation (k_p) and termination (k_t) rate coefficients are assumed to be chain length and conversion independent. [11, 12]

The overall homopolymerization rate constant, k , is based on the kinetic expression for homopolymerization. [13]

$$R_p = k[I]^{1/2}[M] \quad (1.18)$$

The rate constant for the overall polymerization process can be expressed as follows ;

$$k = \frac{k_p}{k_t^{1/2}} (fk_d)^{1/2} \quad (1.19)$$

1.4. Experimental Behavior of the Monomers Modeled

α -substituted acrylates are stabilized radicals by a carbalkoxy group and α -substituents at the same time. Although formation of highly stabilized polymer radicals is expected, there is a fast propagation for the α -substituted acrylates.

A decrease in the propagation rate constant of methyl methacrylate by α -methyl substitution of methyl acrylate is expected since hyperconjugation, due to the presence of the methyl group, increases the stability and reduces the reactivity of the polymer radicals. [16] However the α -chloro, α -cyano and α -fluoro substitutions which can stabilize the polymer radicals as well, result in greater k_p values. This contradiction is the subject of another concept-captodative effect. The captodative (cd) effect promotes the radical polymerization in spite of resonance stabilization of the resulting radicals and sterically hindered 1,1-disubstituted molecules. Cd substitution gives a push-pull resonance stabilization due to a geminal substitution with both electron withdrawing (captive) and electron donating (dative) groups on the same atom. [14, 15]

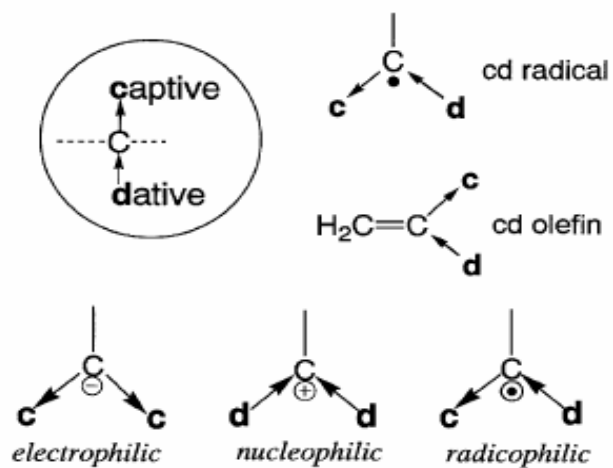
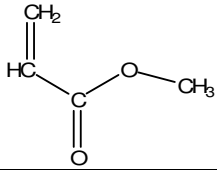
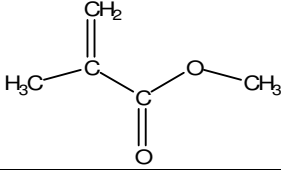
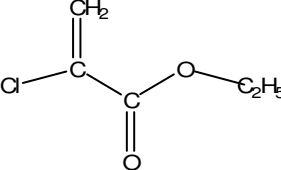
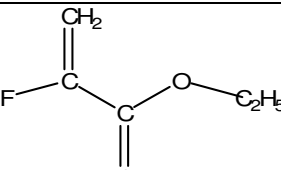
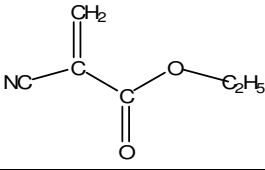


Figure 1.2. Captodative substitution

Cd substitution also brings a synergistic and asymmetric polarization effect to the radicals. These steric hindrance and resonance stabilization assist polymerization since the termination and side reactions are depressed.

The monomers tabulated in Table 1.1 are modeled in order to understand the effect of the structure and substituents on the polymerizability behavior.

Table 1.1. Monomers modeled

No	Structure	Name	k_p (mol L ⁻¹ s ⁻¹)	k_t (mol L ⁻¹ s ⁻¹)	Reference
M1		Methyl acrylate	720	0.34	[14]
M2		Methyl (α - methyl) acrylate	450	4.20	[14]
M3		Ethyl (α - chloro) acrylate	1660	33.30	[14]
M4		Ethyl (α - fluoro) acrylate	1120	48.00	[14]
M5		Ethyl (α - cyano) acrylate	1622	41.10	[14]

The 9 radicals in Table 1.2 are also modeled in order to understand the usage of the Density Functional Theory descriptors related to cyclization.

Table 1.2. Radicals modeled

No	Structure	Name	E _a (5exo) kcal/mol	E _a (6endo) kcal/mol	Reference
M6		N,N-diallylamine radical	7.20	10.90	[38]
M7		N,N-diallylammonium radical	8.60	11.60	[38]
M8		N,N-diallyl N,N-dimethylamine radical	6.20	10.30	[38]
M9		N,N-diallyl N-methylamine radical	5.00	10.60	[38]
M10		N,N-diallyl N-methylammonium radical	6.40	10.20	[38]
M11		N-methyl-N-allyl-2-(methoxycarbonyl) allylamine radical	8.68	12.20	[39]
M12		N-methyl-N-methallyl-2-(methoxycarbonyl) allylamine radical	14.02	11.59	[39]
M13		α-(allyloxymethyl) acrylate radical	5.33	10.23	[40]
M14		Alkyl α-propoxymethyl acrylate radical	9.82	12.08	[40]

1.5. Experimental Methods Used To Measure The Rate Constants

Four widely used methods can be considered in the measurement of the rate constants.

- (1) Pulsed Laser Polymerization
- (2) Laser Flashed Photolysis
- (3) Time Resolved Electron Spin Resonance Spectroscopy
- (4) Simple Dilatometric Method

The monomer solution (containing a photo initiator) is irradiated with a sequence of evenly spaced laser pulses producing a regular flux of radicals in pulsed laser polymerization. The majority of polymer chains initiated during one laser pulse produce a characteristic molecular weight distribution. The molecular weight distribution contains a peak corresponding to the dark time between pulses. If the degree of polymerization of the chains which is terminated is identified, the value of k_p can be found from a knowledge of the monomer concentration $[M]$ and the time between pulses, t_d . [16, 17]

$$(\text{Degree of polymerization}) = k_p \times [M] \times t_d \quad (1.20)$$

Flash photolysis is a commonly used fast reaction technique for photochemical reactions. For reactions with a moderate rate, flash lamps provide sufficient time response. An example of a typical flash lamp is the xenon lamp in a standard camera. For very fast reactions, however, the slow decay time of the light emission from a flash lamp covers the progress of the reaction. In general, the pulse width of the light source must be much shorter than the half-time of the chemical reaction. For faster reactions, specially designed lasers must be used that have pulse widths in the

nanosecond range. Reactants in photochemical reactions can have a wide variety of absorption wavelengths, some of which may not be accessible to a given laser source. Therefore, several different types of lasers are often necessary to provide coverage of the UV range of common organic and inorganic reactants. Many different techniques are available for monitoring the progress of photochemical reactions. Conductivity, IR, Raman, mass spectrometry, and chemiluminescence are all used. [18] However, the most commonly used technique is the UV/Visible spectrophotometry. Flash photolysis experiments are monitored at a single wavelength. However, it is often desired to determine the UV/Visible absorption spectrum of the products. There is not time enough to scan the wavelength of the monochromator of a traditional spectrophotometer during the acquisition of each time point. Diode array spectrometers are often used to acquire all the data points in a spectrum at one time. Unfortunately, the time response of diode array detectors is not sufficient for fast pulse studies. However, the experiment can easily be repeated at a series of wavelengths to piece together the spectrum of the products as a function of time. The only requirement is that enough time is allowed between experiments that the solution can return to equilibrium, usually by diffusion of reactants into the optical path of the laser.

Another technique is the electron paramagnetic resonance (EPR) spectroscopy which is also known as electron spin resonance (ESR) spectroscopy. EPR/ESR is the name given to the process of resonant absorption of microwave radiation by paramagnetic ions or molecules, with at least one unpaired electron spin, in the presence of a static magnetic field. EPR spectroscopy provides an experimental route to study the magnetic interactions in paramagnetic materials. The elucidation of parameters like the electronic Zeeman interaction (g), hyperfine (A), nuclear quadrupole (Q) and zero-field or electronic quadrupole (D) tensors, which characterise the interactions, can lead to an understanding of atomic and molecular structure at magnetic sites. [19]

The dilatometric method is the simplest kinetic way for determining the propagation and termination rate coefficients. This method is also called after-effect experiment which is using a means of initiation to build up a relatively high concentration of free radicals. Then switching off the source of initiation, the free radical concentration is observed as it decreases if propagation stops and termination occurs. [20]

2. AIM OF THE STUDY

The aim of this work is to understand the relationship between the structure of the monomers and their polymerizability behavior by using the quantum chemical tools.

The factors which play an important role in the polymerization of acrylates will be discussed by modeling the experimentally synthesized, polymerized compounds for which propagation and termination rate constants are measured by experimental techniques.

Another task of this study is to test the DFT descriptors in understanding the polymerizability behavior of a set of radicals. It is desirable to predict the site selectivity in cyclization polymerization by the usage of DFT descriptors.

3. METHODOLOGY

All the geometry optimizations have been carried out by using the density functional theory with the B3LYP/6-31+G* methodology. Harmonic frequencies have been computed in order to identify the stationary points as minima (with all real frequencies) or transition states (with only one imaginary frequency) and to obtain thermal energy and entropy contributions. IRC calculations have been performed to confirm the nature of the transition state structures for the propagation reactions. All radicals and transition states have been treated with the spin-unrestricted UB3LYP formalism. All computations have been carried out by using the Gaussian (G03) program.

The energetic results are reported as the change in the electronic energy at 298 K (ΔE_{298}), sum of the electronic energy and zero point energy at 298 K ($\Delta E_{298+ZPE}$).

The reaction rate constants are calculated by using the conventional Transition State Theory (TST). [21, 22] In the conventional TST formalism, the zero point energy contributions are included by direct addition to the energies on the minimum potential energy surface. [23, 24] Such formalism presumes that, contributions of the zero point energies added to the electronic energies do not vary the position of the maxima along the zero point energy corrected hyper surface.

The rate constant in the conventional TST is calculated as follows ;

$$k = \frac{k_B T}{h} \frac{q_{TS}}{q_A q_B} e^{-[E_{TS} - (E_A + E_B)]/RT} \quad (3.1)$$

where k_B represents the Boltzman's constant, T is the temperature, h is Planck's constant, R is the ideal gas constant, and E_o is the critical energy (energy difference at 0 K between reactants and transition state with inclusion of the zero point vibrational energies). The frequency factor is determined by the molecular partition functions for the transition state, (q_{TS}), the alkene (q_A) and the radical (q_B) respectively. These partition functions are approximated as products of electronic, vibration, rotation and translational partition functions generated with Gaussian 03.

3.1. Density Functional Theory

The DFT functional used is the Becke 3-parameter-Lee-Yang-Parr exchange-correlation functional (B3LYP) [25, 26] as implemented in the Gaussian 03 package. This functional has been successfully applied to the radical addition reactions to the unsaturated carbon atom and hydrogen abstraction reactions. [27, 28]

The density functional theory is based on the Kohn-Hohenberg theorems proposed in 1964. [31, 32] The first theorem states that the electron density $\rho(r)$ determines the external potential $v(r)$, i.e. the potential due to the nuclei. The second theorem introduces the variational principle. Hence, the electron density can be computed variationally and the position of nuclei, energy, wave function and other related parameters can be calculated. [29, 30]

The electron density is defined as:

$$\rho(x) = N \int \dots \int |\Psi(x_1, x_2, \dots, x_n)|^2 dx_1 dx_2 \dots dx_n \quad (3.2)$$

where x represents both spin and spatial coordinates of electrons.

The electronic energy can be expressed as a functional of the electron density:

$$E[\rho] = \int v(r)\rho(r)dr + T[\rho] + V_{ee}[\rho] \quad (3.3)$$

where $T[\rho]$ is the kinetic energy of the interacting electrons and $V_{ee}[\rho]$ is the interelectronic interaction energy. The electronic energy may be rewritten as:

$$E[\rho] = \int v(r)\rho(r)dr + T_s[\rho] + J[\rho] + E_{xc}[\rho] \quad (3.4)$$

with $J[\rho]$ being the coulomb energy, $T_s[\rho]$ being the kinetic energy of the non-interacting electrons and $E_{xc}[\rho]$ is the exchange-correlation energy functional. The exchange-correlation functional is expressed as the sum of an exchange functional $E_x[\rho]$ and a correlation functional $E_c[\rho]$, although it contains also a kinetic energy term arising from the kinetic energy difference between the interacting and non-interacting electron systems.

In the Kohn-Sham density functional theory, a reference system of independent non-interacting electrons in a common, one-body potential V_{KS} yielding the same density as the real fully-interacting system is considered. More specifically, a set of independent reference orbitals ψ_i satisfying the following independent particle Schrödinger equation are imagined:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS} \right] \psi_i = \varepsilon_i \psi_i \quad (3.5)$$

with the one-body potential V_{KS} defined as:

$$V_{KS} = v(r) + \frac{\partial J[\rho]}{\partial \rho(r)} + \frac{\partial E_{xc}[\rho]}{\partial \rho(r)} \quad (3.6)$$

$$V_{KS} = v(r) + \frac{\rho(r')}{|r - r'|} dr' + v_{xc}(r) \quad (3.7)$$

where $v_{xc}(r)$ is the exchange-correlation potential. The independent orbitals ψ_i are known as Kohn-Sham orbitals and give the exact density by:

$$\rho(r) = \sum_i^N |\psi_i|^2 \quad (3.8)$$

if the exact form of the exchange-correlation functional is known. However, the exact form of this functional is not known and approximate forms are developed starting with the local density approximation (LDA). This approximation gives the energy of a uniform electron gas, i.e. a large number of electrons uniformly spread out in a cube accompanied with a uniform distribution of the positive charge to make the system neutral. The energy expression is:

$$E[\rho] = T_s[\rho] + \int \rho(r)v(r)dr + J[\rho] + E_{xc}[\rho] + E_b \quad (3.9)$$

where E_b is the electrostatic energy of the positive background. Since the positive charge density is the negative of the electron density due to uniform distribution of particles, the energy expression is reduced to:

$$E[\rho] = T_s[\rho] + E_{xc}[\rho] \quad (3.10)$$

$$E[\rho] = T_s[\rho] + E_x[\rho] + E_c[\rho] \quad (3.11)$$

The kinetic energy functional can be written as:

$$T_s[\rho] = C_F \int \rho(r)^{5/3} dr \quad (3.12)$$

where C_F is a constant equal to 2.8712. The exchange functional is given by:

$$E_x[\rho] = -C_x \int \rho(r)^{4/3} dr \quad (3.13)$$

with C_x being a constant equal to 0.7386. The correlation energy, $E_c[\rho]$, for a homogeneous electron gas comes from the parametrization of the results of a set of quantum Monte Carlo calculations.

