İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

A DFT INVESTIGATION OF THE TACTICITY OF ACRYLAMIDES IN FREE RADICAL POLYMERIZATION

M.Sc. Thesis by
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Programme : Polymer Science and Technology

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AKRİLAMİDLERİN SERBEST RADİKAL POLİMERİZASYONUNUN TAKTİSİTESİNİN DFT İLE İNCELENMESİ

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FOREWORD

I would like to thank my advisor Nurcan TÜZÜN whom support and concern I have always had throughout writing this thesis.

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Polymer Science and Technology

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ABBREVIATIONS

AM1	**:** Austen Model 1
CNDO	**:** Complete Neglect of Differential Overlap
DFT	**:** Density Functional Theory
DMAAm	**:** N,N-Dimethylacrylamide
DPAAm	**:** N,N-Diphenylacrylamide
ESP	**:** Electrostatic Potential
HF	**:** Hartree Fock
LCAO	**:** Linear Combination of Atomic Orbitals
MA	**:** Methylacrylate
MMA	**:** Methylmethacrylate
MNDO	**:** Modified Neglect of Differential Overlap
MphAAM	: N-methyl-N-phenylacrylamide
NMAAm	**:** N-methlacrylamide
PM3	**:** Parametric Method 3
SCF	**:** Self Consistent Field
ZDO	**:** Zero Differential Overlap

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A DFT INVESTIGATION OF THE TACTICITY OF ACRYLAMIDES IN FREE RADICAL POLYMERIZATION

SUMMARY

Tacticity control in free radical polymerization is an important topic since it affects the physical, thermal and mechanical properties of the final product. These properties such as the glass transition and melting temperatures, mechanical strength, the amount of crystallinity and solubility determine the application area of the polymers. In order to obtain the desired product in both laboratory and industrial scale, stereoregularity of the polymer chain should be controlled during the reaction because temperature, solvent, monomer/initiator concentration ratio or additives affect and determine whether a polymer is a tactic polymer (isotactic and syndiotactic) or an atactic polymer.

Quantum mechanical calculations is a very convenient way to understand and identiy the reaction mechanisms because it gives chance to explore the individual reactions by taking the reaction conditions into account.

In this study, the tacticities of a series of acrylamide monomers; DMAAm (N,N-Dimethylacrylamide), MphAAm (N-methyl-N-phenylacrylamide) and DPAAm (N,N-diphenylacrylamide) is investigated with quantum chemical tools. A DFT (Density Functional Theory) at 6-31+G(d,p) level of theory is used for optimization of the geometries, frequency and single point solvent calculations to evaluate the propagation steps of the reactions.

The calculations in this study aim to show the effect of substituent bulkiness, temperature, solvent and stereospecific inducers on the stereospecific addition modes of acrylamides.

The results of our calculations identify the mechanisms of the polymerizations of these three types of acrylamides at specific reaction conditions and reproduce the corresponding experimental findings with a good agreement.

AKRİLAMİDLERİN SERBEST RADİKAL POLİMERİZASYONUNUN TAKTİSİTESİNİN DFT İLE İNCELENMESİ

ÖZET

Serbest radikal polimerizasyonlarında, taktisitenin kontrolü; nihai ürünün fiziksel, termal ve mekanik özelliklerini etkilemesi bakımından önemli bir husustur. Bu özellikler; örneğin camsı geçiş ve erime sıcaklığı, mekanik kuvvet, kristallik oranı ve çözünebilirlik, polimerlerin kullanım alanlarını belirlerler. Hem laboratuvar hem endüstriyel düzeyde, istenilen özellikte ürün elde edebilmek için, polimer zincirinin stereoregularitesi reaksiyon sırasında kontrol edilebilmelidir. Çünkü sıcaklık, çözücü, monomer/başlatıcı konsantrasyon oranı, ya da reaksiyon ortamına eklenen katkı maddeleri, bir polimerin taktik (isotaktik ya da sindiotaktik) ya da ataktik oluşunu etkiler.

Kuantum mekaniksel hesaplamalar, değişik reaksiyon koşullarını da hesaba katarak, her bir reaksiyonu ayrı ayrı incelemeye imkan vermesi bakımından, reaksiyon mekanizmalarının anlaşılabilmesi ve aydınlatılabilmesi için oldukça elverişli bir yöntemdir.

Bu çalışmada, bir seri akrilamid monomerinin, N,N-dimetilakrilamid (DMAAm), N-metil-N-fenilakrilamid (MphAAm) ve N,N-difenilakrilamid (DPAAm), serbest radikal polimerizasyonundaki taktisiteleri kuantum kimyasal yöntemle incelenmiştir. Reaksiyonların propagasyon adımlarını değerlendirmek amacıyla, 6-31+G(d,p) seviyesinde DFT (Yoğunluk Fonksiyoneli Teorisi) metodu ile geometri optimizasyonları, frekans ve solvent hesaplamaları yapılmıştır.

Bu çalışmadaki hesaplamalar, akrilamidlerin stereospesifik katılma modları üzerinde sübstitüent, sıcaklık, solvent ve stereospesifik yapıcı moleküllerin etkisini incelemeyi amaçlamıştır.

Yapılan hesaplamalar neticesinde, belirli reaksiyon koşularında, üç farklı sübstitüye akrilamid monomerinin polimerizasyonunun mekanizması aydınlatılmış, ilgili deneysel verilerle karşılaştırılmış ve deneysel olarak bulunan sonuçlarla uyum gösterilmiştir.

1. INTRODUCTION

1.1 Free Radical Polymerization

Most synthetic plastics, elastomers and some fibers are prepared by free radical polymerization and obviously this is the most important method from a commercial viewpoint [1]. Due to their great industrial importance, free radical polymerizations are the most studied reactions in all of the chemistry. The free radical polymerization has attracted so much attention because it can be used to polymerize a very wide range of monomers and generally require moderate reaction conditions. Additionally, it does not have a high sensitivity to additives or impurities and gives possibility to use water as a solvent or dispersant. In general, it can be stated that the free radical polymerization has an advantage of practicability over the other polymerization types.

1.2 Mechanism and Kinetics of Free Radical Polymerization

A free radical polymerization has three main steps [2] :

i)Initiation of the active monomer

ii)Propagation or growth of the active (free radical) chain by sequential addition of monomers

iii)Termination of the active chain to give the final polymer product

i)Initiation of the active monomer: A radical is essential to start free radical polymerization. Radicals are entities with an unpaired electron. They are obtained by heterolytic or usually homolytic bond cleavage of species called 'intiators'. This covalent bond cleavage is achived by UV irridation or usually by heat:

$$I\text{–}I \xrightarrow{k_d} 2I. \qquad \textbf{(1.1)}$$

Then these radicals react with monomer molecules to give the active monomer.

$$I. + M \xrightarrow{k_a} IM. \quad \textbf{(1.2)}$$

$$R_i = d[I.] / d[t] = 2 f k_d [I] \quad \textbf{(1.3)}$$

where;

R_i : rate of inition

f : initiator efficiency

k_d : dissociation rate constant

ii)Propagation: Monomers subsequently attach to the initiated monomer species until some termination process occurs:

$$IM. + M \longrightarrow IMM. \quad \textbf{(1.4)}$$

$$IM_x. + M \xrightarrow{k_p} IM_xM. \quad \textbf{(1.5)}$$

Assuming that the rate of propagation is independent from the chain size; rate of polymerization becomes equal to rate of propogation:

$$R=R_p = k_p [IM_x.] [M] \quad \textbf{(1.6)}$$

where ;

R=rate of polymerization

R_p : rate of propogation

k_p : propogation rate constant

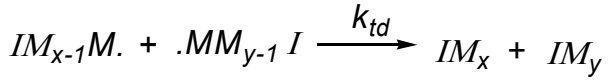
iii)Termination: Termination process may occur by three different ways:

1)Termination by Combination: Two growing polymer chains combine to give dead polymer:

$$IM_{x-1}M. + .MM_{y-1}I \xrightarrow{k_{tc}} IM_{x-1}M\text{—}MM_{y-1}I. \quad \textbf{(1.7)}$$

Two different radicals having different chain lengts react and as a result of this termination process, the propagating step ceases and polymerization stops. The resulting radical then reacts with different species.

2)Termination by disproportionation: Two terminated chains are formed by disproportionation reaction between two different propogating chains. One of the terminated chains has an unsaturated carbon group while the other one is saturated.



$$IM_{x-1}M. + .MM_{y-1}I \xrightarrow{k_{td}} IM_x + IM_y \quad \textbf{(1.8)}$$

3)Termination by Chain Transfer: Chain transfer may occur between the propogating radical and the other molecules such as solvent, initiator, monomer or polymer.

$$IM_{x-1}M. + XH \xrightarrow{k_{tr}} IM_{x-1}MH + X. \quad \textbf{(1.9)}$$

Neglecting the termination by chain transfer,

$$R_t = - d [IM_x.] / d [t] = 2 k_t [IM_x .]^2 \quad \textbf{(1.10)}$$

where ;

R_t : rate of termination

k_t : $k_{tc} + k_{td}$

k_{tc} : combination rate constant

k_{td} : disproportionation rate constant

Using stedy state approximation, assuming that the total radical concentration stays constant during the polymerization reaction, rate of initiaton becomes equal to rate of termination:

$$R_i = R_t \quad \textbf{(1.11)}$$

Substituting (1.11) to (1.3) ;

$$[IM_x ..] = (f k_d / k_t)^2 [I]^{½} \quad \textbf{(1.12)}$$

and polymerization rate is given in (1.13) :

$$R=k_p (f k_d / k_t)^{1/2} [I]^{1/2} [M] \quad \textbf{(1.13)}$$

1.3 Tacticity in Free Radical Polymerization

Tacticity refers to the stereoregularity of a polymer chain. It deals with the relationship between two adjacent monomer units which could be meso (m) or racemo (r) dyad.