The LDA method underestimates the exchange energy by about 10 per cent and does not have the correct asymptotic behavior. The exact asymptotic behavior of the exchange energy density of any finite many-electron system is given by:

$$\lim_{x \rightarrow \infty} U_x^\sigma = -\frac{1}{r} \quad (3.14)$$

U_x^σ being related to $E_x[\rho]$ by:

$$E_x[\rho] = \frac{1}{2} \sum_{\sigma} \int \rho_{\sigma} U_x^{\sigma} dr \quad (3.15)$$

A gradient-corrected functional is proposed by Becke:

$$E_x = E_x^{LDA} - \beta \sum_{\sigma} \int \rho_{\sigma}^{4/3} \frac{x_{\sigma}^2}{1 + 6\beta x_{\sigma} \sinh^{-1} x_{\sigma}} dr \quad (3.16)$$

where σ denotes the electron spin, $x_{\sigma} = \frac{|\nabla \rho_{\sigma}|}{\rho_{\sigma}^{4/3}}$ and β is an empirical constant ($\beta=0.0042$).

This functional is known as Becke88 (B88) functional. [31]

The adiabatic connection formula connects the non-interacting Kohn-Sham reference system ($\lambda=0$) to the fully-interacting real system ($\lambda=1$) and is given by:

$$E_{xc} = \int_0^1 U_{xc}^{\lambda} d\lambda \quad (3.17)$$

where λ is the interelectronic coupling-strength parameter and U_{xc}^{λ} is the potential energy of exchange-correlation at intermediate coupling strength. The adiabatic connection formula can be approximated by:

$$E_{xc} = \frac{1}{2} E_x^{exact} + \frac{1}{2} U_{xc}^{LDA} \quad (3.18)$$

since $U_{xc}^0 = E_x^{exact}$, the exact exchange energy of the Slater determinant of the Kohn-Sham orbitals, and $U_{xc}^1 = U_{xc}^{LDA}$. [32]

The closed shell Lee-Yang-Parr (LYP) correlation functional [33] is given by:

$$E_c = -a \int \frac{1}{1+d\rho^{-1/3}} \left\{ \rho + b\rho^{-2/3} \left[C_F \rho^{5/3} - 2t_w + \left(\frac{1}{9} t_w + \frac{1}{18} \nabla^2 \rho \right) \right] e^{-c\rho^{-1/3}} \right\} dr \quad (3.19)$$

where

$$t_w = \frac{1}{8} \frac{|\nabla \rho(r)|^2}{\rho(r)} - \frac{1}{8} \nabla^2 \rho \quad (3.20)$$

and $a=0.04918$, $b=0.132$, $c=0.2533$ and $d=0.349$.

The mixing of LDA, B88, E_x^{exact} and the gradient-corrected correlation functionals to give the hybrid functionals [34] involves three parameters:

$$E_{xc} = E_{xc}^{LDA} + a_0 (E_x^{exact} - E_x^{LDA}) + a_x \Delta E_x^{B88} + a_c \Delta E_c^{non-local} \quad (3.21)$$

where ΔE_x^{B88} is the Becke's gradient correction to the exchange functional. In the B3LYP functional, the gradient-correction ($\Delta E_c^{non-local}$) to the correlation functional is included in LYP. However, LYP contains also a local correlation term which must be subtracted to yield the correction term only:

$$\Delta E_c^{non-local} = E_c^{LYP} - E_c^{VWN} \quad (3.22)$$

where E_c^{VWN} is the Vosko-Wilk-Nusair correlation functional, a parametrized form of the LDA correlation energy based on Monte Carlo calculations. The empirical coefficients are $a_0=0.20$, $a_x=0.72$ and $a_c=0.81$. [35]

3.2. Basis Sets

In the present study the geometry optimizations were carried out with B3LYP/6-31+G*. The non-scaled frequencies were used to compute zero-point energies (ZPE). The 6-31+G* basis set is used in the determination of the structural parameters of acrylates, and the polymerization reactions.

The 6-31+G* basis set for the first row atoms describes the core orbitals by a combination of six primitive Gaussian functions and the valence shell is split into two orbitals consisting of three and one primitive Gaussian functions. This set is augmented by a set of d orbitals and diffuse functions. For the hydrogen atoms 6-31+G* basis set uses two sets of s orbitals containing three and one primitive Gaussian functions.

3.3. DFT Based Reactivity Descriptors

Density Functional Theory descriptors have been used to understand the reactivity of radical cyclization reactions. The concept is a generalization of the frontier molecular orbital reactivity indices, where all responses to any change of charges and geometry which take place in the HOMO (Highest Molecular Orbital) and LUMO (Lowest MolecularOrbital). The core orbitals remain unaffected. [36, 37]

In order to investigate the chemical reactivity of the monomers in free radical addition reactions, global reactivity parameters like electronegativity or hardness is used, on the other hand site selectivity is usually understood in terms of local functions like the Fukui function $f(r)$ and local softness $s(r)$.

Among the above parameters, electronegativity is the negative of the chemical potential which is the derivative of the energy with respect to the number of electrons at constant external potential.

$$\chi = -\mu = \left(\frac{\partial E(N, \nu(r))}{\partial N} \right)_{\nu(r)} \quad (3.23)$$

In this expression $E(N, \nu(r))$ is the energy of the system as a function of N , the number of electrons and $\nu(r)$ is the external potential.

The other global index hardness describes the resistance to changes in electronic charge. Hardness is expressed as the second derivative of energy with respect to the number of electrons.

$$\eta = \left[\frac{\partial^2 E(N, v(r))}{\partial N^2} \right]_{v(r)} = \left(\frac{\partial \mu}{\partial N} \right)_{v(r)} \quad (3.24)$$

In a system, the second derivative of energy is taken at the fixed external potential and this is a simple tool for HSAB (Hard-Soft Acid Base) principle. This principle states that “among the potential partners of the same electronegativity, hard likes hard and soft likes soft”. In other words, the interaction between two systems will be favored in case of global softnesses that are close to each other.

By using finite difference approximation and quadratic $E=E(N)$ curve, the equation (3.24) reduces to

$$\eta = \frac{IE - EA}{2} \quad (3.25)$$

where IE and EA are the Ionization Energy and Electron Affinity respectively. The equation (3.25) can be expressed as well for closed shell molecules

$$\eta = \frac{\epsilon_{HOMO} - \epsilon_{LUMO}}{2} \quad (3.26)$$

where $\epsilon_{HOMO} - \epsilon_{LUMO}$ is the energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital.

The inverse of the global hardness is called the global softness.

$$S = \frac{1}{\eta} \quad (3.27)$$

In order to understand the reaction mechanism, besides global properties, the local parameters can also be used as a measure of reactivity of the different sites within a molecule is needed.

It's necessary to describe the local softness which gives the local response of the electron density $\rho(r)$ upon a change in the electronic chemical potential.

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu} \right) \quad (3.28)$$

Equation (3.28) can be rewritten as

$$s(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} \left(\frac{\partial N}{\partial \mu} \right)_{v(r)} \quad (3.29)$$

where $\left(\frac{\partial N}{\partial \mu} \right)_{v(r)}$ is equal to global softness and $\left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)}$ is described as the Fukui function $f(r)$. So the equation becomes

$$s(r) = f(r) \cdot S \quad (3.30)$$

This descriptor, the Fukui function represents the response of the chemical potential of a system to any change in external potential.

$$f(r) = \left(\frac{\partial N}{\partial v(r)} \right)_N = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} \quad (3.31)$$

Fukui function also gives information about local change in the electron density of an atom or molecule upon changing the total number of electrons. Since $\left(\frac{\partial \rho(r)}{\partial N} \right)$ is a discontinuous function of N, finite difference approximation leads to three types of Fukui function for a system, one value from the right, one from the left and an average at some integral value of N.

$$f^+ = \left[\frac{\partial \rho(r)}{\partial N} \right]_{v(r)}^+ \quad (\text{When } N \text{ goes from } N_0 \text{ to } N_0 + \delta) \quad (3.32)$$

$$f^- = \left[\frac{\partial \rho(r)}{\partial N} \right]_{v(r)}^- \quad (\text{When } N \text{ goes from } N_0 - \delta \text{ to } N_0) \quad (3.33)$$

$$f^0 = \frac{1}{2} [f^+(r) + f^-(r)]^0 \quad (\text{Average}) \quad (3.34)$$

By using the finite difference approximation, these equations can be written as

$$f^+(r) = \rho_{N+1}(r) - \rho(r) \quad (3.35)$$

$$f^{-}(r) = \rho_N(r) - \rho_{N-1}(r) \quad (3.36)$$

$$f^0(r) = \frac{1}{2}[\rho_{N+1}(r) - \rho_{N-1}(r)] \quad (3.37)$$

Condensed forms of Fukui functions for an atom k can be written as follows by using the atomic population q_k .

$$f^{+}(r) = q_k(N+1) - q_k(N) \quad (3.38)$$

$$f^{-}(r) = q_k(N) - q_k(N-1) \quad (3.39)$$

$$f^0(r) = \frac{1}{2}[q_k(N+1) - q_k(N-1)] \quad (3.40)$$

In these equations, $f^{+}(r)$ is the reactivity index for a nucleophilic attack, $f^{-}(r)$ for an electrophilic attack and $f^0(r)$ for a radical attack.

4. RESULTS AND DISCUSSION

The free radical process is a combined complex reaction including initiation, propagation, chain transfer and termination reactions. It is clear that control of the product (the molecular weight, the chain architecture and the sequence distribution of the resulting polymer) requires knowledge of the respective rates of these reactions. The factors that affect the propagation and termination rate constants of the chosen monomers M1, M2, M3, M4 and M5 are discussed via modeling these reactions.

4.1. The Effect of Pendant Groups and Capto-dative Effect on the Polymerization Rate

Photoinitiated radical polymerization is preferred and is very common since the process is reproducible and can occur in various types of solvents, even in water, over a wide range of reaction temperatures under mild conditions with convenient apparatus. Furthermore, photoinitiated radical polymerization can be used for many types of monomers. It is inevitable to control photoinitiated radical polymerization mechanism by kinetics to have high performance and high quality polymers. The best way to control the mechanism is to strengthen the radical species by adding some pendant groups. In this study, the free radical polymerizability of a series of acrylates (methyl acrylate, methyl (α -methyl) acrylate, ethyl (α -floro) acrylate, ethyl (α -chloro) acrylate, ethyl (α -cyano) acrylate)) is investigated in an attempt to analyze in details the effects exerted by the pendant groups on the polymerizability (Table 4.1). The experimental photopolymerization behavior of various methyl (α -substituted) acrylates is shown in Table 4.2. The monomer itself is used as the attacking radical to model the propagation and the disproportionation reactions. After locating all the ground state and transition state geometries on the potential energy surface, the kinetic parameters are evaluated. The overall polymerization rate coefficient ($k_p/k_d^{1/2}$) is used to understand the polymerization behavior of the monomers under study.

Table 4.1. α -(substituted) acrylate monomers modeled

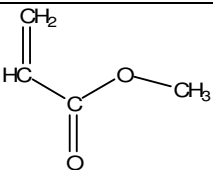
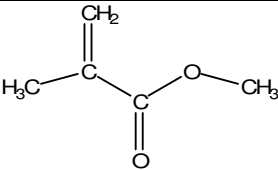
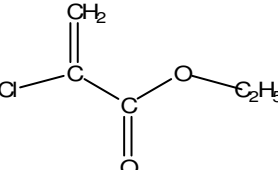
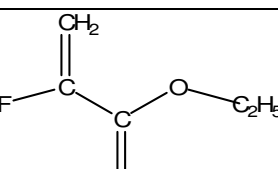
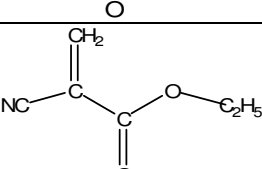
No	Structure	Name
M1		Methyl acrylate
M2		Methyl (α -methyl) acrylate
M3		Ethyl (α -chloro) acrylate
M4		Ethyl (α -fluoro) acrylate
M5		Ethyl (α -cyano) acrylate

Table 4.2. Photopolymerization results for monomers M1, M2, M3, M4 and M5

No	k_p (mol L ⁻¹ s ⁻¹)	k_t (mol L ⁻¹ s ⁻¹)	Reference
M1	720	0.34	[14]
M2	450	4.20	[14]
M3	1660	33.30	[14]
M4	1120	48.00	[14]
M5	1622	41.10	[14]

4.1.1 3D-structures of M1, M2, M3, M4 and M5

In alkyl (α -substituted) acrylates, various conformers exist since there is free rotation around the C₁-C₅ and C₅-O₇ bonds (C₁-C₅ and C₅-O₈ bonds for methyl (α -methyl) acrylate). These conformers are examined and the most stable ones are chosen for each monomer. These stable geometries are presented with the dihedral angles. (Table 4.3-Table 4.7) Based on B3LYP/6-31+G* calculations, the anti and syn conformers with respect to C₁-C₅ bond are also located and it is found that except for methyl (α -methyl) acrylate monomer, the syn conformers are more stable (Table 4.8). The numbering system used in alkyl (α -substituted) acrylates is shown in Figures 4.1–4.5

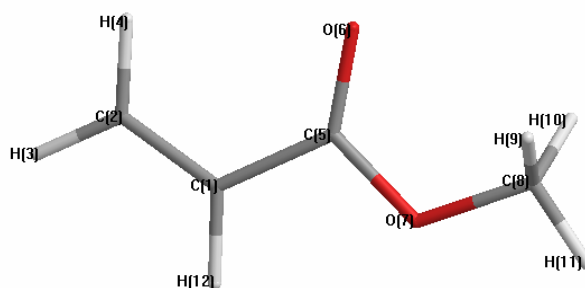


Figure 4.1. Numbering system used for methyl acrylate

Table 4.3. Dihedral angles for M1

Dihedral angles	M1
C ₅ C ₁ C ₂ H ₄	-0.1
C ₅ C ₁ C ₂ H ₃	-179.9
H ₁₂ C ₁ C ₅ O ₆	-179.9
O ₆ C ₅ O ₇ C ₈	-0.1
C ₅ O ₇ C ₈ H ₁₁	-179.9

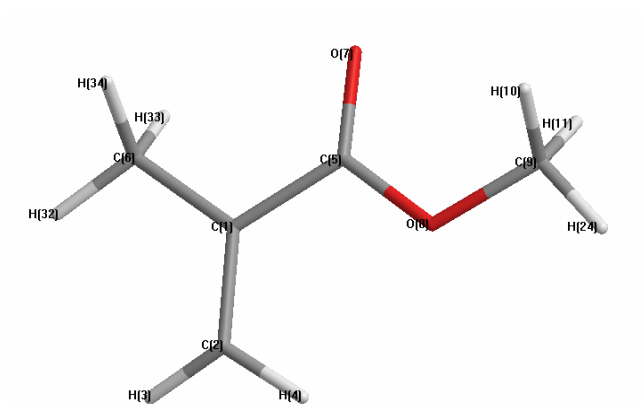


Figure 4.2. Numbering system used for methyl (α -methyl) acrylate

Table 4.4. Dihedral angles for M2

Dihedral angles	M2
$H_{32}C_6C_1C_5$	178.4
$H_{32}C_6C_1C_2$	2.4
$C_6C_1C_5O_7$	-0.4
$C_6C_1C_2H_3$	14.9
$C_2C_1C_5O_7$	-179.6
$C_2C_1C_5O_8$	2.0
$O_7C_5O_8C_9$	1.2
$C_5O_8C_9H_{24}$	-178.5

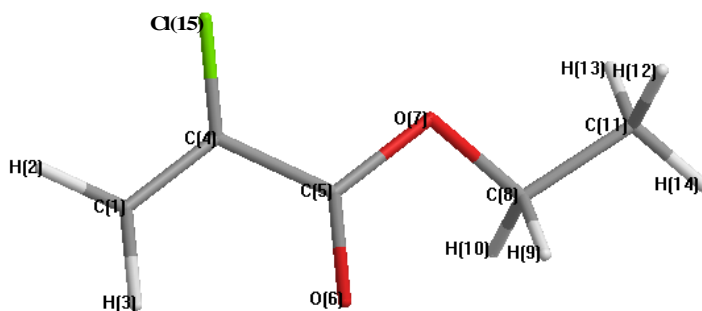


Figure 4.3. Numbering system used for ethyl (α -chloro) acrylate

Table 4.5. Dihedral angles for M3

Dihedral angles	M3
$\text{Cl}_{12}\text{C}_1\text{C}_2\text{H}_3$	-0.1
$\text{Cl}_{12}\text{C}_1\text{C}_2\text{H}_4$	180.0
$\text{C}_2\text{C}_1\text{C}_5\text{O}_7$	-179.8
$\text{C}_2\text{C}_1\text{C}_5\text{O}_6$	0.2
$\text{Cl}_{12}\text{C}_1\text{C}_5\text{O}_6$	-179.8
$\text{Cl}_{12}\text{C}_1\text{C}_5\text{O}_7$	0.2
$\text{C}_1\text{C}_5\text{O}_7\text{C}_8$	-180.0
$\text{C}_5\text{O}_7\text{C}_8\text{H}_{11}$	179.5

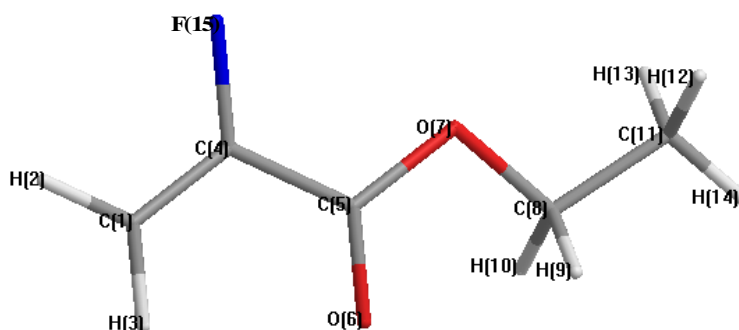
Figure 4.4. Numbering system used for ethyl (α -fluoro) acrylate

Table 4.6. Dihedral angles for M4

Dihedral angles	M4
$\text{F}_{12}\text{C}_1\text{C}_2\text{H}_3$	-0.0
$\text{F}_{12}\text{C}_1\text{C}_2\text{H}_4$	179.9
$\text{C}_2\text{C}_1\text{C}_5\text{O}_7$	180.0
$\text{C}_2\text{C}_1\text{C}_5\text{O}_6$	-0.0
$\text{F}_{12}\text{C}_1\text{C}_5\text{O}_6$	180.0
$\text{F}_{12}\text{C}_1\text{C}_5\text{O}_7$	-0.0
$\text{C}_1\text{C}_5\text{O}_7\text{C}_8$	178.0
$\text{C}_5\text{O}_7\text{C}_8\text{H}_{11}$	180.0

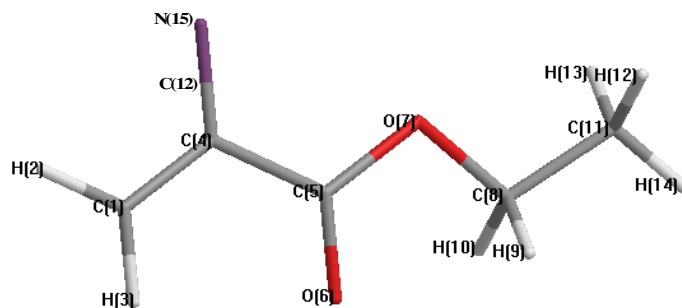


Figure 4.5. Numbering system used for ethyl (α -cyano) acrylate

Table 4.7. Dihedral angles for M5

Internal Coordinates	M5
C ₁₂ C ₁ C ₂ H ₃	-0.1
C ₁₂ C ₁ C ₂ H ₄	180.0
C ₂ C ₁ C ₅ O ₇	180.0
C ₂ C ₁ C ₅ O ₆	-0.0
C ₁₂ C ₁ C ₅ O ₆	180.0
C ₁₂ C ₁ C ₅ O ₇	-0.0
C ₁ C ₅ O ₇ C ₈	-180.0
C ₅ O ₇ C ₈ H ₁₁	-179.9

Table 4.8. Relative energies (kcal/mol) for the *anti* and *syn* conformers of M1, M2, M3, M4 and M5

Monomer	Anti conformer	Syn conformer
M1	0.64	0.00
M2	0.00	0.23
M3	0.56	0.00
M4	0.55	0.00
M5	1.41	0.00

The alkyl (α -substituted) acrylate monomers that were modeled prefer to be syn except for methyl (α -methyl) acrylate as seen from the dihedral angles from Table 4.4 to Table 4.7.

4.1.2 3D-structures of the radical derivatives of M1, M2, M3, M4 and M5

In the radical derivatives of methyl (α -substituted) acrylates, there is also free rotation around the C₂-C₆ and C₆-O₈ bonds (C₁₃-C₁₇ and C₁₇-O₂₈ bonds for methyl (α -methyl) acrylate) and various conformers exist. Based on B3LYP/6-31+G* calculations, the anti and syn conformers with respect to C₂-C₆ bond (C₁₃-C₁₇ bond for methyl (α -methyl) acrylate) are also located and it is found that all the radical derivatives prefer the syn conformers. On the other hand, the methyl group (-CH₃) which comes from methyl radical attached to the C-C double bond of the monomer prefers to be out of face of the radical structure as seen from the dihedral angles from Table 4.9.

The numbering system of the atoms of radical derivatives of the alkyl (α -substituted) acrylates is shown in Figures 4.6-4.10. All the dihedral angles of the radical derivative of monomers M1, M2, M3, M4 and M5 are given in Table 4.9.

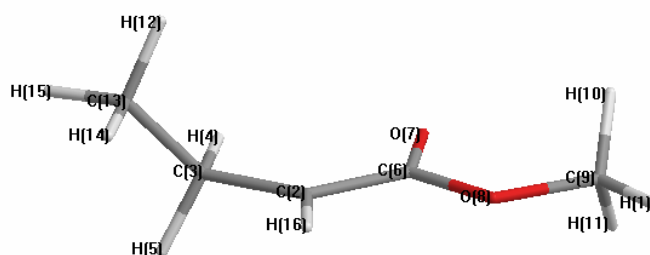


Figure 4.6. Numbering system used for the radical derivative of methyl acrylate

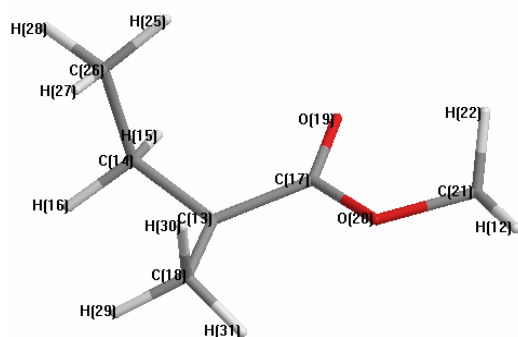


Figure 4.7. Numbering system used for the radical derivative of methyl (α -methyl) acrylate

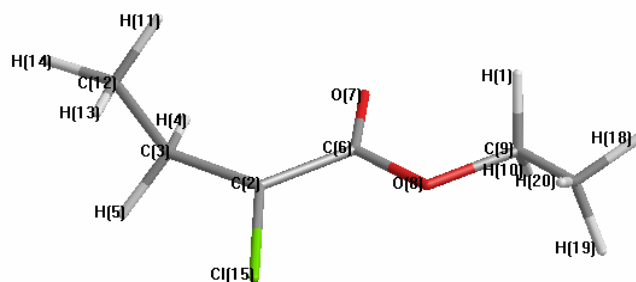


Figure 4.8. Numbering system used for the radical derivative of methyl (α -chloro) acrylate

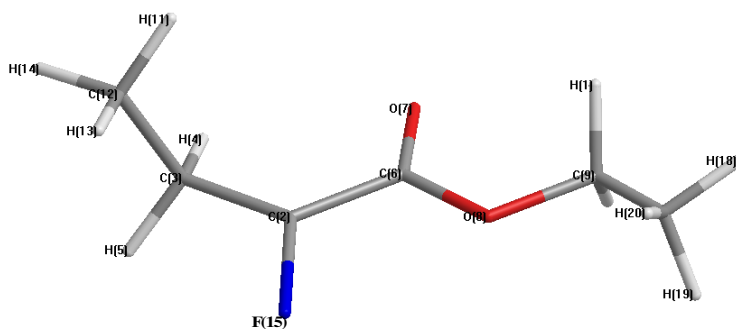


Figure 4.9. Numbering system used for the radical derivative of ethyl (α -fluoro) acrylate

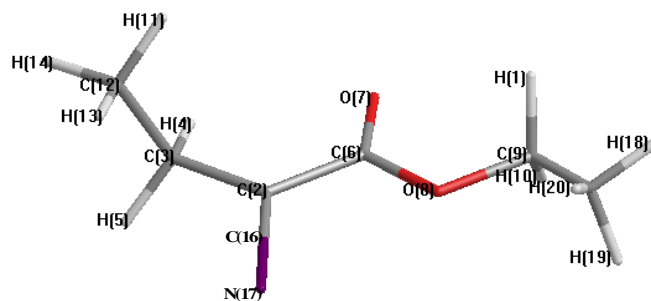


Figure 4.10. Numbering system used for the radical derivative of ethyl (α -cyano) acrylate

Table 4.9. Dihedral angles for the radicals **M1R**, **M2R**, **M3R**, **M4R** and **M5R**

	Radical				
Dihedral angles	M1R	M2R	M3R	M4R	M5R
C ₁₃ C ₃ C ₂ C ₆ (C ₂₈ C ₁₄ C ₁₃ C ₁₇ *)	-125.5	-101.8	-102.3	-114.1	-91.9
H ₁₁ C ₉ O ₈ C ₆	-60.3	-63.3	-60.3	-60.5	-60.3
C ₉ O ₈ C ₆ O ₇	-0.0	-5.0	-0.1	-0.0	-0.0
O ₇ C ₆ C ₂ C ₃	-0.6	-17.2	-1.2	-0.3	-1.7
O ₇ C ₆ C ₂ C ₁₈ * O ₇ C ₆ C ₂ F ₁₆ ** O ₇ C ₆ C ₂ Cl ₁₆ *** O ₇ C ₆ C ₂ C ₁₆ ****	-	-165.1	-178.1	-179.4	-178.8

*The numbering system used for M2R

**The numbering system used for M4R

***The numbering system used for M3R

****The numbering system used for M5R

4.1.3 Propagation reaction of M1, M2, M3, M4 and M5

The radical derivatives of the monomers are used to model the transition structures of the propagation reactions. (Figure 4.11) Radicals that are used for modelling the propagation transition state are produced by attaching the methyl radical to the less substituted C-C double bond of the monomers.

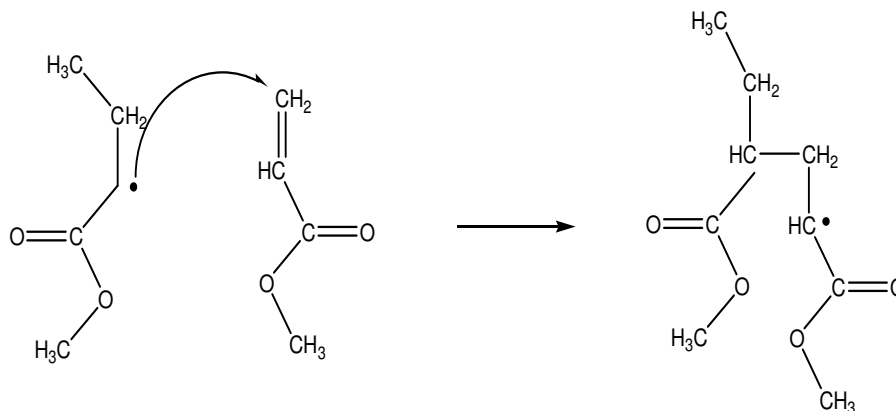


Figure 4.11. Schematic representation of the propagation reaction for methyl acrylate

Although all the monomers prefer to be planar as it can be seen from Table 4.3 to Table 4.7, the direction of attack of the methyl radical to the C-C double bond of the monomer is monitored by addition of the methyl radical to methyl acrylate. (Figure 4.12)

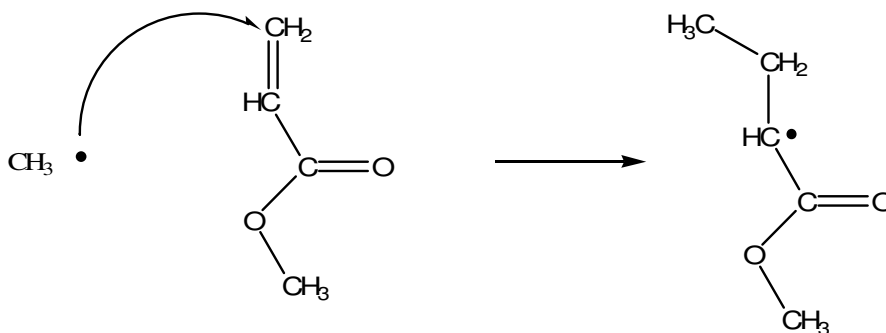


Figure 4.12. Schematic representation of the methyl addition reaction to methyl acrylate

Figures 4.13 and 4.14 show the direction which the methyl radical attacks the methyl acrylate monomer. The transition state energies are tabulated in Table 4.10.

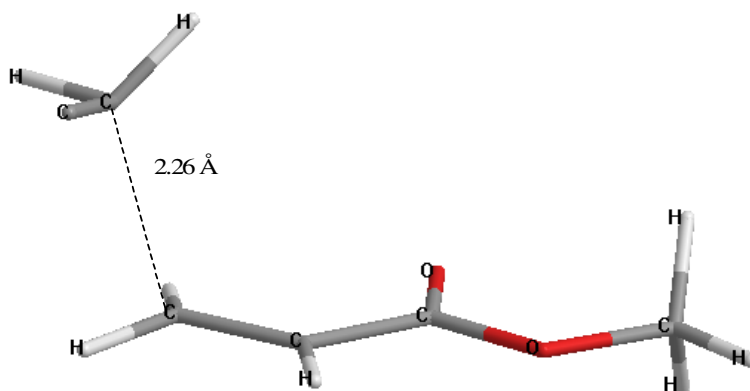


Figure 4.13. Radical addition to **M1** from the upper face

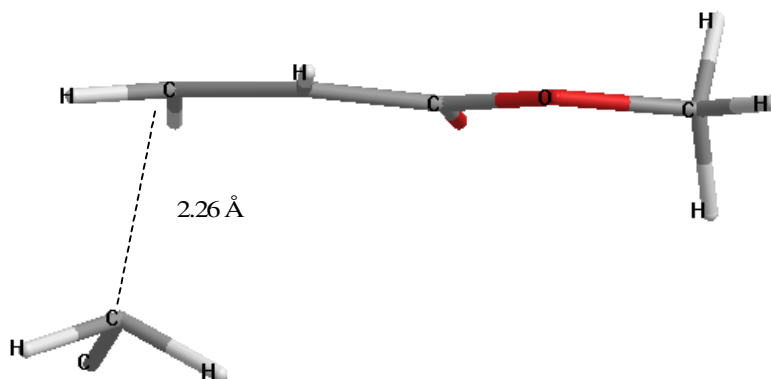


Figure 4.14. Radical addition to **M1** from the bottom face

Table 4.10. Relative transition state energies (kcal/mole) of the radicals that attack the C-C double bond of methyl acrylate from the upper and bottom faces

	M1
upper face	0.00
bottom face	0.24

Although the relative transition state energies of the radicals attacking the C-C double bond of methyl acrylate from the upper and bottom faces are close to each other, the

transition states in this work are the ones for upper face attack of the radical to the C-C double bonds of the monomers. Figures 4.15 – 4.19 illustrate the propagation reaction transition states of monomers **M1**, **M2**, **M3**, **M4** and **M5**.