There are four types of molecular configurations with different tacticities in monosubstitued ethylenes. Isotactic polymers consists of entirely meso diads and syndiotactic polymers consist of entirely racemo diads.

Heterotactic polymers consists of meso and racemo diads located alternatingly along the polymer chain. Polymers having equal amounts of m and r dyads are called atactic.

Tacticity can be shown by drawing the polymer chain with a planar zig zag conformation, Figure 1.1, Figure 1.2, Figure 1.3, Figure 1.4. The structures shown below have head to tail configuration which is known to be the most favored addition for vinyl monomers.

Actually, polymers cannot usually adopt planar zigzag conformation which requires the dihedral angles between the neighbouring carbon atoms to be 180°. In order to prevent overlapping of the substituent groups, rotations around carbon carbon single bonds occur and this causes deviations from planar zigzag conformation. For example, isotactic polymers with bulky substituents are known to have helix conformation in the crystal form [3].

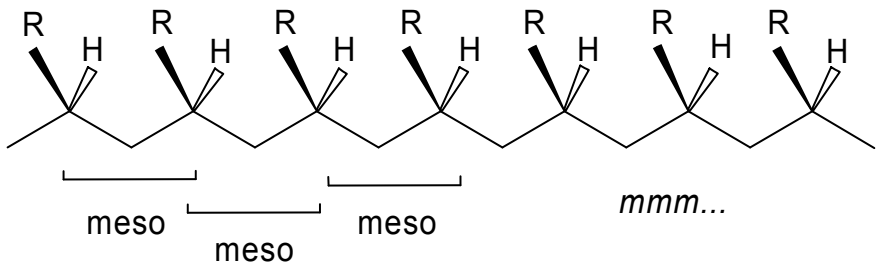


Figure 1.1 : Substituents lie on the same side of the planar in isotactic placement.

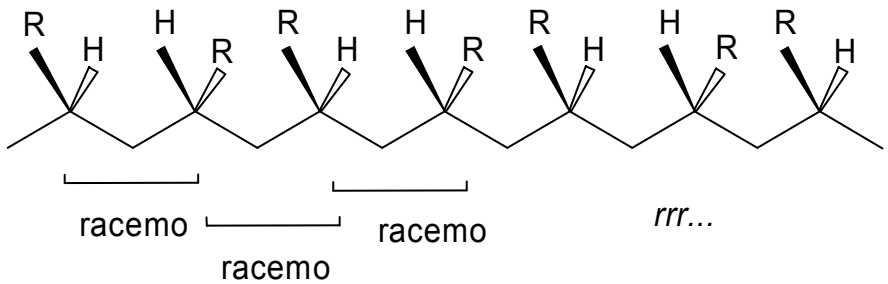


Figure 1.2 : Substituents regularly alternate from side of the plane to the other in syndiotactic placement.

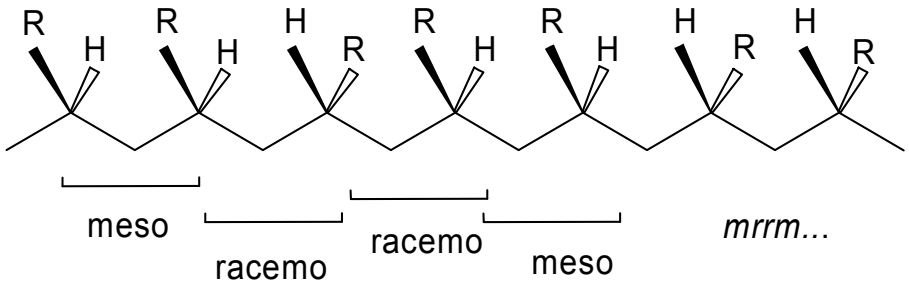


Figure 1.3 : Substituents ramdomly lie along the polymer chain in atactic placement.

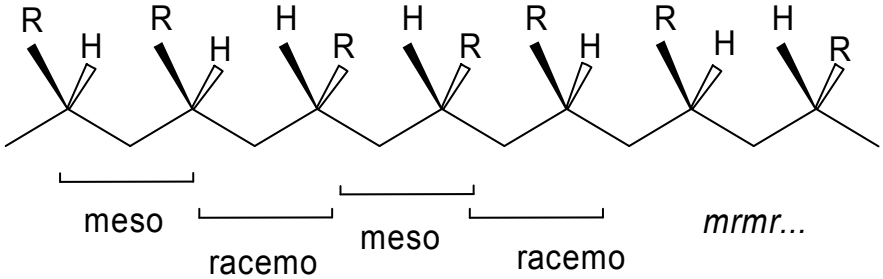


Figure 1.4 : Meso and racemo dyads alternate along the polymer chain in heterotactic placement.

The polymerization of a monosubstituted ethylene, CH_2=CHR (where R is any substituent other than H), leads to polymers in which every tertiary carbon atom in the polymer chain is a stereocenter. The stereocenter in each repeating unit is denoted as C* in **a** and **b**. A stereocenter is an atom bearing substituents of such identity that a hypothetical exchange of the positions of any two substituents would convert one stereoisomer into another. Thus, an exchange of the R and H groups converts **a** into **b** and vice versa. Each such site in a polymer chain can exhibit either of two different configurations, Figure 1.5.

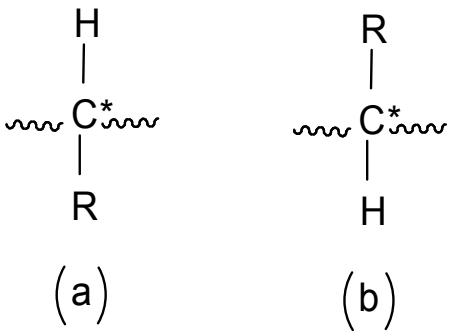


Figure 1.5 : Two different configurations around a stereocenter carbon radical.

Isotactic placement corresponds to meso placement for a pair of consecutive stereocenters. Syndiotactic placement corresponds to racemo placement for a pair of consecutive stereocenters [4].

The pioneering work in the recognition and polymerization of isotactic, crystalline vinyl polymers is due to Ziegler and Natta, who were awarded the Nobel Prize for Chemistry in 1963 [3]. In general, α-olefins such as polypropylene cannot be polymerized by either radical or ionic catalysts. While atactic polypropylene can be produced by the use of Lewis acid or organometalic compound, the product is a branched and rubbery polymer (T_g = -20° C) at ambient temperature with no important commercial applications [2]. On the other hand, isotactic polypropene is a strong, crystalline polymer having a high melting temperature (165°C), which enables it to be used as both a plastic and a fiber [4].

Syndiotactic and isotactic polymers are termed as tactic polymers. Compared to the syndiotactic polymers, isotactic polymers have attracted much more attention due to relatively easy formation and at the same time satisfying the properties that synthesizers desire. On the other hand, heterotactic polymers are found rarely but there exists few examples. For example, heterotactic stereospecific free radical polymerization of N-isopropylacrylamide has been achived [5].

Control of stereochemistry in free radical polymerization reactions has been of interest after Staudinger' findings that the tertiary carbons formed in vinyl free polymerization reactions could have two different stereochemical arrangements, Figure. 1.6 [6].

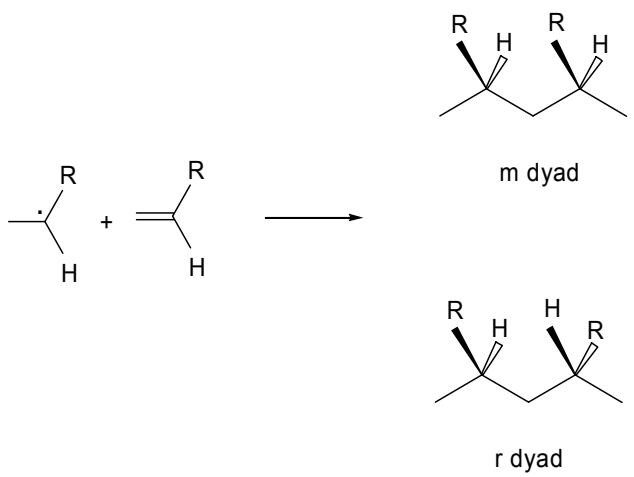


Figure 1.6 : Two different stereochemical arrangements in free radical polymerization of vinyl monomers.

However, most of the polymers produced by free radical polymerization lack tacticity and are mostly atactic polymers. The reason underlying this phenomenon is the structure of the propagating polymer chains which makes it hard to control the stereospecific addition mode of the polymerization reaction because the sp^2-planar or planar-like propagating radical species do not support efficient control of the addition mode compared to the ionic or coordination polymerizations in which the selectivity of the growing polymer can be regulated with electronic interactions with counterion [7]. The difference between the activation barriers for the addition to the diastereopic faces of the radical determines the selectivity of the polymerization but due to the conformational mobility of the chain, the steric interaction between the incoming monomer and the propagating chain stereocenter is overcome [6]. So most of the free radical polymerization reactions produce atactic polymers due to the almost equal possibility for formation of two different stereochemical arrangements.