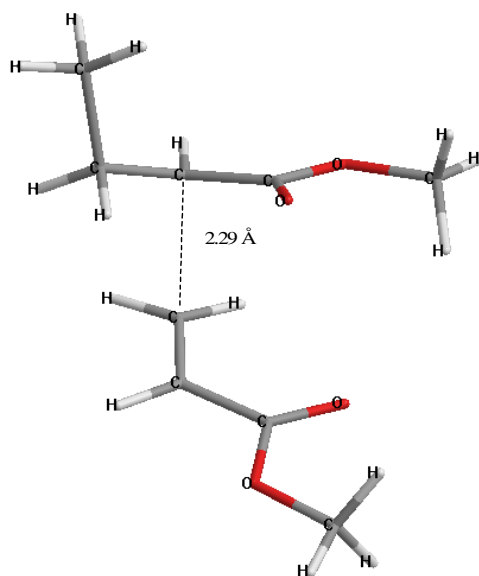


Figure 4.15. Radical addition to **M1**

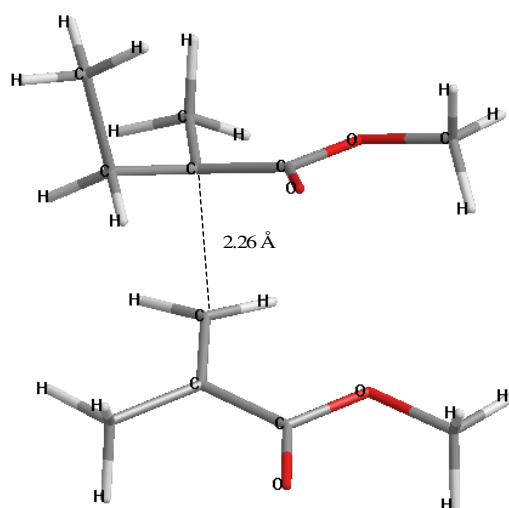
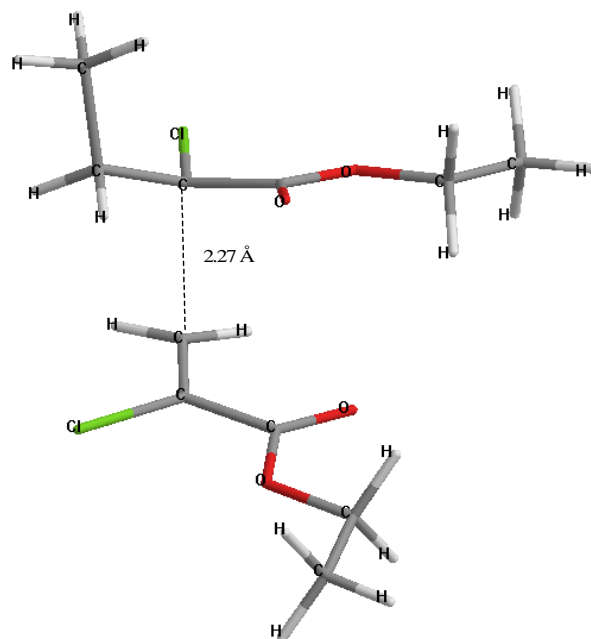
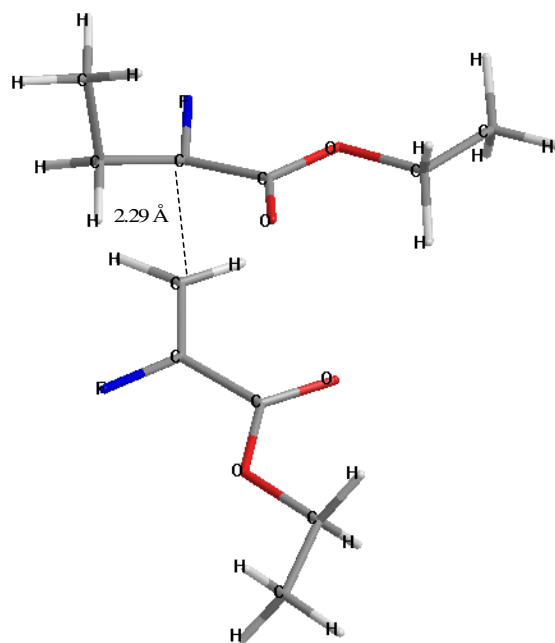


Figure 4.16. Radical addition to **M2**

Figure 4.17. Radical addition to **M3**Figure 4.18. Radical addition to **M4**

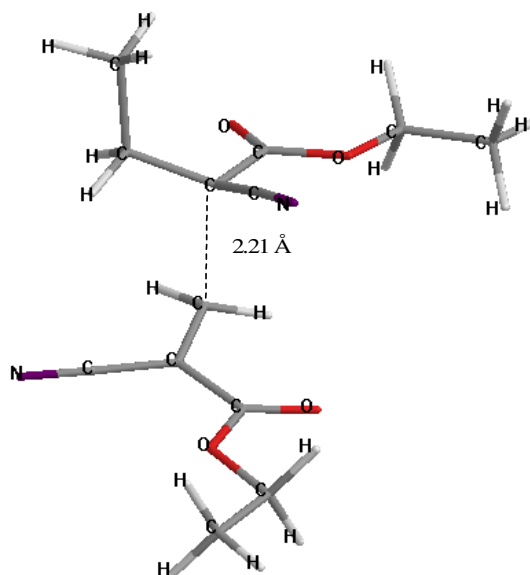


Figure 4.19. Radical addition to **M5**

Intrinsic reaction coordinate (IRC) calculations have been performed in order to confirm the identity of the structures as transition state structures which connect the proposed reactants to the proposed products. The monomer-radical prereactive complex structure located as the reactants of the IRC calculations have been used to calculate the rate constants for the propagation reactions. The rate constant in the conventional TST was calculated as follows:

$$k = \frac{k_B T}{h} \frac{q_{TS}}{q_A q_B} e^{-[E_{TS} - (E_A + E_B)]/RT} \quad (4.1)$$

For the calculation of the rate constant for propagation reaction the monomer-radical complex structure is used and equation (4.1) becomes:

$$k = \frac{k_B T}{h} \frac{q_{TS}}{q_{complex}} e^{-[E_{TS} - (E_{complex})]/RT} \quad (4.2)$$

In the formula $\frac{k_B T}{h} \frac{q_{TS}}{q_{complex}}$ is called the preexponential factor, A is the Arrhenius constant and equation (4.2) becomes:

$$k = A e^{-[E_{TS} - (E_{complex})]/RT} \quad (4.3)$$

Rate constant calculations are performed in a specific temperature range between 300 K-600 K. The temperature range is chosen in accordance with the experimental temperature range. Table 4.11 shows the calculation steps for M3. Table 4.12 displays the total partition functions for the IRC prereactive complex, addition transition state and ln(k) values for each temperature in the range of 300-600 K.

Table 4.11. Calculation steps for M3

IRC prereactive complex	HF (energy) = -1650.6919572 Hartree
	Zero point correction = 0.2689460 Hartree
	Total energy = -1650.423011 Hartree
	Total enthalpy = -1650.399811 Hartree
IRC product	HF (energy) = -1650.7125895 Hartree
	Zero point correction = 0.272621 Hartree
	Total energy = -1650.439969
	Total enthalpy = -1650.418656
Transition state	HF (energy) = -1650.6779690
	Zero point correction = 0.2695050
	Total energy = -1650.947474
	Total enthalpy = -1650.38688
Forward barrier (T= 0 K)	E _{TS} -E _{IRC complex} = 1.45E-02 Hartree

Table.4.12. Partition functions and $\ln(k)$ values for 300 K < T < 600 K

T (K)	q (IRC complex)	q (Transition state)	$\ln(k)$
300	1.95E+28	2.79E+24	1.59E+00
310	4.41E+28	5.96E+24	2.10E+00
320	9.85E+28	1.26E+25	2.57E+00
330	2.18E+29	2.65E+25	3.02E+00
340	4.76E+29	5.51E+25	3.44E+00
350	1.03E+30	1.14E+26	3.83E+00
360	2.21E+30	2.33E+26	4.21E+00
370	4.69E+30	4.73E+26	4.56E+00
380	9.89E+30	9.56E+26	4.90E+00
390	2.07E+31	1.92E+27	5.22E+00
400	4.29E+31	3.82E+27	5.52E+00
410	8.83E+31	7.56E+27	5.82E+00
420	1.80E+32	1.49E+28	6.09E+00
430	3.66E+32	2.91E+28	6.36E+00
440	7.39E+32	5.67E+28	6.61E+00
450	1.48E+33	1.10E+29	6.85E+00
460	2.95E+33	2.12E+29	7.09E+00
470	5.84E+33	4.05E+29	7.31E+00
480	1.15E+34	7.73E+29	7.52E+00
490	2.25E+34	1.47E+30	7.73E+00
500	4.38E+34	2.78E+30	7.93E+00
510	8.49E+34	5.22E+30	8.12E+00
520	1.64E+35	9.79E+30	8.30E+00
530	3.14E+35	1.83E+31	8.48E+00
540	6.00E+35	3.39E+31	8.65E+00
550	1.14E+36	6.28E+31	8.81E+00
560	2.16E+36	1.16E+32	8.97E+00
570	4.06E+36	2.13E+32	9.13E+00
580	7.61E+36	3.89E+32	9.28E+00
590	1.42E+37	7.09E+32	9.42E+00
600	2.64E+37	1.29E+33	9.56E+00

When $\ln(k)$ is plotted versus $1/T$, the slope gives the energy of activation (E_a) for the reaction and the intercept gives the pre-exponential factor A . As seen from Table 4.13 the energy of activation, E_a , for M3 is $9.13 \text{ E}+00 \text{ kcal/mol}$, whereas the pre-exponential factor A is $3.98 \text{ E}+07$. By using E_a and A , the rate constant at $T = 298.15 \text{ K}$ is calculated easily as $4.29 \text{ E}+00 \text{ mol L}^{-1}\text{s}^{-1}$. Table 4.13 shows both the experimental and the calculated rate constants for propagation reactions. As it can be seen from the table clearly the size and the bulkiness of the monomer increases the rate of propagation decreases.

Table 4.13. The experimental and calculated propagation rate constants
for M1, M2, M3, M4 and M5

No	Calculations				Experiment		
	E_a (kcal/mol)	A	$k_p \text{ calc.}$ (mol L ⁻¹ s ⁻¹)	$k_p \text{ calc.}^a$	$k_p \text{ exp.}$ (mol L ⁻¹ s ⁻¹)	$k_p \text{ exp.}^a$	Reference
M1	8.63E+00	2.09 E+04	1.49E-01	1.00	7.20E+02	1.00	[16]
M2	1.73 E+01	1.78 E+12	3.57E-02	0.24	4.50E+02	0.63	[16]
M3	9.13 E+00	3.98 E+07	4.29E+00	2.88E	1.66E+03	2.31	[16]
M4	1.24 E+01	6.90 E+08	2.32E+00	1.56E	1.12E+03	1.56	[16]
M5	8.04 E+00	1.29 E+08	7.75E+00	5.20E	1.62E+03	2.25	[16]

^aRelative to M1.

The propagation reaction for the monomers have been rationalized on the basis of different criteria. The relation between E_a and $\ln(k_{\text{exp}})$ and $\ln(k)$ vs $\Delta(\text{SOMO-LUMO})$ -the single occupied molecular orbital, SOMO, and the lowest unoccupied molecular orbital, LUMO, energy have been considered separately.

The dependence of the propagation rate constant $\ln(k_{\text{exp}})$ on the calculated barrier E_a is shown in Figure 4.20.

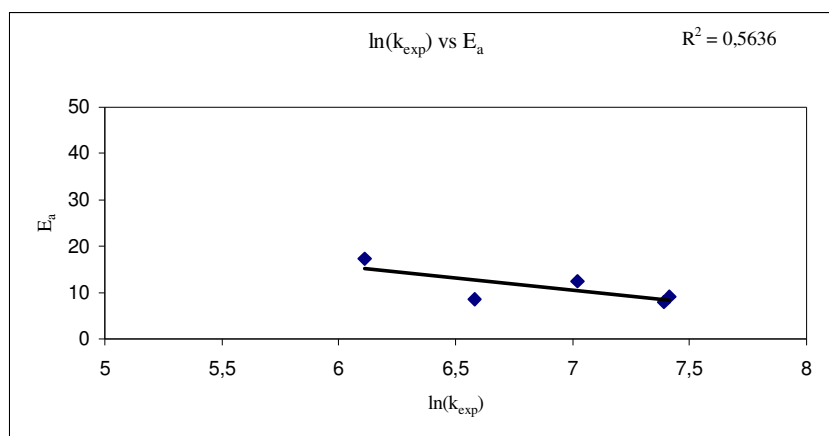


Figure 4.20. Experimental rate constant $\ln(k_{\text{exp}})$ vs the computed energy barriers E_a

Despite the well-known difference in the preexponential factors (A) for monomers, the quite good correlation observed gives confidence to the ability of the theoretical method used to reproduce the experimental results.

For the propagation reaction, the proper overlap between the highest occupied molecular orbital of the propagating radicals (SOMO) and the lowest unoccupied molecular orbital of the monomers (LUMO) is necessary. The energy difference between the SOMO of the propagating radical and the LUMO of the monomer is calculated (Table 4.14).

Table 4.14. The energy of the SOMO and LUMO of the propagating radicals and the monomers

	SOMO	LUMO	Δ (SOMO-LUMO)
M1	-0.28783	-0.06127	0.17578
M1R	-0.23705	0.00445	
M2	-0.27756	-0.05521	0.16329
M2R	-0.2185	0.00236	
M3	-0.27729	-0.06999	0.15883
M3R	-0.22882	0.00029	
M4	-0.28645	-0.06563	0.16121
M4R	-0.22684	0.00133	
M5	-0.30457	-0.09666	0.16440
M5R	-0.26106	-0.01321	

Figure 4.21 shows the relation between SOMO-LUMO energy difference with calculated rate constants. As it can be clearly observed, monomer M1 which propagates slower compared to the others has the highest SOMO-LUMO energy difference. For M3, M4 and M5 there is no distinct difference for SOMO-LUMO energy difference as well as their propagation rate constants are almost close to each other.