Experimental works reveal that in order to control the stereospecifity of free radical polymerization, reaction conditions such as the temperature, solvent, monomer/initiator ratio or stereospecifity additives should be regulated since they all affect the tacticity of the polymer.

Tacticity of a polymer has significiant effect on the physical, thermal and mechanical properties of that polymer. Tactic polymers have significiantly distinct properties than atactic polymers because spatial arrangement of the atoms in a molecule influences the morphology of a polymer and determines the amount of crystalline and amorphous regions. Generally tactic polymers (having a regular sequence of relative distrubition of adjacent diads) have higher crystallinity which produce higher glass transition and melting temperatures. For example syndiotacticity increases the glass transition temperature of poly(methyl methacrylate) [2] given in Table 1.1.

Table 1.1 : The effect of tacticity on glass transition temperature of poly (methyl methacrylate).

Tacticity of PMMA	Glass Transition Temperature (° C)
atactic	105
isotactic	45
syndiotactic	115

However atactic polymers are usually amorphous materials. Mechanical properties of a polymer such as tensile strength, stiffness and modulus are also dependent on the tacticity of a polymer. Generally isotactic and syndiotactic versions of a specific polymer is harder, stiffer and tougher than the atactic version. Physical behaviors of a polymer such as solubility is also affected by the tacticity.

Thus, it is a crucial point to control the relative distribution of adjacent monomeric units along the polymer chain.

Stereoregularity of a polymer chain could only be controlled during the polymerization reaction so polymer synthesizers have been working for decades to find the appropriate reaction medium (solvent or stereospecifity inducers), temperature or other factors that could give the desired tacticity of the specific polymer.

Quantum chemical calculations is an advantageous way to study the tacticity phenomenon comprehensively because it enables to explore all of the possible addition modes of the monomer to the propogating radical together with the chance of investigating the effect of any solvent, temperature and stereospecific additives on the tacticity.

In this study, the tacticities of a series of acrylamide monomers'(N,N-Dimethylacrylamide, N-methyl-N-phenylacrylamide and N,N-Diphenhylacrylamide) free radical polymerization are studied to identify the structure-tacticity relationship and reproduce the experimentally declared tacticites of these monomers.

Solvent and temperature effects are also investigated and compared with experimental results. It is known that appropriate additives can be used as stereospecifity inducers.

For DMAAm, the favorable stereopecifity mode of the polymer chain is varied from isotactic to syndiotactic in the absence and presence of tartrate molecules respectively. The effect of tartrates on the addition mode of the monomer to the propogating radical is also studied and reproduced.

The bulkiness of the substituent in acrylamide derivatives determine the favorable addition mode which may lead a polymer to be isotactic, syndiotactic or atactic, Figure 1.7.

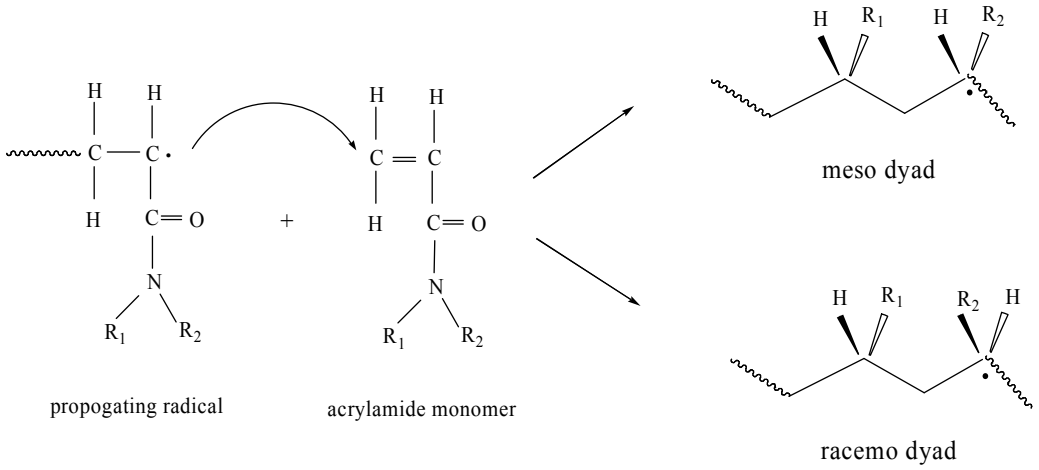


Figure 1.7 : Possible attachements of incoming monomer to the propogating radical in acrylamide derivatives' free radical polymerization.

In this study, experimentally [8,9,10] determined tacticities of DMAAm, MphAAm and DPAAm is reproduced and the effect of bulkiness of the substituent on the stereospecific addition mode (m or r additions) is explained. Clear substituent size effect on the stereospecifity of the polymerization is found as the R groups vary from $-CH_3$ to –phenyl groups for DMAAm, MphAAm and DPAAm monomers respectively. It has been shown experimentally [8,11] that NMAAm gives atactic polymer regardless of the solvent and temperature. The substituent effect on tacticity of free radical polymerization of acrylamide monomers can be summarized in Table 1.2.

Table 1.2 : Substituent effect on the tacticity of acrylamide derivatives [8,9,10,11].

	Substituent Groups		
Monomer	**R_1**	**R_2**	**Tacticity**
NMAAm	H	H	Atactic (m≈r)
DMAAm	CH_3	CH_3	Isotactic (m>r)
MphAAm	CH_3		Syndiotactic (r>m)
DPAAm			Syndiotactic (r>>m)

Also it was shown by our calculations that as the temperature decreases from 0° C to -80° C the content of m and r dyad ratios of DMAAm and MphAAm polymers increase respectively as stated in the experimental results too.

Additionally, a relationship between the solvent polarity and the content of m and r dyads in the polymer chain of DMMAm is constructed and discussed with experimental results.

2. THEORY

All quantum chemical calculations start with solving Schrödinger equation:

$$\hat{H}\Psi=E\Psi \tag{2.1}$$

where $\hat{H}$ is the Hamiltonian operator, Ψ is the wavefunction of the system that has all the information that the system possess, E is the total energy of the system. The Hamiltonian operator includes the kinetic and potential energy terms. Actually the wavefunction depends on both the spatial coordinates of the system (x,y,z) and time at a specific state given in a time-dependent Schrödinger given in equation (1.2) . However time-independent Schrödinger equation is used in quantum chemical problems generally; taken into account that the state of a system does not change with time.

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi \tag{2.2}$$

where ħ is h/2π and h is the Planck' s constant.

The Schrödinger equation has exact analytical solutions for a few problems such as the harmonic oscillator or one-electron systems (e.g .Hydrogen Atom) but when dealing with multielectron and multinuclear systems some approximations should be introduced.

The Molecular Hamiltonian comprises of potential energy term (V) and kinetic energy terms (T) :

$$\hat{H}=T+V \tag{2.3}$$

where;

$$V = \frac{1}{4\pi\,\varepsilon_o} \sum_j \sum_{k<j} \frac{e_j e_k}{\Delta r_{jk}} \tag{2.4}$$

Potential energy term could be written in more detail where the terms are explained as follows.

Explicitly;

$$V=\frac{1}{4\pi\,\varepsilon_o}\left\{-\sum_i\sum_l\frac{Z_l\,e^2}{\Delta r_{il}}+\sum_i\sum_{j<i}\frac{e^2}{\Delta r_{ij}}+\sum_l\sum_{j<l}\frac{Z_l\;Z_j\;e^2}{\Delta R_{ij}}\right\} \quad \textbf{(2.5)}$$

where ε_0 is vacuum permittivity, Z is the atomic number of the atom, e is the charge on the particles, r is the distance between the electrons, electrons and the nuclei, R is the distance between the nuclei. The nucleus of the atoms are regarded as an aggregate charged mass. The potential energy term includes the Culomb attraction between electrons and nuclei, repulsion between electrons and aelectrons and nuclei and nuclei.

The kinetic term includes the kinetic energy of all of the moving particles in x,y,z coordinates with mass m :

$$T=-\frac{h^2}{8n^2}\sum_k\frac{1}{m_k}\left(\frac{\partial}{\partial x_k^2}^{2}+\frac{\partial}{\partial y_k^2}^{2}+\frac{\partial}{\partial z_k^2}^{2}\right) \quad \textbf{(2.6)}$$

Because of the electron-electron repulsion terms in Hamiltonian operator some approximations should be introduced to solve the Schrödinger equation:

2.1 The Born-Oppenheimer Approximation

The nuclear and electronic motions are seperated and treated distinctly with Born-Oppenheimer approximation. It states that the mass of the nuclei is much heavier than the mass of the electron so the nuclei of an atom move very slowly compared to electrons' motions. This leads to the assumption that the positions of the nuclei are fixed and experience the motions of the electrons at fixed coordinates. Then the electronic wavefunction depends on the positions of the nuclei not on the velocity of the nuclei.

The positions of the nuclei are incorporated into the Schrödinger equation as parameters. So Schrödinger equation for electrons are solved seeing the fixed electric potential arising from nuclei; and this prosess is repeated many times to obtain the potential energy surface of the moleculer system.

And then nuclear Schrödinger equation is solved to obtain the vibrational, rotational and translational states of the nuclei.

Since exact solution of the Schrödinger equation is not possible, some methods are developed with some approximations and the way that approaches the chemical problems.

These electronic structure methods could be classified into three groups:

i.Semi Emprical Theory

ii.Ab Initio Theory

iii.Density Functional Theory

2.2 Ab Initio Theory

Ab initio calculations treat the many electron problems by solving the Schrödinger equation without using experimental parameters. The procedure of ab initio calculation is [12]: First, the correct Hamiltonian operator of the system is written; and then a trial wavefunction (Ψ) is constructed, this trial wavefunction has adjustable parameters ; and the energy (E) of the system is minimized according to the equation:

$$E = \frac{\int \Psi^* \hat{H} \Psi dT}{\int \Psi^* \Psi dT} \qquad \textbf{(2.7)}$$

The Variational Principle states that an approximate wavefunction (Ψ) has an energy above or equal to the exact energy of the system. As the wavefunction of a system has adjustable parameters, the calculations are repeated until the best trial function that gives the minimum energy is obtained.

Self-consistent method (SCF) is one of the most performed method within the ab initio calculations [12]. The SCF method aims to find the set of molecular orbitals that give the lowest energy of the system [13]. The wavefunction for a SCF calculation is one or more antisymmetrized product of one electron spin orbitals. Since molecules are made up with atoms the molecular orbitals can be constructed with linear combinations of atomic orbitals (LCAO).

2.2.1 Linear combinations of atomic orbitals (LCAO)

For restricted case of a closed shell single determinal wavefunction, the variatonal method leads to the construction of Hartree-Fock equations [12] ;

$$\hat{F}\phi_i = \epsilon_i \phi_i \tag{2.8}$$

Explicitly;

$$\hat{F}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{\mu} Z_\mu / r_{\mu 1} + \sum_{j=1}^{n} (2\hat{J}_j - \hat{K}_j) \tag{2.9}$$

Molecular orbitals (Q) are eigenfunctions of the Fock operator and Fock operator is hamiltonian operator.

where; F is called Fock operator, Q_i is the molecular orbital, $\mathcal{E}_i$ the eigenvalue, i and j are indices for the N electrons, μ is an index for the N nuclei, J_j and K_j are operators related to the $1/r_{ij}$ in molecular Hamiltonian operator , $\hat{H}$:

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n} \nabla_i^2 - \sum_{\mu=1}^{N}\sum_{i=1}^{n} Z_\mu / r_{\mu i} + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} 1/r_{ij} \tag{2.10}$$

J_j is called 'coulumb operator' because it leads to energy terms corresponding to charge cloud repulsions :

$$\hat{J}_j = \int \phi_j^*(2)\left(1/r_{12}\right)\phi_j(2)d\tau(2) \tag{2.11}$$

K_j is called exchange operator which leads to the formation of exchange integrals:

$$\hat{K}_j\phi_i(1) = \int \phi_j^*(2)(1/r_{12})\phi_i(2)d\tau(2)\,\phi_j(1) \tag{2.12}$$

As a result,

$$\langle \phi_i | \hat{J}_j | \phi_i \rangle = \langle \phi_i(1)\,\phi_j(2)\,|1/r_{12}|\,\phi_i(1)\,\phi_j(2)\rangle = J_{ij} \tag{2.13}$$

and,

$$\langle \phi_i | \hat{K}_j | \phi_i \rangle = \langle \phi_i(1)\,\phi_j(2)\,|1/r_{12}|\phi_i(2)\,\phi_j(1)\rangle = K_{ij} \tag{2.14}$$

Since the Fock operator is itself a function of the MOs Φ and the requirement to find

Φ_i is the *Fock operator* itself and Φ_i is needed to know the *Fock operator ;* an iterative process is utilized and an initial guess is made , MOs Φ. After defining the MOs Φ,the Fock operator is constructed which then leads to the calculation of the new MOs Φ. This process goes on until no significiant change is occured between the two iterative steps.

The orbital energy or a one-electron energy (ε_i) is the energy of an electron in Φ_i . It is the sum of its kinetic energy, the energy caused by the attraction between itself and the nuclei, repulsion caused by the other electrons and exchange energies arised from the other electrons in their electrical charge clouds:

$$\epsilon_i = \langle \phi_i \left| -\frac{1}{2}\nabla_1^2 \right| \phi_i \rangle - \sum_{\mu} \langle \phi_i \left| Z_u / r_{\mu 1} \right| \phi_i \rangle + \sum_{j=1}^{n} \left(2J_{ij} - K_{ij} \right) \qquad \textbf{(2.15)}$$

The inadequate side of the Hartree-Fock SCF calculations is that it does not consider the instantaneous interactions between the electrons. It means that electrons' movement in the molecule interacts with other and they repel to each other and cancel each other's way. But Hartree-Fock approximations sees this effect in an average way which cause the resulting energy deviate 'much' from the correct value. So the term electron correlation must be taken into account to derive a better wavefunction that describes the system. Correlation energy is the difference between the hartree fock energy and the exact energy.

Because of the lack of electron correlation term in the Hartree-Fock calculations, this method is not suitable for modeling the reactions. Hartree Fock geometries and energies for equilibrium structures are in good agreement with experiment often but it is an inadequate method when studying intermolecular interactions or modeling reactions [14].

Post Hartree Fock theories are developed such as Configuration interaction and Moller Plesset Perturbation Theory. These methods extend the Hartree Fock theory by mixing ground state and excited state wavefunctions [13].

2.3 Semi Emprical Theory

Semi emprical methods are relatively inexpensive when compared with the Hartree Fock calculations because they reduce the number of two-electron integrals used

when constructing the Fock matrix [15]. In semi-emprical methods, the experimental parameters and simpler Hamiltonian is used than the correct Hamiltonian. This brings an advantageous situation when dealing with large systems. Semi-emprical theories were developed for conjugated π electron systems first and the most famous semi-emprical π electron theory is the Hückel molecular orbital theory.

Semi-emprical methods start with HF and LCAO approximations resulting in Roothaan-Hall equations [16] Roothaan equations give the energy of an electron in a molecular orbital of the molecule as a function of orbital coefficients [17].

Let an electron(1) occupy a spatial function Ψ_a (1) ;

$$f_1\psi_a(1) = \varepsilon_a\psi_a(1) \tag{2.16}$$

Where f_1 is the fock operator ;

$$f_1 = h_1 + \sum_u \{2J_u(1) - K_u(1)\} \tag{2.17}$$

Where h is the hydrogenic hamiltonian for electron(1), J_u is the coloumb operator and K_u is the exchange operator.

Spatial wavefunctian may be defined as the summation of the orbital ceffcients(c_{ij}) multiplied by M basis functions(θ_j) ;

$$\psi_i = \sum_{j=1}^{M} c_{ji}\theta_j \tag{2.18}$$

yields;

$$f_1 \sum_{j=1}^{M} c_{ja}\theta_j(1) = \varepsilon_a \sum_{j=1}^{M} c_{ja}\theta_j(1) \tag{2.19}$$

and multiplied both sides with θ_i^* and integration over r_1 ;

$$\sum_{j-1}^{M} c_{ja} \int \theta_i^*(1) f_1 \theta_j(1)\, \mathrm{d}r_1 = \varepsilon_a \sum_{j-1}^{M} c_{ja} \int \theta_i^*(1)\theta_j(1)\, \mathrm{d}r_1 \tag{2.20}$$

introducing the overlap matrix (S) and Fock matrix (F) respectively;

$$S_{ij} = \int \theta_i^*(1)\theta_j(1)\,\mathrm{d}r_1 \tag{2.21}$$

$$F_{ij} = \int \theta_i^*(1)f_1\theta_j(1)\,\mathrm{d}r_1 \tag{2.22}$$

As a result a set of M simulteneous Roothaan equations are obtained, given below;

$$\sum_{j=1}^{M} F_{ij}c_{ja} = \varepsilon_a \sum_{j=1}^{M} S_{ij}c_{ja} \tag{2.23}$$

Modern semiemprical methods are based on the MNDO (Modified neglect of differential overlap) approach [18]. In this method, parameters are assigned for different atomic types and are fitted to reproduce properties such as heats of formation, geometrical variables, dipole moments, and first ionization energies. MNDO approximation ignored the differential overlap when the basis functions belong to different atoms [16] AM1 and PM3 methods are the most popular MNDO methods .

Several other semiemprical approximations exist such as the CNDO (Complete Neglect of Differential Overlap) which take into account Slater type orbitals as minimal sets [19] and ZDO (Zero Differential Overlap) which ignores the two electron integrals and simpley the many electron problems [18].

2.4 Density Functional Theory (DFT)

Density Functional Theory is based on Hohenberg Kohn Theorem; states that the ground state electronic energy of a system is a functional of electron probability density (ρ_o) which is function of three variables (x,y,z) :ρ_o(x,y,z).

So all of the molecular electronic proporties and wave function of the ssystem can be calculated from electron probability density [20]. Hohenberg and Kohn showed that there is a relationship between the electron probability density and the external potential [12].

DFT methods aim to form functionals that will connect the electron density with the energy [15]. The wavefunction of a molecular system and electron density are functions whereas the energy is a functional of these functions.