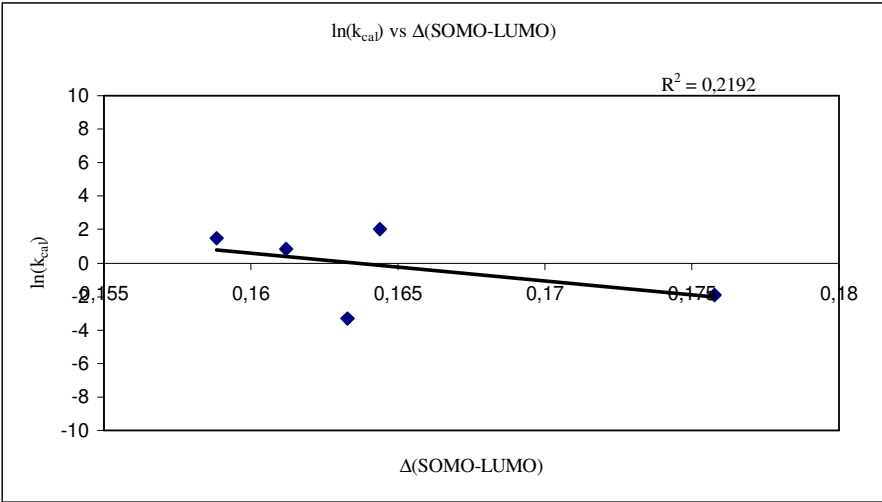


Figure 4.21. Calculated rate constant $\ln(k_{\text{calc}})$ vs the SOMO-LUMO energy difference

The small energy difference between the SOMO of the reacting radicals and the LUMO of the monomers indicates a better overlap of the reacting radicals and the monomers.

The size of the α -substituent is expected to play a role in the propagation reaction. The possibility of the approach of the propagating radical to the monomer can be reduced due to the presence of a bulky group attached to the α carbon atom. In this work M1 has no α -substituent and has higher propagation rate constant as compared to M2 [Methyl(α -methyl)acrylate] which has one methyl group attached to C_α and a clear decrease in the rate of propagation can be observed. The same discussion can be made for chloro substituted M3 [Methyl(α -chloro)acrylate], fluoro substituted M4 [Methyl(α -fluoro)acrylate] and cyano group substituted M5 [Methyl(α -cyano)acrylate].

It is expected that when the propagating radical is stabilized by some factors, the attack of this radical to the monomer is less favorable compared to the less stable radical. Capto-dative substituent on the α carbon atom is a stabilizing factor for the propagating radicals. In this work M1R radical can be called non-cd (non-capto dative) acrylate radical. On the other hand α -methyl substituent on M2R has a capto-dative effect and α -cyano substituent on M5 has a captive-captive effect on the radical. The propagating radical can be stabilized more when capto-dative substituent is present than when captive-captive one is substituted. M5R is less stable radical due to captive-captive effect compared to M2R which has capto-dative substituent effect due to the presence of α -methyl group. This stabilizing effect renders M1 (non-cd) less reactive than M2 and M2 (capto-dative) less reactive than M5 (captive-captive) for the propagation reaction.

The next radical stabilization discussion can be made for M3 [Methyl (α -chloro) acrylate] and M4 [Methyl (α -fluoro) acrylate]. The difference in the propagation rate constants can be interpreted in terms of greater stabilizing effect of the chloride by the capability of undergoing octet expansion, which can not be expected for fluoride. The α -chloro and α -fluoro substituted radicals are displayed by the following resonance structures (Figure 4.22)

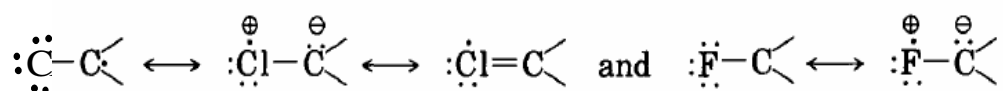


Figure 4.22. Resonance structures for α -chloro and α -fluoro substituted radicals

This stabilization effect can be discussed for the resulting radical after propagation reaction. Since the resulting radical after propagation reaction for M3 monomer is more stable than M4, the propagation reaction for M3 is more favorable than M4.

4.1.4 Disproportionation reaction of M1, M2, M3, M4 and M5

Disproportionation reaction occurs between two radical species such that one radical center abstracts a hydrogen from C atom of the other radical (Figure 4.23).

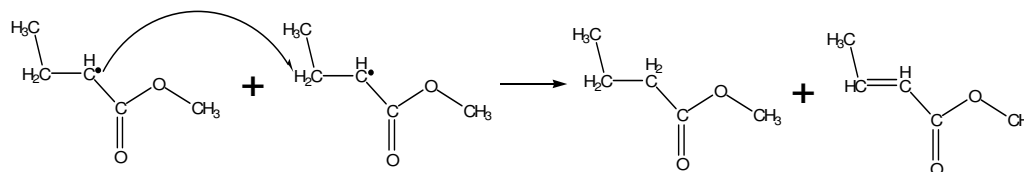


Figure 4.23. Schematic representation of the disproportionation reaction for methyl acrylate

There are two available hydrogen atoms on the radical derivatives M1R, M3R, M4R and M5R whereas the radical derivative of methyl (α -methyl) acrylate (M2R) has 5 possible hydrogen atoms. Figures 4.24-4.28 show the Mulliken charges of the labile hydrogen atoms of **M1R**, **M2R**, **M3R**, **M4R** and **M5R**.

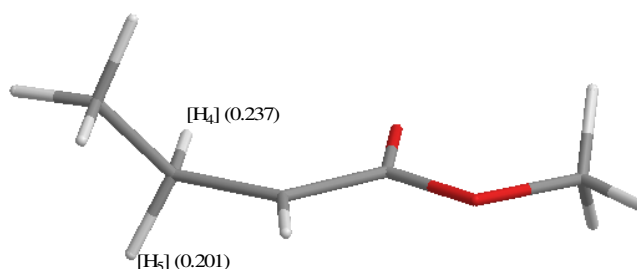


Figure 4.24. Mulliken charges of the labile hydrogen atoms on the radical M1R

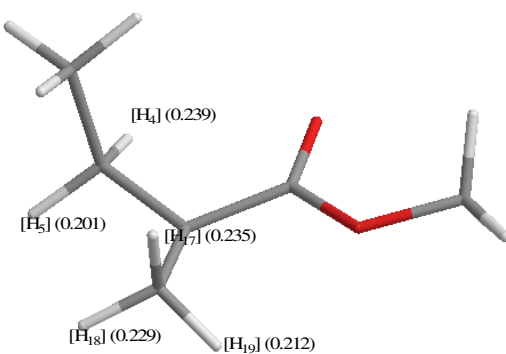


Figure 4.25. Mulliken charges of the labile hydrogen atoms on the radical M2R

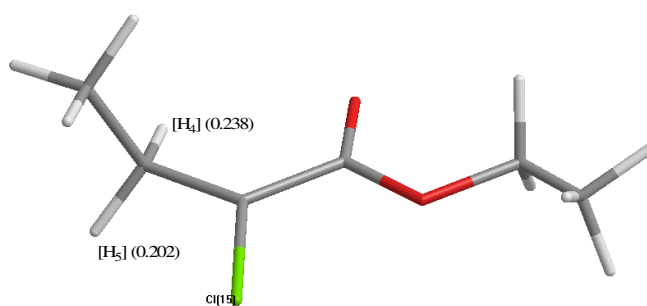


Figure 4.26. Mulliken charges of the labile hydrogen atoms on the radical M3R

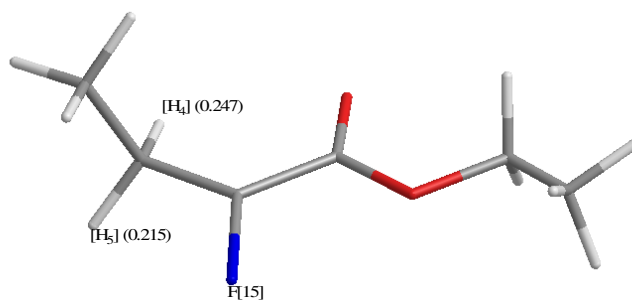


Figure 4.27. Mulliken charges of the labile hydrogen atoms on the radical M4R

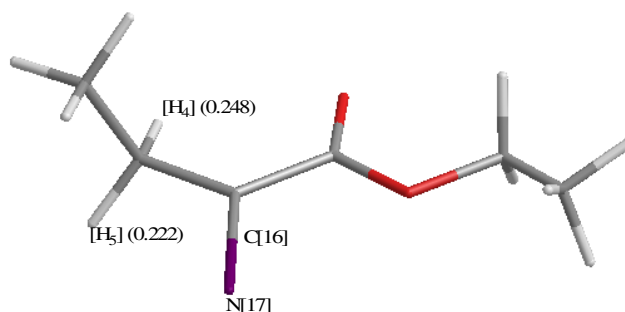


Figure 4.28. Mulliken charges of the labile hydrogen atoms on the radical M5R

Mulliken charges indicate that the most labile hydrogen atom on the radical derivatives of the monomers M1, M3, M4 and M5 is H₄ since this H atom is more positively charged as compared with the other labile H atoms.

On the other hand, the hydrogen abstraction transition states of the abstractable hydrogens are modelled with methyl radical to see which hydrogen atoms on the α -C atom is more likely to be abstracted. (Figure 4.29-Figure 4.33) Table 4.15 shows that there is no difference between the hydrogen abstraction barriers for H₄ and H₅ hydrogen atoms for M1R, M3R, M4R and M5R since all the monomers show symmetry according to the monomer plane. On the other hand, for M2R, the hydrogen abstraction barriers for H₄ and H₅ hydrogen atoms are smaller than the hydrogen abstraction barriers for H₁₇, H₁₈ and H₁₉ hydrogen atoms.

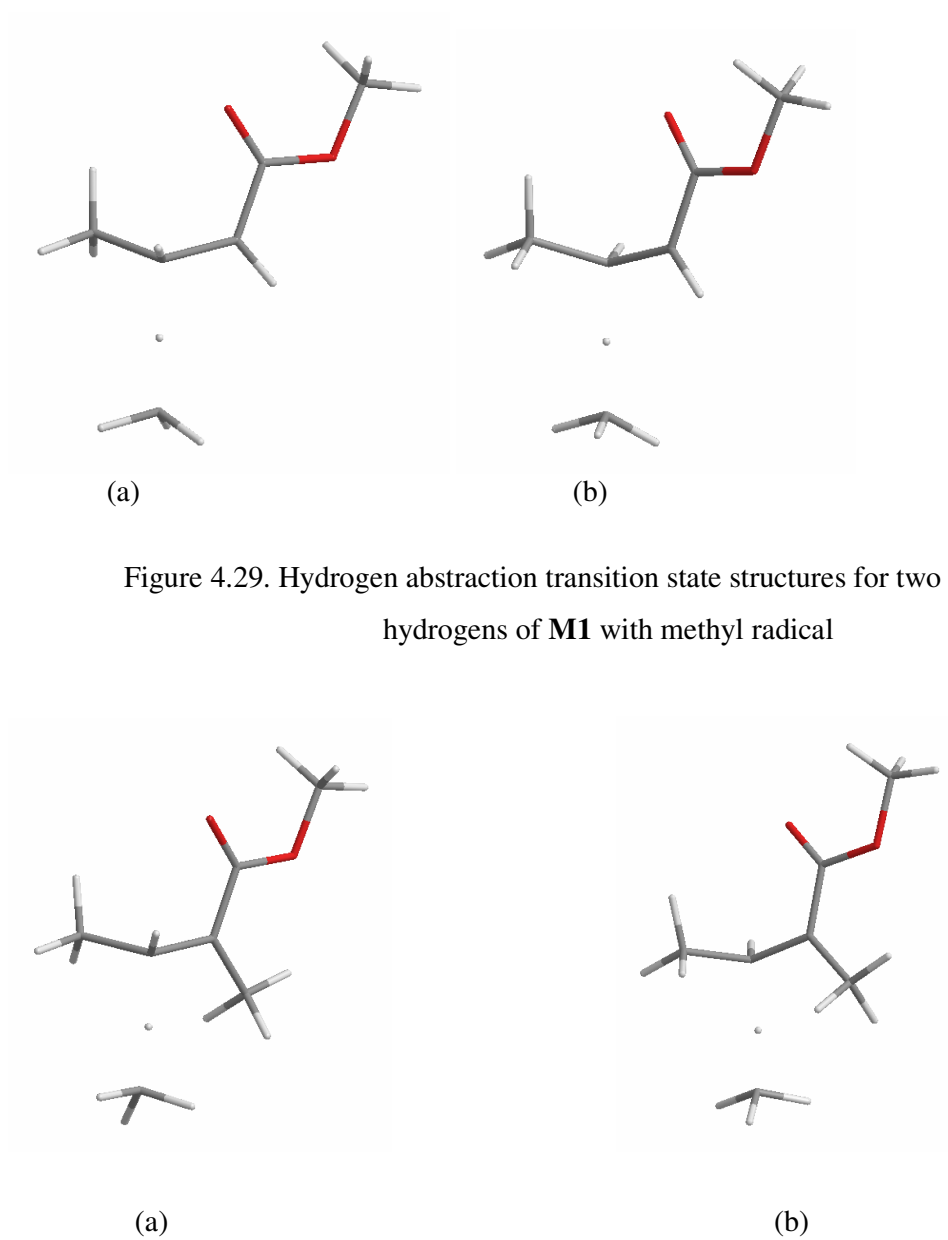


Figure 4.29. Hydrogen abstraction transition state structures for two abstractable hydrogens of **M1** with methyl radical

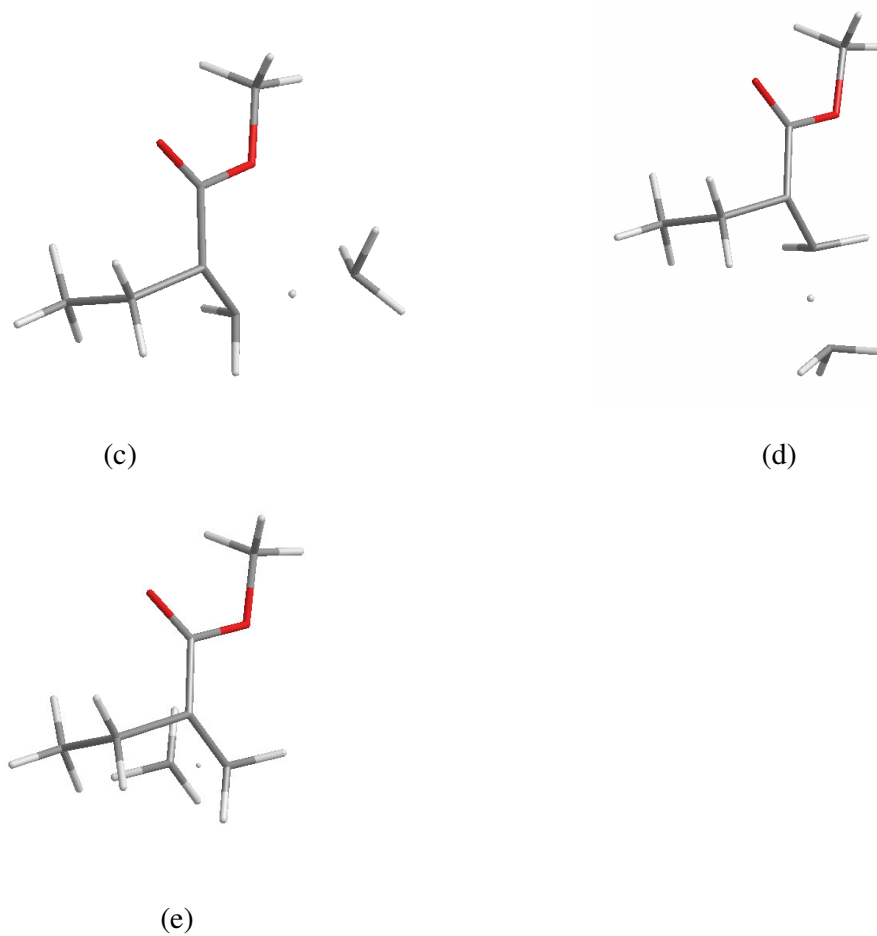


Figure 4.30. Hydrogen abstraction transition state structures for five abstractable hydrogens of **M2** with methyl radical