The difference between Hartree-Fock theory and Density Functional Theory is that in HF Theory the wavefunction of a many-electrons system is given in a Slater determinant that is composed of single electron wavefunctions and calculate these wavefunctions by solving Schrödinger equation. However in DFT total electronic energy and the whole electronic density distribution is calculated [14].

The energy functional could be written as the sum of external potential and kinetic energy of electrons and interelectronic interactions :

$$E[\rho(\mathbf{r})] = \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} + F[\rho(\mathbf{r})] \tag{2.24}$$

where E[ρ(**r**)] is the energy functional, ρ(**r**) is the electron density, V_{ext} is the external potential. The first term impiles the interactions of electrons with an external potential, $V_{ext.}$

F[ρ(**r**)] is the sum of kinetic energy of electrons and also interelectronic interactions are incorporated. The minimum energy then corresponds to the ground state electron density.

Using variational approach to minimize the energy,

$$\frac{\delta}{\delta\rho(\mathbf{r})}\left[E[\rho(\mathbf{r})] - \mu\int \rho(\mathbf{r})\, d\mathbf{r}\right] = 0 \tag{2.25}$$

where ;

$$N = \int \rho(\mathbf{r})\, d\mathbf{r} \tag{2.26}$$

denotes that the number of electrons(N) restricting the electon density; μ *is* Langrange multiplier given below;

$$\left(\frac{\delta E[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})}\right)_{V_{\text{ext}}} = \mu \tag{2.27}$$

Kohn and Sham suggested a way to find the $F[\rho(\mathbf{r})]$;

$$F[\rho(\mathbf{r})] = E_{KE}[\rho(\mathbf{r})] + E_{H}[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})] \tag{2.28}$$

where, $E_H[\rho(\mathbf{r})]$ repreent the electron-electron energy(Hartree electrostatic energ) and $E_{XC}[\rho(\mathbf{r})]$ functional represents the exchange and correlation energies and $E_{KE}[\rho(\mathbf{r})]$ represents the kinetic energy of a system of non interacting electrons with the real system's electron density :

$$E_{KE}[\rho(\mathbf{r})] = \sum_{i=1}^{N} \int \psi_i(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \psi_i(\mathbf{r})\, d\mathbf{r} \tag{2.29}$$

So the energy of a N electron system is given as follows;

$$E[\rho(\mathbf{r})] = \sum_{i=1}^{N} \int \psi_i(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \psi_i(\mathbf{r})\, d\mathbf{r} + \frac{1}{2} \int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 \quad \mathbf{r}_2|}\, d\mathbf{r}_1\, d\mathbf{r}_2 + E_{XC}[\rho(\mathbf{r})]$$
$$- \sum_{A=1}^{M} \int \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \rho(\mathbf{r})\, d\mathbf{r} \tag{2.30}$$

The density of a system is given with one-electron orthonormal orbitals ;

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \tag{2.31}$$

The following Kohn-Sham expression is obtained with combining the density with the variational approach;

$$\left\{ -\frac{\nabla_1^2}{2} - \left(\sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{XC}[\mathbf{r}_1] \right\} \psi_i(\mathbf{r}_1) = \varepsilon_i \psi_i(\mathbf{r}_1) \tag{2.32}$$

where ε_i is the orbital energy.

Exchange correlation functional is related to the exchange correlation energy as;

$$V_{XC}[\mathbf{r}] = \left(\frac{\delta E_{XC}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \right) \tag{2.33}$$

Then a self consistent approach which utilizes iteration process is applied to solve equation 2.30. At first the density is guessed and then a set of orbitals is derived. The density value is improved with iterations and iterations go on and calculation comes to an end when the convergence is achieved.

Density Functional methods have been widely used in quantum chemical calculations in a wide range of area. The popularity of this method comes from the fact that it counts for the electron correlation with significiantly less computational cost than the HF methods [17]. It also enables to make calculations on large systems.

2.5 Basis Sets

Basis functions are one-electron functions that are used to construct the molecular orbitals in quantum mechanical calculations. A linear combinations of these basis functions yield the molecular orbitals:

$$\phi_i = \sum_{\mu=1}^{N} c_{\mu i} \chi_{\mu} \qquad \textbf{(2.34)}$$

where φ_i *is* the molecular orbital, χ is the basis functions , $c_{\mu i}$ is the molecular orbital expansion coefficients. The basis set choice is one of the crucial points when proceeding quantum chemical calculations. There are two types of basis functions: Slater type orbitals and Gaussian type orbitals. Gaussian type basis sets dominate the STO because they speed up the calculations.

Several basis sets are developed such as the minimal basis sets (STO-3G, STO-4G and STO-3G$^{*...}$), pople basis sets (3-21g, 6-31g* , 6-31+g* ... ; where * denotes "polarized" , + denotes "diffuse' functions, split valance basis sets [18].

Minimal basis sets use fixed size atomic orbitals [21]. On the other hand, split valance basis sets allow the orbitals to change their sizes. However, polarized basis sets allow to change the shape of the orbitals as they add extra functions on heavy atoms. Diffuse basis functions are chosen if the species have lone pair electrons that are far away from the nucleus [14].

2.6 Methodology

Throughout this study Gaussian 03 software package is used for all of the calculations. Conformer searches and theormodynamic functions such as the Gibbs Free Energy, Enthalpy and Entropy for monomers (DMAAm, MphAAm and DPAAm), monomeric radicals and transition structures were performed with the B3LYP functional at 6-31+G(d,p) level of theory. The reactants (monomer and monomeric radicals) were located as global mimimum structures that are the lowest energy structures along the potential energy surface. In each modelling of the propagating reaction of these three monomers, monomer and monomeric radical were taken as the reactants which then combine and form the dimeric chain. Methyl group is attached to the monomer to generate the monomeric radical which may be thought as the growing chain. All propagating reactions were modelled with the most stable monomer and monomeric radical because in each case they would give the most stable transition structures for both isotactic (m dyad) and syndiotactic (r dyad) stereospecific addition modes. In order to ensure that the transition structures that were found actually connect the reactants and the products on the reaction pathway, IRC (Intrinsic Reaction Coordinate) calculations were performed. Intrinsic reaction coordinate is the minimum energy path that can be thought as a classical particle sliding downhill with infinitesimal velocity from the transition state to each of the minima that corresponds to reactants and products [20].

To show the solvent effect on the tacticities of DMAAm, MphAAm and DPAAm free radical polymerizations, the optimized geometries for the gas phase were considered and all the structures located on the reaction coordinate were subjected to solvent medium without changing the optimized geometries. For this purpose Single Point Energy Calculations were done with B3LYP functional at 6-31+G(d,p) level of theory. IEF-PCM (Integral Equation Formalism-Polarizable Continuum Model) is used as a Solvation model. This model is a SCRF (Self Consistent Reaction Field) method which models the solvent as a continuum of uniform dielectric constant by creating the solute cavity as a set of overlapping spheres. Necessary parameters that define the solvent accurately such as the solvent density, solvent radius, Eps (static dielectric constant of a solvent) are defined. As long as the dielectric constant of a solvent determines the polarity of a solvent, solvent polarity effect on the rate of

propagation could be determined from the corresponding energy of the system in various solvents.

The optimization of a molecule is started with an initial geometry which is defined with the bond angle, dihedral angle and the bond distance and drawn as the input structure. The coordinates of the atoms in each structure is given as the only defined parameter. For the conformer searches, many input structures having different defined coordinates are prepared and optimized to be able to get the global minimum structure on the potential surface of the molecule. Then the electronic energies which are obtained from the optimization calculations and the Gibbs Free Energies that are obtained from the frequency calculations are compared and the least energetic structures are considered as the reactants and the transition state structures. The overall procedure can be seen in detail in Figure 2.1 [22].

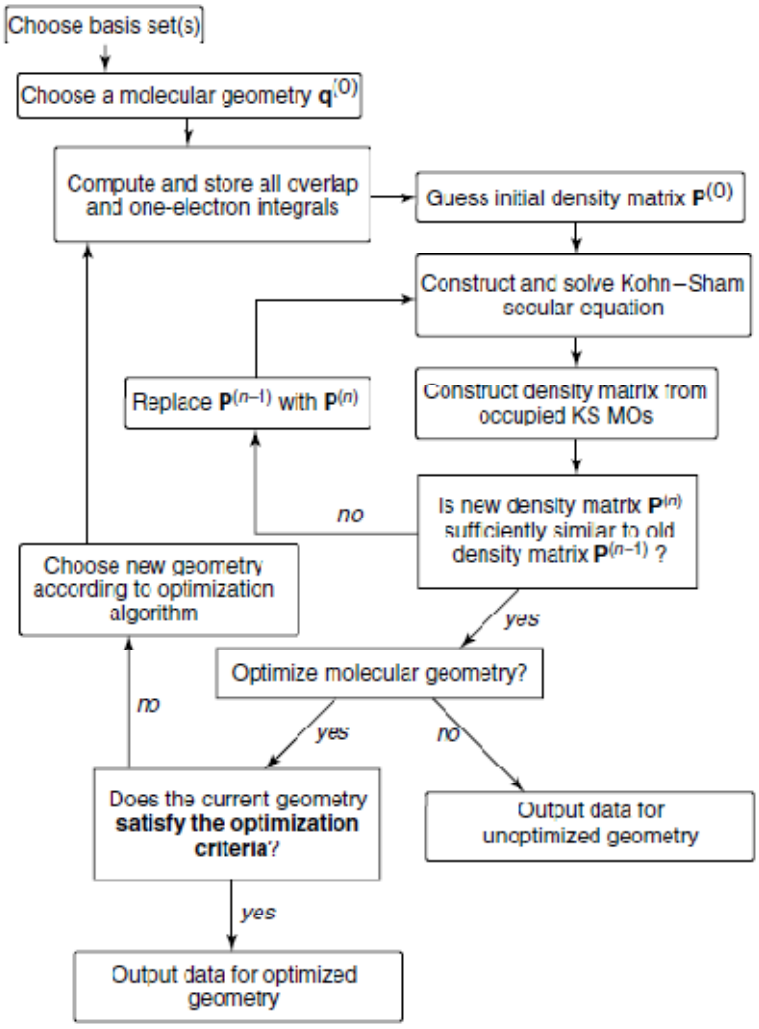


Figure 2.1 : Flow chart of the DFT calculation implemented in this study for the optimization of the species [22].

3. RESULTS AND DISCUSSION

In the free radical polymerization, the propagating radical attacks to the monomer, breaks the C=C double bond of the monomer and the new monomer is added to the propogating chain. The second monomer repeats the same process and this chain growth goes on until some termination reactions occur (Figure 3.1).

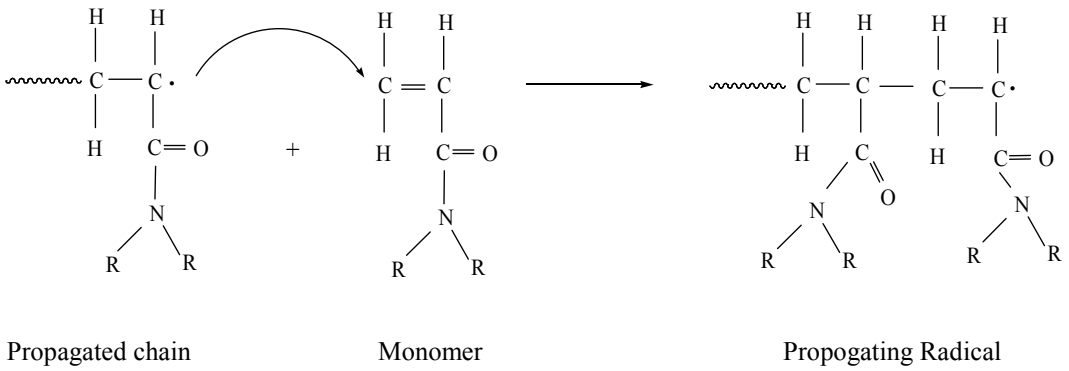


Figure 3.1 : Chain propagating reaction in free radical polymerization of vinyl monomers.

While modeling this radical polymerization, CH_3 radical added monomer is used as a representative propagating chain which then sequentially adds monomer and goes on growing. For this purpose methyl group is attached to the monomer to generate the monomeric radical. Additionally, propogation reactions are modelled according to the head-to-tail regioselective placement (Figure 3.2).

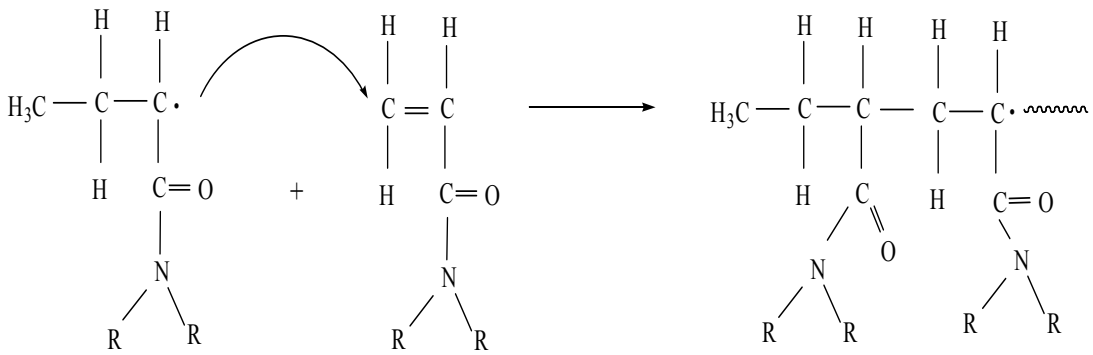


Figure 3.2 : Model chain propagation reaction.

There are three possible different regioselectivites in monosubstituted vinyl polymers given in Fig.3.3. Among these attachements head to tail placement is the most dominant one due to steric effects, resonance effects and inductive effect [4,23,24,25]. Steric effects arise when a propogating radical approaches the monomer, and in the case of head-to-tail attachement, the steric hindrance between the monosubstituted carbon and monomer are reduced compared to the head-to-head approach. Resonance effects give rise to a stabilization of 'a' structure rather then 'b' structure because 'a' structure can be stabilized by the resonance effects of the substituent group since it is bonded to the carbon atom with an unpaired electron.

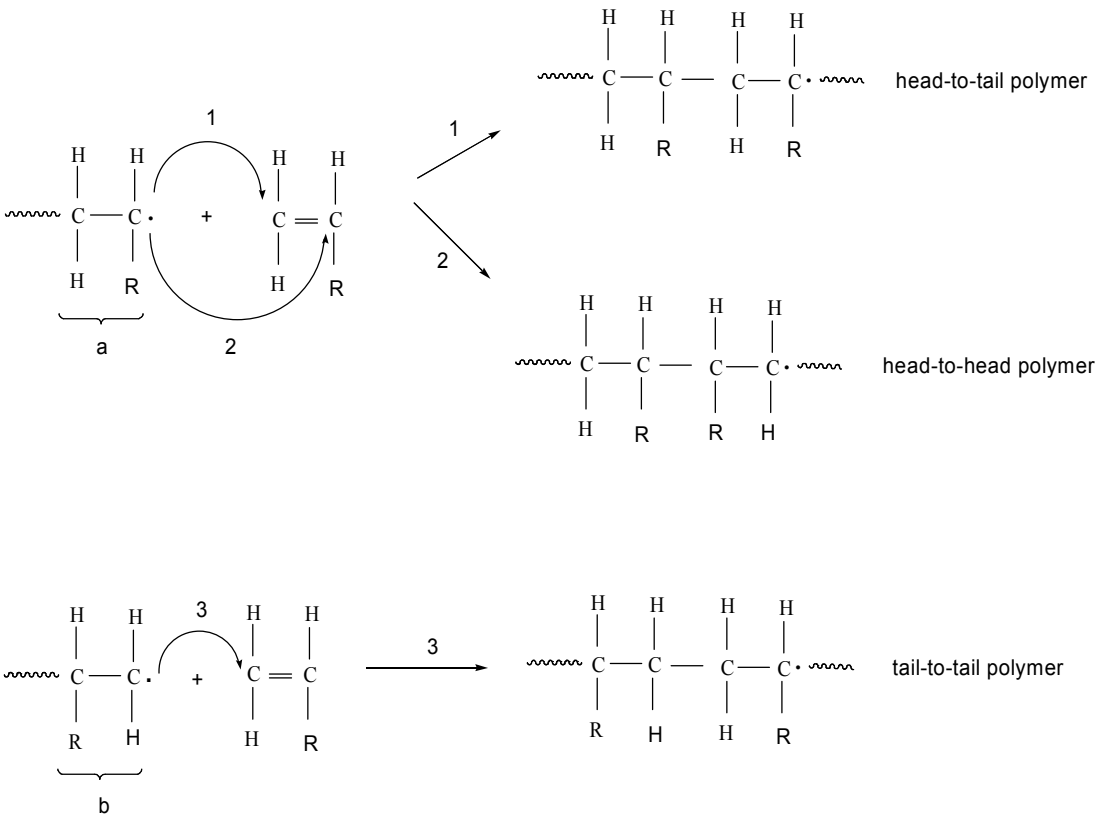


Figure 3.3 : Regioselectivity in monosubstituited vinyl polymers.

In the course of our study, ''terminal model'' is considered to reproduce the substituent, solvent and temperature effect on the tacticities of DMAAm, MphAAm and DPAAm monomers as propagation reactions are modeled at dimeric stage. In terminal model, side reactions are assumed to be not significiant and the propagation reaction kinetics is only affected by the terminal unit of the polymer radical and the nature of the monomer [26].

3.1 Stereospecific Free Radical Polymerization

Tacticity refers to the stereospecific addition of the monomer to the propagating chain. Two different modes of addition is possible in monosubstituted vinyl monomers. One of them leads to a formation of m dyad and the other to r dyad.

Tertiary carbon atom denoted as C* in the polymer chain is a stereocenter and a site of steric isomerism which means that if hydrogen atom and the substituent replace their places with each other in the structure "a", it would give the structure "b". These structures have enantiomeric relationship. They have the same atom placement and the same bonding sequence but their orientation in space is different. This site of steric isomerism leads to the possibility of formation of two kinds of configurational base units (1 and 2) along the polymer chain given in Figure 3.4.