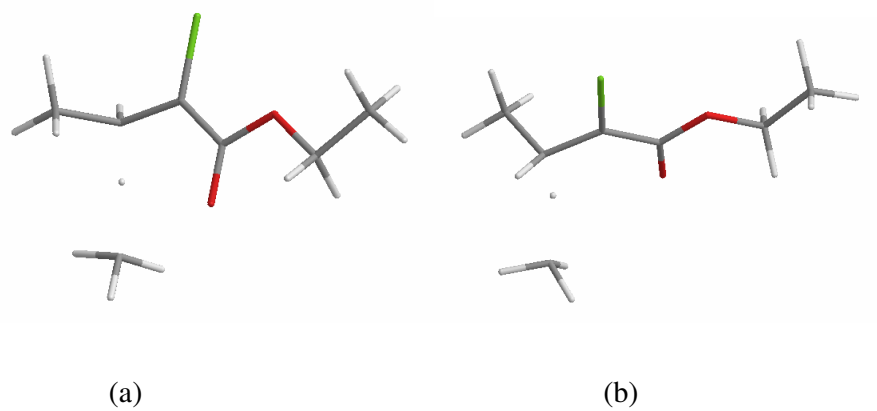


Figure 4.31. Hydrogen abstraction transition state structures for two abstractable hydrogens of **M3** with methyl radical

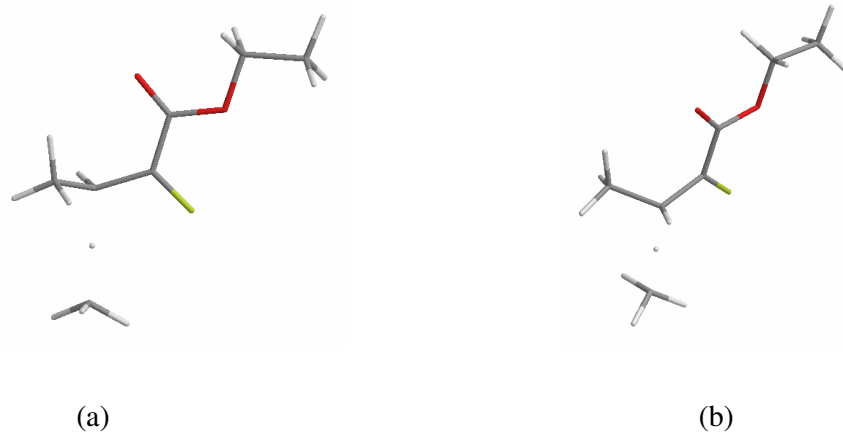


Figure 4.32. Hydrogen abstraction transition state structures for two abstractable hydrogens of **M4** with methyl radical

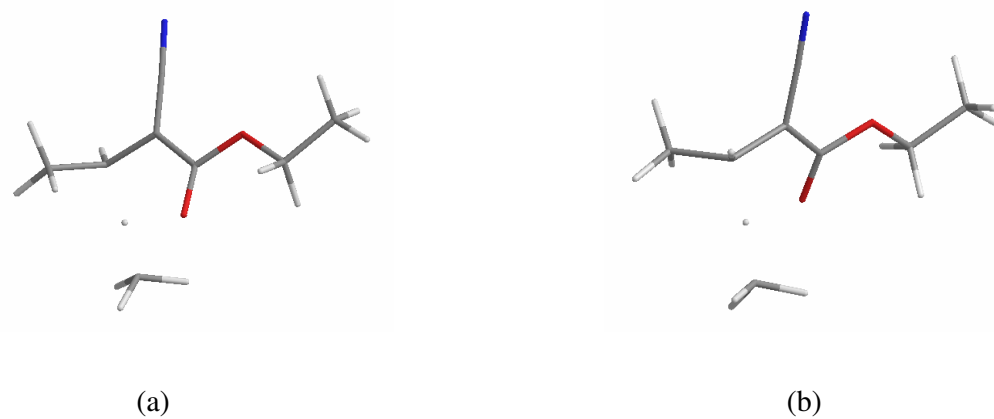


Figure 4.33. Hydrogen abstraction transition state structures for two abstractable hydrogens of **M5** with methyl radical

Table 4.15. Hydrogen abstraction barriers (E_a (kcal/mol)) for available hydrogen atoms of **M1**, **M2**, **M3**, **M4** and **M5** to be abstracted

	a (H₄)	b (H₅)	c (H₁₇)	d (H₁₈)	e (H₁₉)
M1	4.22	4.22	-	-	-
M2	4.63	4.63	4.97	4.97	4.97
M3	5.07	5.07	-	-	-
M4	5.20	5.20	-	-	-
M5	5.21	5.21	-	-	-

Finally the reactivity descriptors of the radical derivatives of the monomers **M1**, **M2**, **M3**, **M4** and **M5** are checked. These descriptors for the hydrogen atoms H₄ and H₅ (additionally H₁₇, H₁₈ and H₁₉ for the monomer **M2**) of the monomers are tabulated in Table 4.16. For all the radicals, the difference between softness values for the radical center C atom for methyl radical and labile H atom ($s_k^0(CH_3) - s_k^0$) is lower for H₄ compared with the other H atoms. We have taken into account all these data and have decided to choose H₄ hydrogen atoms for the radical derivatives of the monomers **M1**, **M2**, **M3**, **M4** and **M5** to model the disproportionation reactions.

Table 4.16. Reactivity descriptors of hydrogen atoms on the α -C atom of the radical derivatives of the monomers **M1**, **M2**, **M3**, **M4** and **M5**

	k	f_k^0	$^*\rho_k(N_o+1)$	$^*\rho_k(N_o-1)$	S	s_k^0	$s_k^0(CH_3) - s_k^0$
M1	H ₄	-0.05185	0.201714	0.305413	8.281573	-0.4294	1.807083
	H ₅	-0.08621	0.148835	0.321246	8.281573	-0.71392	2.091605
M2	H ₄	-0.04526	0.200225	0.290741	9.05551	-0.40983	1.787522
	H ₅	-0.06517	0.143743	0.274092	9.05551	-0.59019	1.967876
M3	H ₁₇	-0.08358	0.158031	0.325193	9.05551	-0.75687	2.134557
	H ₁₈	-0.05607	0.190637	0.302767	9.05551	-0.5077	1.885385
	H ₁₉	-0.06597	0.152844	0.284793	9.05551	-0.59743	1.975121
	H ₄	-0.04402	0.211229	0.299276	8.729431	-0.3843	1.761988
	H ₅	-0.06603	0.160536	0.292593	8.729431	-0.57639	1.954079
M4	H ₄	-0.04535	0.214321	0.305029	8.765394	-0.39755	1.775234
	H ₅	-0.08158	0.155921	0.319074	8.765394	-0.71505	2.092738
M5	H ₄	-0.04929	0.200686	0.299268	8.069397	-0.39775	1.775437
	H ₅	-0.05754	0.172009	0.287084	8.069397	-0.46429	1.841981
CH ₃	C ₁	-0.48757	-0.86268	-0.05890	3.428020	-0.39775	0.000000

* $\rho_k(N_o)$ represents the electronic population (Mulliken) on atom k for the N_o electron system.

After determination of the more labile hydrogen atom on the radicals for the disproportionation reaction with methyl radical, the radical derivatives of the monomers are used to model this reaction. Figures 4.36-4.40 illustrate the disproportionation transition states of the radical derivatives for the monomers M1, M2, M3, M4 and M5.

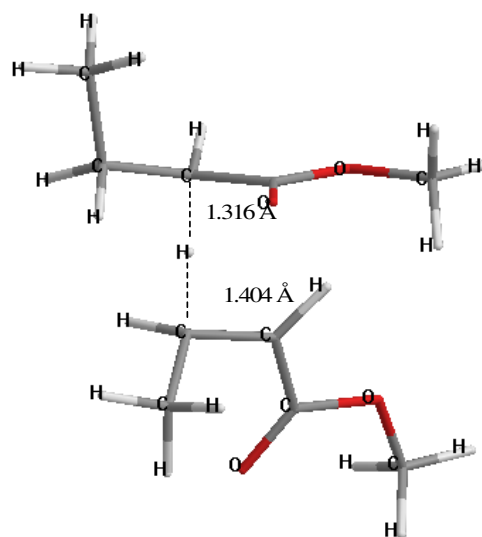


Figure 4.34. Disproportionation reaction for **M1**

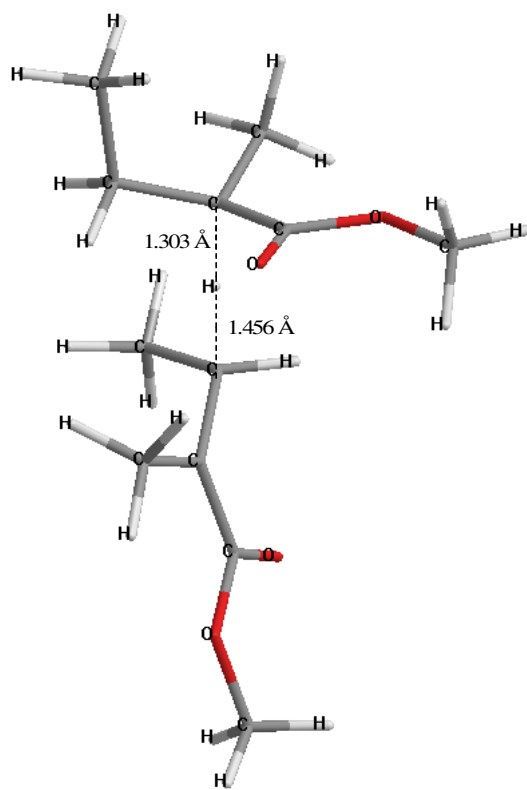


Figure 4.35. Disproportionation reaction for **M2**

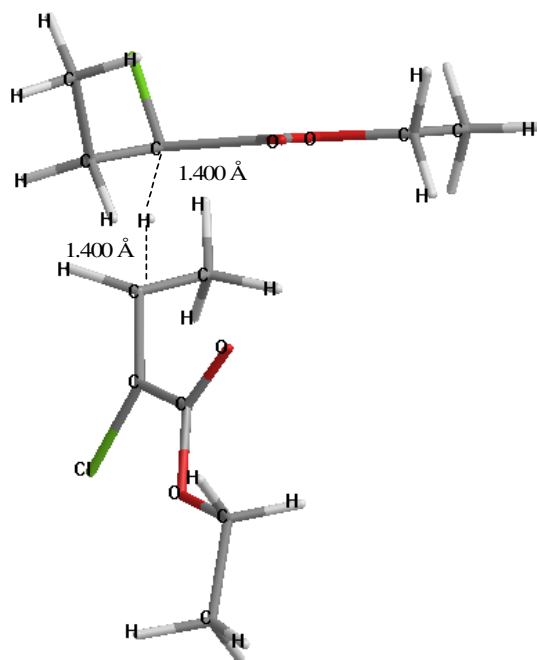


Figure 4.36. Disproportionation reaction for **M3**

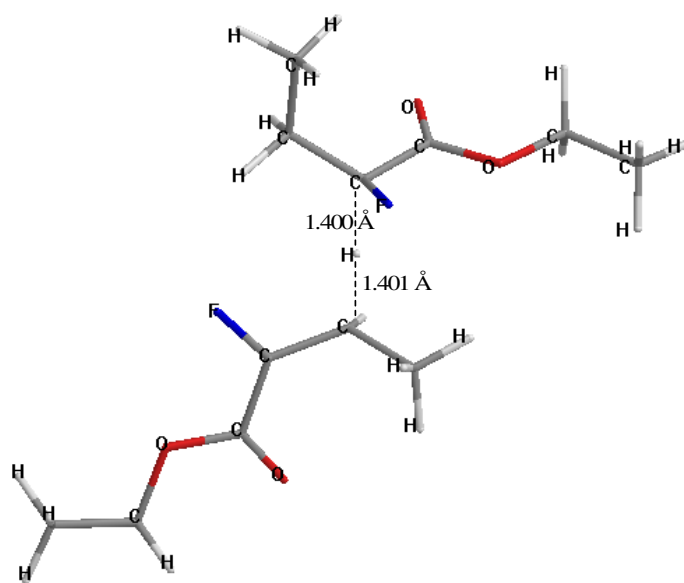


Figure 4.37. Disproportionation reaction for **M4**

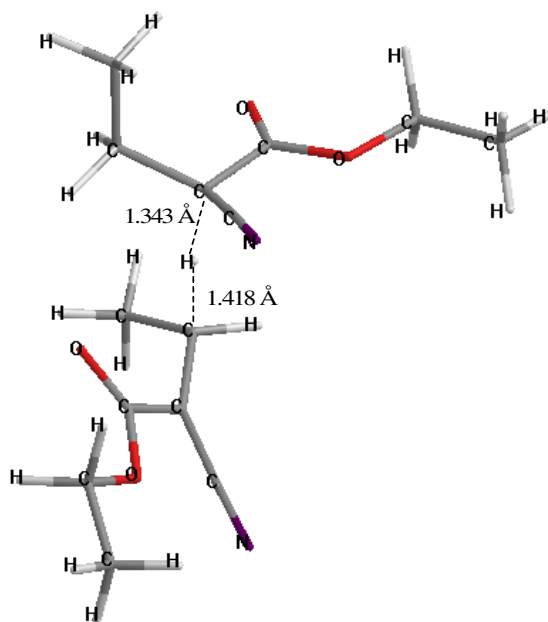


Figure 4.38. Disproportionation reaction for **M5**

For modelling the disproportionation reaction since Intrinsic reaction coordinate (IRC) calculations were not performed in order to confirm the structures, the following equation (4.1) was used to calculate the rate constant:

$$k = \frac{k_B T}{h} \frac{q_{TS}}{q_A q_B} e^{-[E_{TS} - (E_A + E_B)]/RT} \quad (4.1)$$

As two radicals react with each other in disproportionation reaction, A and B in the equation both represent the same radical. In the formula $\frac{k_B T}{h} \frac{q_{TS}}{q_A q_B}$ is called the preexponential constant A (Arrhenius constant) and the equation (4.1) become:

$$k = Ae^{-[E_{TS}-(E_A+E_B)]/RT} \quad (4.4)$$

Rate constant calculations are performed in a specific temperature range in this work 300 K-600 K. Temperature range is chosen in accordance with the experimental temperature range. Table 4.17 shows the calculation steps for M3. Table 4.18 displays the total partition functions for M3R, disproportionation transition state and $\ln(k)$ values for each temperature in the range of 300-600 K.