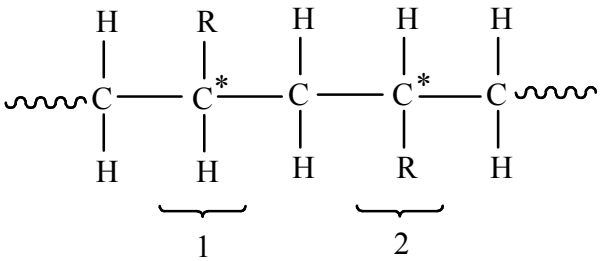


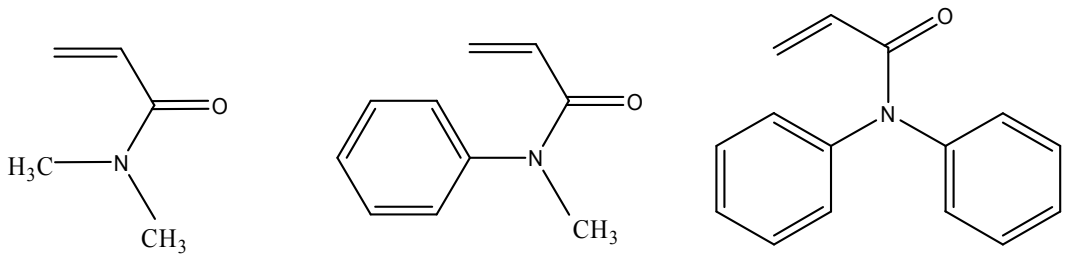
Figure 3.4 : Two different configurational base units in the monosubstituted vinyl monomers.

In isotactic polymers (mmmm…), all of the configurational base units are all identical along the polymer chain. However, in syndiotactic polymers (mrmrmr…), configurational base units are located alternately along the main chain.

To measure the tacticity of a polymer chain, one has to look at the two adjacent configurational base units which form dyads. There are two possible dyad formations. A meso (m) dyad contains two identical adjacent configurational base units; whereas a racemo (r) dyad contains the two alternate configurational units.

In this work, in order to identify the mechanism of stereospecific propagation of the polymer chain, possible addition modes of the propagating radical to the monomer at dimeric stage was considered and all possible conformers for monomer, monomeric radical and transition structures were searched to find the most favorable addition mode which could either be r dyad leading to a syndiotactic polymer or m dyad leading to an isotactic polymer.

Calculations in this work aim to shed light on the reasons of the stereospecific addition modes, bring a detailed perspective of the mechanism of stereospecific free radical polymerization of DMAAm, MphAAm and DPAAm monomers given in Figure 3.5 and reproduce the substituent, solvent and temperature effect on tacticity.



N,N-dimethylacrylamide (DMAAm) | N-methyl-N-phenylacrylamide (MphAAm) | N,N-diphenylacrylamide (DPAAm)

Figure 3.5 : N-substituted acrylamide monomers discussed in this study.

3.2 N,N-Dimethylacrylamide (DMAAm)

In an experimental work [9] free radical polymerization of DMAAm was conducted in toluene at low temperatures in the absence and presence of tartrate molecules. The stereoregularity of the polymer chain was determined for both situations. It was shown that isotactic rich polymer (m dyad) is obtained in the absence of tartrates whereas syndiotactic rich polymer (r dyad) is obtained in the presence (Table 3.1). Additionally, temperature was found to have an effect on the m and r dyad ratios.

Table 3.1: Experimental results [9] for stereospecific free radical polymerization of DMAAm in the presence and absence of tartrates.

Added Tartrate	**Temperature (°C)**	**m**	**r**
None	-80	73	27
L-EtTar	-80	37	63

Activation parameters [9] for isotactic and syndiotactic propagations found by experimentalists for DMAAm free radical polymerization in the absence and presence of L-EtTar are given in Table 3.2.

Table 3.2: Experimental [9] activation parameters (Enthalpy and Entropy) for stereospecific free radical polymerization of DMAAm.

Added Agent	$\Delta H^{\ddagger}_{i} - \Delta H^{\ddagger}_{s}$ (kcal/mol)	$\Delta S^{\ddagger}_{i} - \Delta S^{\ddagger}_{s}$(cal/mol)
None	-0.68±0.03	-1.53±0.14
L-EtTar	0.71±0.03	2.27±0.14

The induction of the isotactic or syndiotactic specificity was attributed to the conformationally limited propogating radicals and also to the extent of hydrogen bonding between tartrates and monomeric units such that it was found to increase the syndiotacticity of the obtained polymers.

In this study, polymerization reaction is modelled both in the absence and presence of tartrates.

3.2.1 Without tartrates

In order to model the free radical polymerization of DMAAm, reactants and transition structures should be located on the reaction coordinate. For this purpose conformer search was performed for DMAAm monomer and DMAAm monomeric radical to find the most stable structures. Optimized geometries of the two conformers of each species can be seen in Table 3.3.

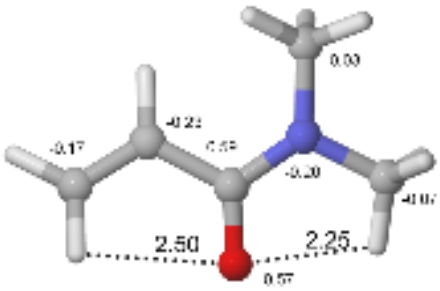
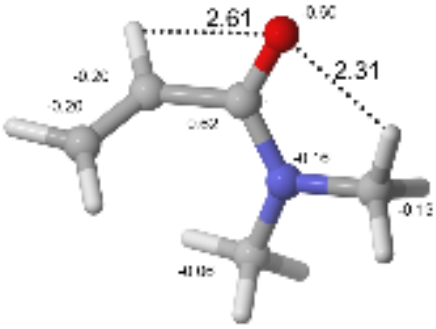
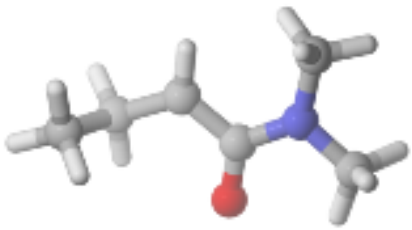
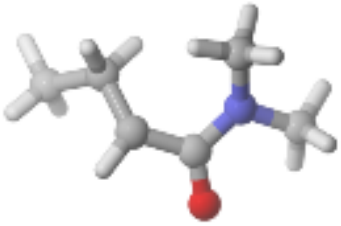
Energetically stable conformer has a planar form with C=O and C=C groups cis to each other as expected for acrylamides [27,28].

Propagation reaction is modelled at dimeric stage considering the most stable monomer (DMAAm-s-cis) and the radical conformer (DMAAm-rad-cis).

Two different configurations may occur in the polymerization reaction of DMAAm.

The relative position of the substituents of the propagating radical and the newly coming monomer determine the specific addition mode (Figure 3.6).

Table 3.3: Relative Electronic and Gibbs Free Energies (in paranthesis) and Enthalpies (in italics) at 25 °C of DMAAm monomer and DMAAm monomeric radical conformers (given in kcal/mole), dipole moments of two monomer conformers given in debye (in bold) and ESP charges on atoms.

 DMAAm-s-cis 0.0 (0.0) *0.0* **3.8374**	 DMAAm-s-tr 1.88 (2.25) *1.77* **4.0407**
 DMAAm-rad-cis 0.0 (0.0) *0.0*	 DMAAm-rad-tr 3.50 (4.31) *3.41*

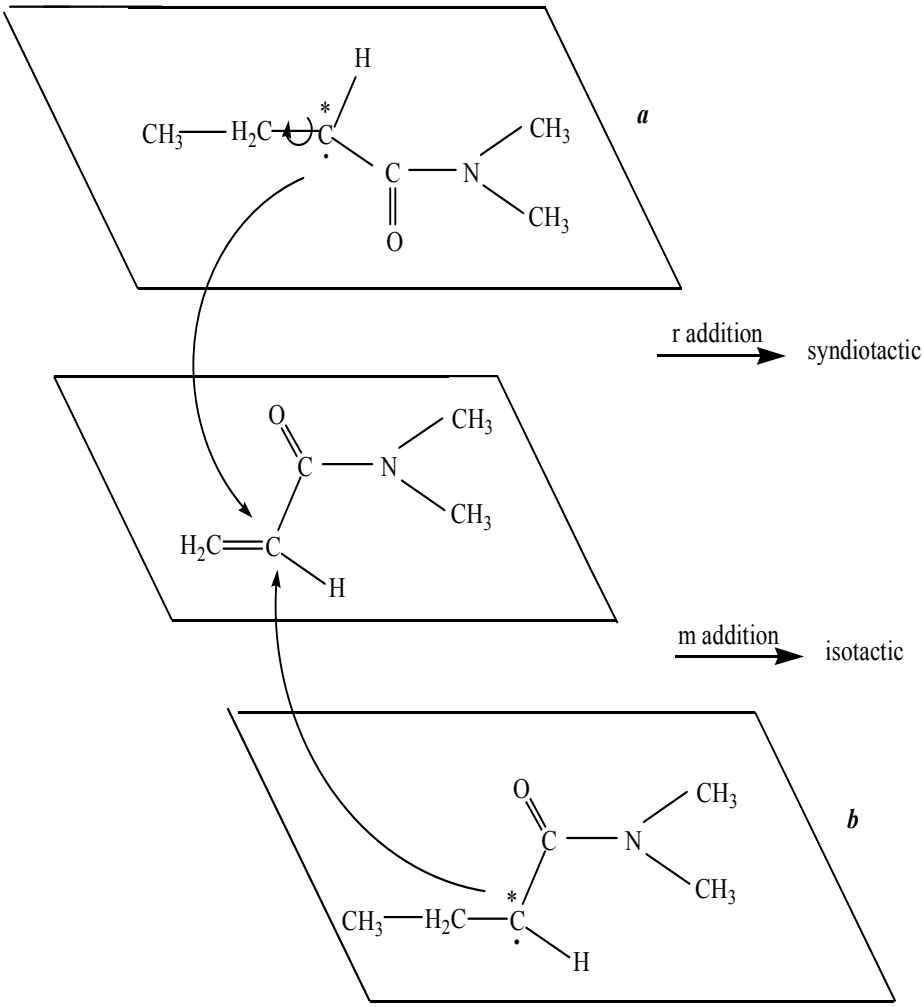
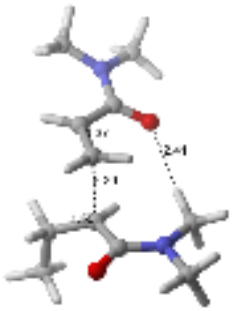
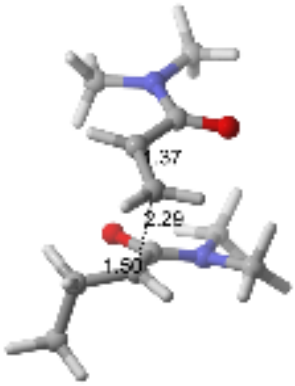
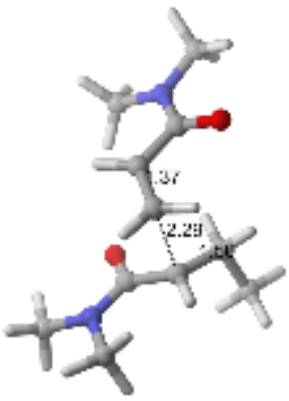