Table 4.17. Calculation steps for M3

<u>M3R</u>	HF (energy) = -845.266775 Hartree
	Zero point correction = 0.125388 Hartree
	Total energy = -845.141387 Hartree
<u>Transition state</u>	HF (energy) = -1690.548597 Hartree
	Zero point correction = 0.302931 Hartree
	Total energy = -1690.245666 Hartree
Forward barrier (T= 0 K)	$E_{TS}-2(E_{M3R}) = 3.71 \text{ E-02 Hartree}$

Table.4.18. Partition functions and $\ln(k)$ values for $300\text{ K} < T < 600\text{ K}$

T (K)	Q (M3R)	Q (transition state)	$\ln(k)$
300	8.33E+17	3.13E+26	-3.48E+01
310	1.27E+18	7.31E+26	-3.35E+01
320	1.91E+18	1.69E+27	-3.22E+01
330	2.88E+18	3.86E+27	-3.10E+01
340	4.30E+18	8.75E+27	-2.99E+01
350	6.40E+18	1.96E+28	-2.89E+01
360	9.47E+18	4.37E+28	-2.79E+01
370	1.40E+19	9.63E+28	-2.69E+01
380	2.05E+19	2.11E+29	-2.60E+01
390	3.00E+19	4.57E+29	-2.52E+01
400	4.37E+19	9.85E+29	-2.43E+01
410	6.34E+19	2.11E+30	-2.36E+01
420	9.18E+19	4.48E+30	-2.28E+01
430	1.32E+20	9.47E+30	-2.21E+01
440	1.90E+20	1.99E+31	-2.14E+01
450	2.72E+20	4.15E+31	-2.08E+01
460	3.89E+20	8.60E+31	-2.01E+01
470	5.55E+20	1.77E+32	-1.95E+01
480	7.88E+20	3.64E+32	-1.90E+01
490	1.12E+21	7.43E+32	-1.84E+01
500	1.58E+21	1.51E+33	-1.79E+01
510	2.23E+21	3.05E+33	-1.74E+01
520	3.13E+21	6.13E+33	-1.69E+01
530	4.39E+21	1.23E+34	-1.64E+01
540	6.15E+21	2.44E+34	-1.59E+01
550	8.59E+21	4.85E+34	-1.55E+01
560	1.20E+22	9.57E+34	-1.50E+01
570	1.67E+22	1.88E+35	-1.46E+01
580	2.31E+22	3.68E+35	-1.42E+01
590	3.20E+22	7.19E+35	-1.38E+01
600	4.43E+22	1.40E+36	-1.34E+01

When $\ln(k)$ is plotted versus $1/T$, the slope gives the energy of activation (E_a) for the reaction and the intercept gives the pre-exponential factor A . As seen from Table 4.19 the energy of activation, E_a , for M3 is $2.23 \text{ E}+01$, whereas the pre-exponential factor A is $2.51 \text{ E}+03$. By using E_a and A , the rate constant at $T = 298.15 \text{ K}$ is calculated easily as $9.99 \text{ mol L}^{-1}\text{s}^{-1}$. Table 4.19 shows both the experimental and the calculated rate constants for propagation reactions.

Table 4.19. The experimental and calculated disproportionation rate constants for M1, M2, M3, M4 and M5

No	Calculations				Experiment		
	E_a (kcal/mol)	A	$k_t \text{ calc.}$ ($\text{mol L}^{-1}\text{s}^{-1}$)	$k_t \text{ calc.}^a$	$k_t \text{ exp. E-07}$ ($\text{mol L}^{-1}\text{s}^{-1}$)	$k_t \text{ exp.}^a$	Reference
M1	2.59E+01	4.38E+03	9.15E-18	1.00E+00	0.34E-07	1.00E+00	[16]
M2	2.37E+01	1.44E+02	2.76E-17	3.02E+00	4.20E-07	1.24E+01	[16]
M3	2.33E+01	2.51E+03	4.96E-16	5.42E+01	3.33E-06	9.79E+01	[16]
M4	2.24E+01	2.28E+04	2.02E-14	2.21E+03	4.80E-06	1.41E+02	[16]
M5	1.87E+01	3.85E+01	7.88E-13	8.61E+04	4.11E-06	1.20E+02	[16]

^a Relative to M1.

4.1.5 Overall Polymerizability Behavior of M1, M2, M3, M4 and M5

In order to have information concerning the kinetics of radical reactions and polymerizability behavior of the monomers, a stationary polymerization system in which the radical concentration is constant during the whole process and the rate of initiation of radicals (generation of active radicals) is equal to the rate of termination of radicals (removal of active radicals resulting dead polymers) is assumed is defined. Since the rate constant for the overall polymerization process is expressed with the following expression (4.5) :

$$k = \frac{k_p}{k_t^{1/2}} (fk_d)^{1/2} \quad (4.5)$$

it is convenient to compare the ($\frac{k_p}{k_t^{1/2}}$) ratio for the monomers M1, M2, M3, M4 and M5.

Table 4.20 shows the experimental and calculated k_p, k_t and $\frac{k_p}{k_t^{1/2}}$ ratios for these monomers.

Table 4.20. The overall rate constant and polymerizability behavior of the monomers M1, M2, M3, M4 and M5

	Calculated				Experimental			
	k_p mol L ⁻¹ s ⁻¹	k_t mol L ⁻¹ s ⁻¹	$\frac{k_p}{k_t^{1/2}}$	$\frac{k_p}{k_t^{1/2}}^a$	k_p mol L ⁻¹ s ⁻¹	k_t mol L ⁻¹ s ⁻¹	$\frac{k_p}{k_t^{1/2}}$	$\frac{k_p}{k_t^{1/2}}^a$
M1	1.49E-01	9.15E-18	4.97E+07	1.00	7.20E+02	0.34E+00	1.23E+03	1.00
M2	3.57E-02	2.76E-17	6.80E+06	0.13	4.50E+02	4.20E+00	2.20E+02	0.18
M3	4.29E+00	4.96E-16	1.93E+08	3.91	1.66E+03	3.33E+01	2.88E+02	0.23
M4	2.32E+00	2.02E-14	1.63E+07	0.33	1.12E+03	4.80E+01	1.62E+02	0.13
M5	7.75E+00	7.88E-13	8.73E+06	0.18	1.62E+03	4.11E+01	2.53E+02	0.20

^aRelative to M1.

The rates of overall polymerization reaction of **M1**, **M2**, **M3**, **M4** and **M5** show a decrease in the order **M3**> **M1**> **M4**>**M5**>**M2** according to the calculations. On the other hand this trend is observed in the order M1>M3>M2>M5>M4 according to experimental findings. M1 has the higher propagation rate constant and lower disproportionation rate constant compared to M2. Since the smallest propagating radical M1R is very active and diffuses the reaction side faster, the H abstraction side reaction (termination) is suppressed for the monomer M1. On the other hand M2 has an α -methyl group and this group stabilizes the propagating radical. That's why M1 is the monomer that polymerizes easily compared to M2. The reactivity differences of the monomers M3, M4 and M5 can be explained with the α -substituents effects. α -chloro substituent on M3 makes this monomer more stable due to the resonance stabilization. The resonance stabilization effect is smaller for α -floro substituent on M4. The most important factor for M5 reactivity is the captodative effect. This effect due to α -cyano substituent (captive-captive effect) makes M5R is

more stable than M2R which has α -methyl substituent (captodative effect). This stabilization effect renders monomer M5 less reactive compared with M1.

4.2. Density Functional Theory Descriptors for Cyclization Reactions of Diallyl Compounds

Allyl monomers are generally considered as poor monomers for radical polymerization, since chain transfer reactions take place by abstraction of allylic hydrogens of monomer by the propagating radical. The radical that is formed by abstraction of allylic hydrogen is more stable because of resonance stabilization. The stability of the resulting radical reduces the polymerization efficiency and the molecular weight of the polymer.

Although monofunctional allyl compounds are not good monomers for polymerization, their difunctional analogues have been found to be polymerized to high molecular weights through cyclopolymerization, as discovered by Butler's pioneering work [41, 42, 43]. The cyclopolymerization reactions of diallyl monomers have interesting features since these bifunctional monomers can form linear polymers with cyclic structures on the backbone, and can introduce important physical properties to the monomer. In radical cyclopolymerization reactions, the radicalic initiator attacks intramolecularly one of the olefinic bonds and produces a secondary carbon radical, which forms either 5-membered or 6-membered ring structures. (Figure 4.39)

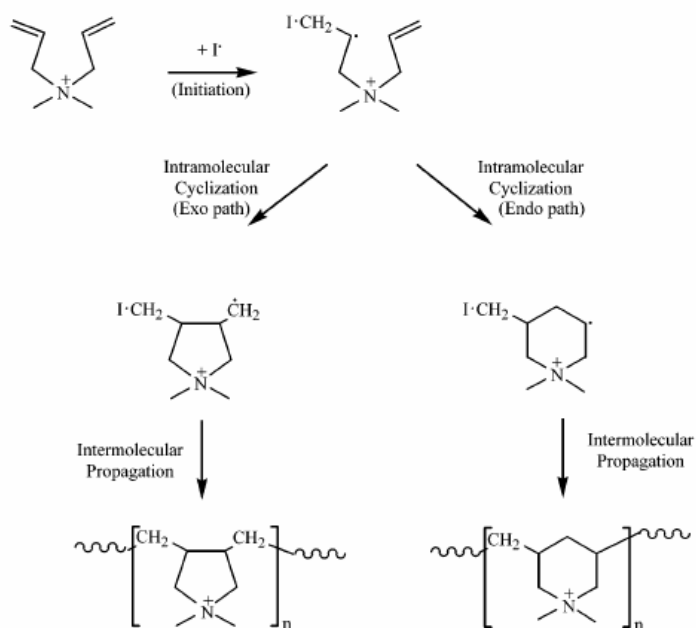


Figure 4.39. Mechanism of Cyclopolymerization

The conformational preferences of the monomers and their consequences on cyclization can be demonstrated by modeling the transition structures leading to 5-membered and 6-membered rings and the activation energies can be calculated for these reactions forming transition states. In this study, the regioselectivity of the monomers is explained with the Density Functional Theory descriptors. Nine radicals (M6....M14) that are chosen for this work have been modeled previously to demonstrate whether the monomers form a five membered ring or six membered rings (Table 4.21). It is clearly realized from Table 4.21 that M6 prefers to make a five-membered ring via cyclopolymerization since the energy of activation for 5 membered ring formation is less than the energy of activation for 6 membered ring formation.

Table 4.21. Radicals modeled for cyclopolymerization

No	Structure	Name	E _a (5exo) kcal/mol	E _a (6endo) kcal/mol	Reference
M6		N,N-diallylamine radical	7.20	10.90	[38]
M7		N,N-diallylammonium radical	8.60	11.60	[38]
M8		N,N-diallyl N,N-dimethylamine radical	6.20	10.30	[38]
M9		N,N-diallyl N-methylamine radical	5.00	10.60	[38]
M10		N,N-diallyl N-methylammonium radical	6.40	10.20	[38]
M11		N-methyl-N-allyl-2-(methoxycarbonyl) allylamine radical	8.68	12.20	[39]
M12		N-methyl-N-methallyl-2-(methoxycarbonyl) allylamine radical	14.02	11.59	[39]
M13		α-(allyloxymethyl) acrylate radical	5.33	10.23	[40]
M14		Alkyl α-propoxymethyl acrylate radical	9.82	12.08	[40]

4.2.1 3D-structures of M6...M14

For the radicals M6-M14, since there are free rotations around single bonds, various conformers exist. Based on B3LYP/6-31+G* calculations, the most stable conformers are chosen. The numbering system used in radicals in Table 4.21 is shown in Figures 4.40 – 4.48

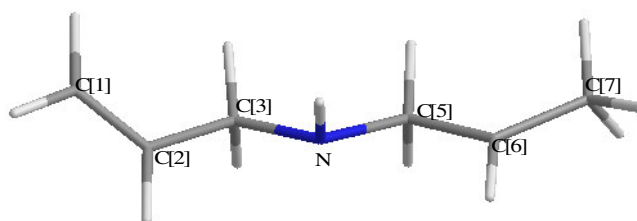


Figure 4.40. Numbering system used for M6

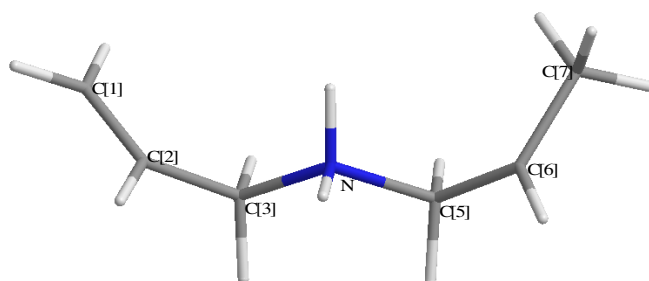


Figure 4.41. Numbering system used for M7

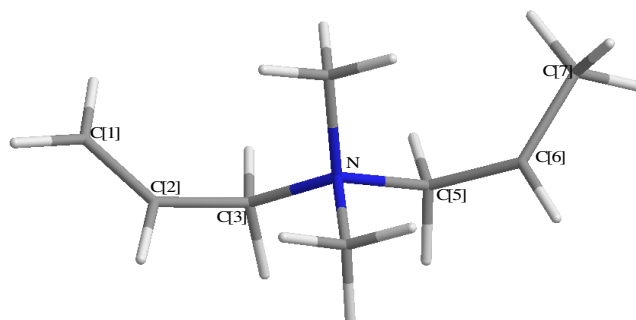


Figure 4.42. Numbering system used for M8

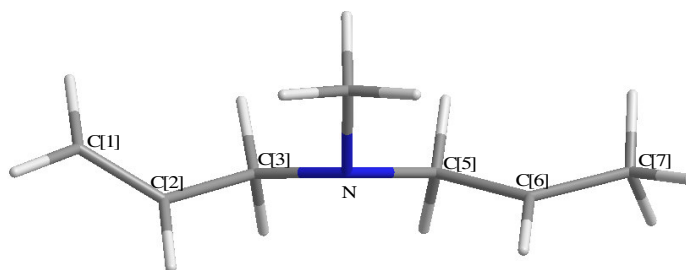


Figure 4.43. Numbering system used for M9

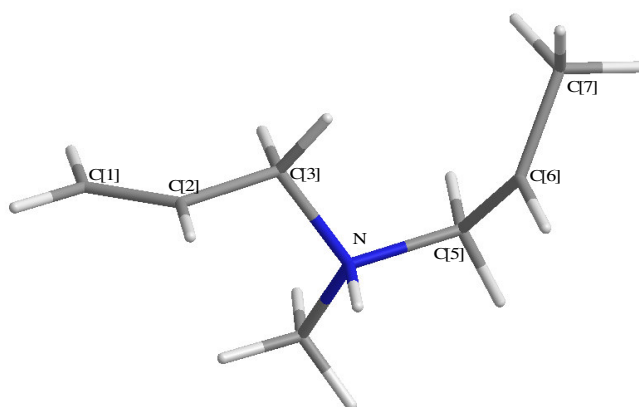


Figure 4.44. Numbering system used for M10

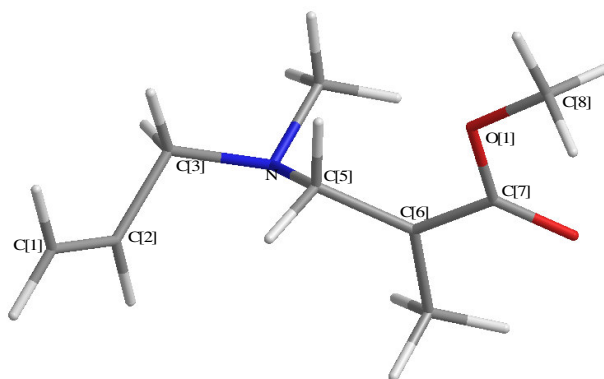


Figure 4.45. Numbering system used for M11

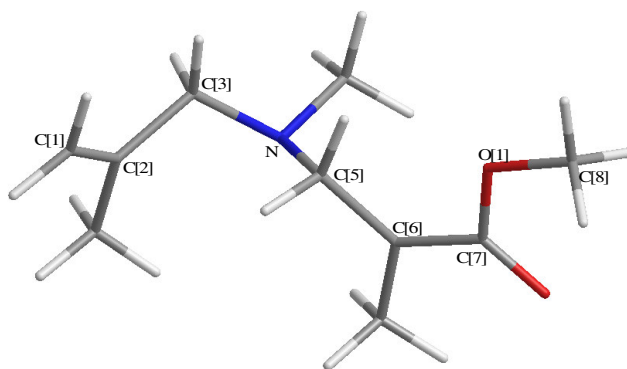


Figure 4.46. Numbering system used for M12

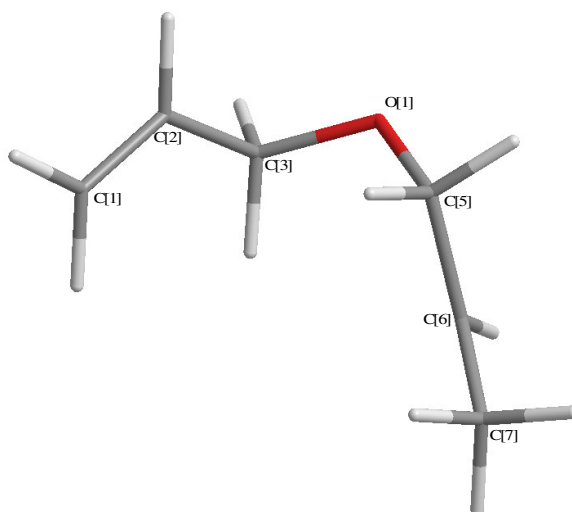


Figure 4.47. Numbering system used for M13

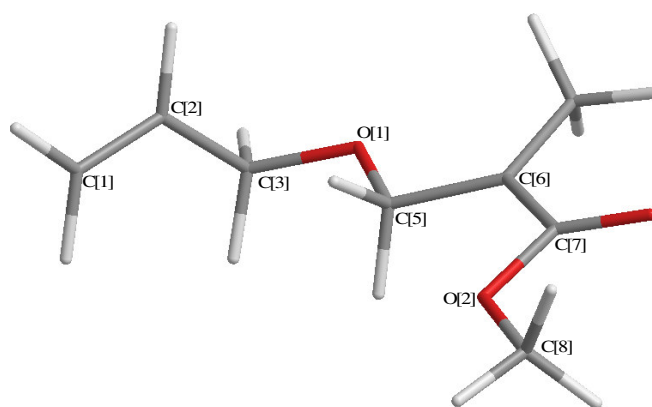


Figure 4.48. Numbering system used for M14

The dihedral angles for the most stable conformers for the 9 radicals are given in Table 4.22. M6, M7, M8, M9 and M10 show the similar structures. The substitutions on these radicals do not affect the backbone structure. On the other hand, M11, M12, M13 and M14 differ in structure as it can be realized from the dihedral angles (Table 4.22) due to the carbonyl attachment and ester linkage on these radicals.

Table 4.22. Dihedral angles for M6-M14

	M6	M7	M8	M9	M10	M11	M12	M13	M14
C ₁ C ₂ C ₃ N									
*C ₁ C ₂ C ₃ O ₁	125.0	111.6	113.7	130.2	118.7	-128.7	-122.7	128.1	127.7
C ₂ C ₃ NC ₅									
*C ₂ C ₃ O ₁ C ₅	177.7	179.7	177.9	165.3	165.8	68.9	70.3	-73.3	-71.8
C ₃ NC ₅ C ₆									
*C ₃ O ₁ C ₅ C ₆	-180.0	179.9	179.3	165.6	165.5	-162.8	-164.7	-71.9	-78.6
NC ₅ C ₆ C ₇									
*O ₁ C ₅ C ₆ C ₇	-162.9	-95.4	-106.7	-161.3	-120.1	-136.1	-133.8	162.1	179.2
C ₅ C ₆ C ₇ O ₁									
*C ₅ C ₆ C ₇ O ₂	-	-	-	-	-	2.6	1.9	-	-0.2
C ₆ C ₇ O ₁ C ₈									
*C ₆ C ₇ O ₂ C ₈	-	-	-	-	-	179.8	179.8	-	179.9

*The numbering system for M13 and M14.

4.2.2 DFT Reactivity Descriptors

The reactivity descriptors which are calculated for M6-M14 are given in Table 4.23.

s_k^0 is calculated with the following equation (4.6)

$$s_k^0 = f^0(r) \times S \quad (4.6)$$

where $f^0(r) = \frac{1}{2} [q_k(N+1) - q_k(N-1)]$ and $S = \frac{2}{\epsilon_{HOMO} - \epsilon_{LUMO}}$. s_k^0 is calculated for

both the radical center C atom and two C atoms in the double bond to understand whether the 5 membered or 6 membered ring forms via cyclopolymerization.

Table 4.23. DFT Descriptors for M6-M14

	k	$f^0(r)$	$\rho_k(N_o+1)$	$\rho_k(N_o-1)$	S	s_k^0	$\Delta s_k^0(exo)$	$\Delta s_k^0(endo)$
M6	C ₁	-0.086070	-0.359800	-0.187660	4.931939239	-0.424484	0.192003	0.4569072
	C ₂	-0.032360	-0.127740	-0.063030		-0.159580		
	C ₆ [*]	0.0065740	-0.088790	-0.101940		0.032422		
M7	C ₁	-0.058881	-0.201934	-0.084173	4.98852600	-0.293727	-0.809279	-1.123179
	C ₂	-0.221109	-0.392631	0.049586		-1.103006		
	C ₆ [*]	0.004044	-0.168839	-0.176927		0.020174		
M8	C ₁	-0.049905	-0.193321	-0.093511	4.90629000	-0.244848	-0.149700	0.138630
	C ₂	0.008863	-0.168732	-0.186457		0.043482		
	C ₆ [*]	-0.021650	-0.172082	-0.128783		-0.106219		
M9	C ₁	-0.076640	-0.362100	-0.208820	4.947555907	-0.379173	0.169689	0.437960
	C ₂	-0.022420	-0.113250	-0.068420		-0.110902		
	C ₆ [*]	0.011882	-0.074770	-0.098540		0.058787		
M10	C ₂	0.013005	-0.248810	-0.274820	4.793863854	0.062342	-0.053809	1.055884
	C ₃	0.001780	-0.177480	-0.181040		0.008533		
	C ₁₅ [*]	-0.218480	-0.414510	0.022448		-1.047351		
M11	C ₁₃	-0.086096	-0.359842	-0.187651	4.78996000	-0.412394	0.431765	0.688993
	C ₁₁	-0.032394	-0.127769	-0.062981		-0.155166		
	C ₄ [*]	0.057746	-0.031989	-0.147480		0.276599		
M12	C ₁₃	0.058881	0.201934	0.084173	4.988526389	0.293727	0.875818	0.561918
	C ₁₁	-0.004040	0.168839	0.176927		-0.020174		
	C ₄ [*]	0.171523	0.392631	0.049586		0.855644		
M13	C ₁	0.016494	-0.326310	-0.359300	4.988526389	0.082280	-0.295416	-0.274429
	C ₂	0.020701	-0.066900	-0.108300		0.103267		
	C ₆ [*]	-0.038520	-0.125630	-0.048600		-0.192148		
M14	C ₉	0.021916	0.041322	-0.002510	4.793863854	0.105060	-0.710657	-0.113293
	C ₁₀	0.146526	-0.117710	-0.410760		0.702423		
	C ₄ [*]	-0.001720	0.009114	0.012549		-0.008234		

* The radical center C atom.

$\rho_k(N_o)$ represents the electronic population (Mulliken) on atom k for the N_o electron system, s_k^0 represents local softness and S represents global softness.

The relation between the Δs_k^0 and the activation energy of the cyclopolymerization reactions was investigated with reactivity descriptor calculations. $\Delta s_k^0(exo)$ values are smaller than $\Delta s_k^0(endo)$ values for the all radicals except M12 which is the only one that prefers 6 membered ring via cyclopolymerization. Among these 9 radicals, there is also a

linear relation (Figure 4.49) with activation energy and Δs_k^0 except M13 and M14 since the ether linkages play an important role on the conformations of these two radicals as it can be realized from the dihedral angles (Table 4.22).

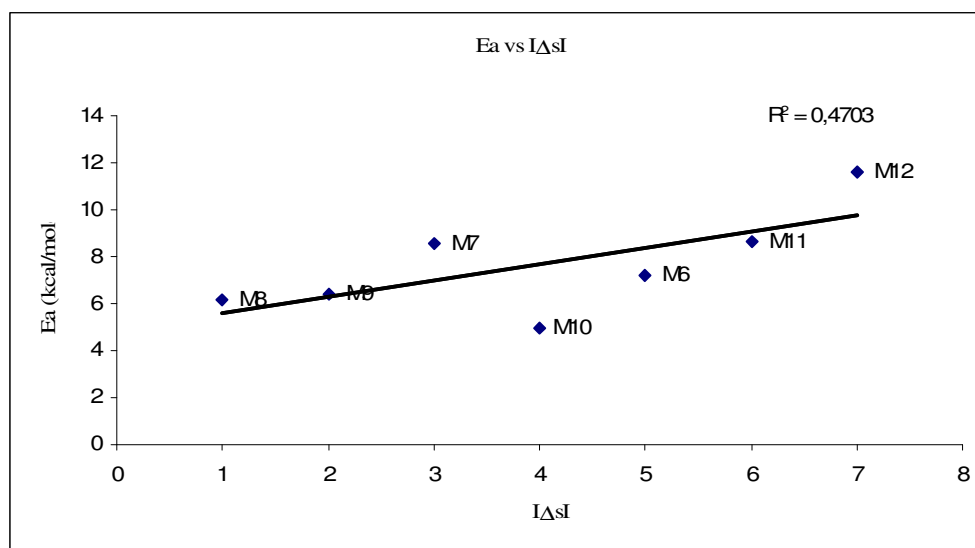


Figure 4.49. Relation between E_a and Δs_k^0 for M6, M7, M8, M9, M10, M11 and M12

It can be clearly observed that there is a deviation from the linearity for the negative Δs_k^0 values which were calculated for M7, M8, and M10. If we also ignore these values for M7, M8 and M10, the remaining 4 radicals (M6, M9, M11, M12) show perfect relation for the activation energy and Δs_k^0 (Figure 4.50).

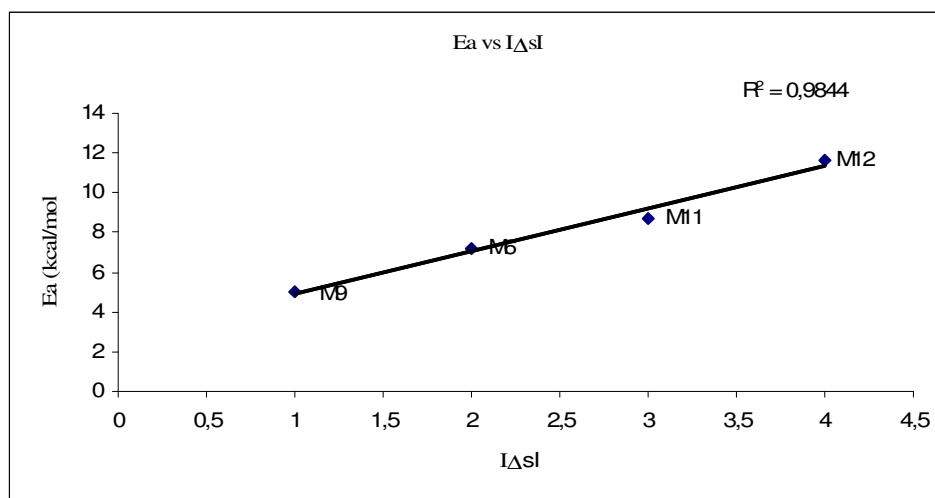


Figure 4.50. Relations between E_a and Δs_k^0 for M6, M9, M11 and M12

5. CONCLUSIONS

In this study, α -substituted acrylate monomers have been modeled by using the quantum mechanical methods in order to understand the structure reactivity relationship on propagation and the dispropagation reactions. The polymerization kinetics has been considered in order to understand whether correlations between the theoretical and experimental findings can be established.

The propagation reaction is modeled by considering the radical attack to the least substituted C of the C-C double bond of the monomer. On the other hand, the termination reaction which is modeled considering the α -methylene hydrogen abstraction between two radicals. The rate constants k_p , k_t and $k_p/k_t^{1/2}$ are evaluated in order to obtain quantitative understanding of the reactivity structure relationship. The results show that k_p and k_t do not perfectly mimic quantitatively the experimental rates but they follow the experimental findings qualitatively. The ratio $k_p/k_t^{1/2}$ is used to understand the overall polymerizability trend in the monomers of interest.

The other task of this study is to use the DFT descriptors in order to understand the cyclopolymerizability of diallylic monomers. DFT descriptors have been used in order to predict the site selectivity in cyclic polymerization.

Overall, this study has allowed to test with success the methodologies so far established in order to predict the polymerizability behavior of acrylate derivatives. Higher levels of calculation may be necessary for quantitative predictions.

SUGGESTIONS FOR FUTURE WORK

The following suggestions can be made for future work:

- Extending the methodology used in this study to larger monomers whose experimental behavior is known and if again perfect agreement with experiment is achieved predictions for new monomers can be done.
- Carrying out the kinetics with a higher basis set (B3LYP/6-311G**) for the first 5 monomers.
- Re-modeling the second set of radicals (9 radicals for cyclopolymerization reaction) with a higher basis set (B3LYP/6-31+G*)
- Assessing the effect of basis set on the kinetics of each step.

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