Figure 3.6 : Syndiotactic and isotactic addition for stereospecific radical polymerization of DMAAm.

In this study, tacticity of DMAAm is evaluated by constituting the possible m and r dyads at dimeric stage. Diads are formed with the monomer and the monomeric radical. The transition structures belonging to all addition modes of m and r dyads are formed; Electronic and Gibbs Free Energies of the transition structures are calculated to decide the more favorable addition mode. Among the transition structures located, the most stable two are obtained with DMAAm-s-cis and DMAAm-rad-cis species given in Table 3.4.

The monomeric radical attacks to the monomer in a gauche fashion in the case of m dyad formation (in transition state structure DMAAm-ts-iso1) as expected for most isotactic polymers due to steric repulsions between the substituent of the monomer and the substituent of the ultimate monomeric unit of the propagating radical.

Table 3.4: Relative Gibbs Free Energies and Enthalpies (in italics) at 25 °C and Electronic Energies (in paranthesis) of the most stable transition structures for syn and iso addition of DMAAm polymerization given in (kcal/mole).

Syn addition	Iso addition
 DMAAm-ts-syn-1 0.79 (1.00) *1.02*	 DMAAm-ts-iso-1 0.0 (0.0) *0.0*
 DMAAm-ts-syn-2 1.80 (1.34) *1.40*	 DMAAm-ts-iso-2 2.22 (1.31) *2.19*

However, in the case of r dyad formation a trans conformation of the backbone (as in DMAAm-ts-syn1) of the polymer chain, leading to a torsion angle of nearly 180° for the backbone may be preferred since this conformation allows the occurence of the critical intermolecular interactions between the monomer and the newly formed

radical substiuents' atoms which adds stabilization of the species and thus lowers the electronic energy.

For example a theoretical study [29] denotes that in the free radical polymerization of methyl acrylate and methyl methacylate, the global minima of MA and MMA transition structures on the potential energy surface of the reaction for isotactic dimeric radical of the MA and MMA are gauche (with θ=49.60°, θ=49.88 °, respectively) with the local minima are again gauche (with θ=-50.70°, θ=-71.63, respectively). On the other hand, for syndiotactic addition, the most favorable dimeric radical for MA is trans with a torsion angle of 176.83; whereas for MMA the backbone prefers gauche (θ =60.13) conformation as in the isotactic addition.

Another work [30] conducted both experimentally and with a DFT calculation shows the same pattern as in MA and MMA polymerization. In this work Poly (N-isopropylacrylamide) prefers r dyad formation over m dyad; having the trans conformation being more favorable over gauche in the case of syndiotactic addition; however the polymer backbone chain prefers gauche fashion when it gives isotactic dimer.

Gauche addition is the most favorable addition mode in the free radical polymerization in most of the cases. For example, the addition of n-alkyl radicals to ethylene is studied with ab initio calculations [31] and as a result of these calculations gauche addition is found to be favored over trans conformation. Another quantum chemical calculations on the addition of gamma-substituted propyl radicals to various alkenes show that the lowest energy transition structures are the conformations with gauche attachements and this is attributed to the stabilizing effect of the gamma substituent when it is close the monomer substituent and unpaired electron [32]. The methyl acrylate and vinyl acetate free radical propagation reaction is studied at dimeric stage theoretically [33] and shown that the gauche addition gives the global minimum transition state structures for both monomers in which hydrogen bonding is playing critical role in stabilizing the crowded conformation in gauche additions.

Similiar effects on the steresoselectivity of free radical polymerization of the methyl acrylate, methyl methacrylate and N-isopropylacrylamide monomers are shown in the literature [29,30,34,35].

The importance of hydrogen bonding interaction effect on stabilizing poly(N-isopropylacrylamide) is pointed out; such that the intramolecular interaction between C=O and H-N groups determine the conformation (in this example it is helical structure) of the main chain of the polymer and also it is shown that the dimers having intramolecular hydrogen bondings are more stable than the ones which don't have when the backbone of the polymers have the same conformation [34,35].

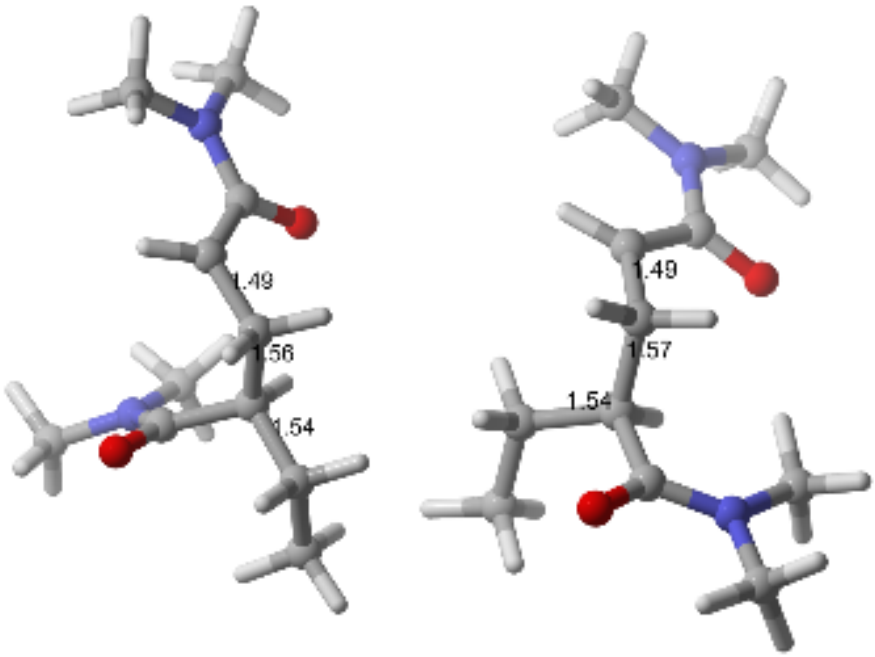
So, the substituent effect (including the bulkiness, interactions such as hydrogen bonding and steric repulsions between the substituent of the newly coming monomer and the ultimate substituent groups) determines the conformation of the backbone and also the configuration of the addition mode which may be meso (m) or racemo(r) .

In this study, same kind of interaction could be observed for both isotactic and syndiotactic additions. In both type of additions, it is observed that the H-bonding between the monomer oxygen and the radical's methyl hydrogen is playing a crucial role in the determination of stereoregularity.

There are two kinds of competative addition modes in the polymerization reaction medium (Figure 3.7). Generally in free radical polymerization of vinyl monomers, the activation barriers between isotactic and syndiotactic additions are small which allows the two kinds of additions in the reaction medium. In this study, it is found that the two polymeric products have different possibilities of formation being in favor of isotactic product (DMAAm-iso-product) over syndiotactic product (DMAAm-syn-product) depicted in reaction profiles in Figure 3.8.

The calculations in this work confirm the presence for the experimentally observed the favorable isotacticity over syndiotacticity in free radical polymerization of DMAAm.

Two competative propagation reactions are both possible in the reaction medium. The relative energies of the transition state structures, pre-reactive complexes and products can be seen in the reaction profile (Figure 3.8) for these two types of addition modes. The reactions of the addition modes (syn and iso) start with the same monomer and monomeric radical. But the propagation rate of these two different additions are different in the reaction medium.



DMAAm-syn-product DMAAm-iso-product

Figure 3.7 : Competative isotactic and syndiotactic dimeric products in free radical polymerization of DMAAm.

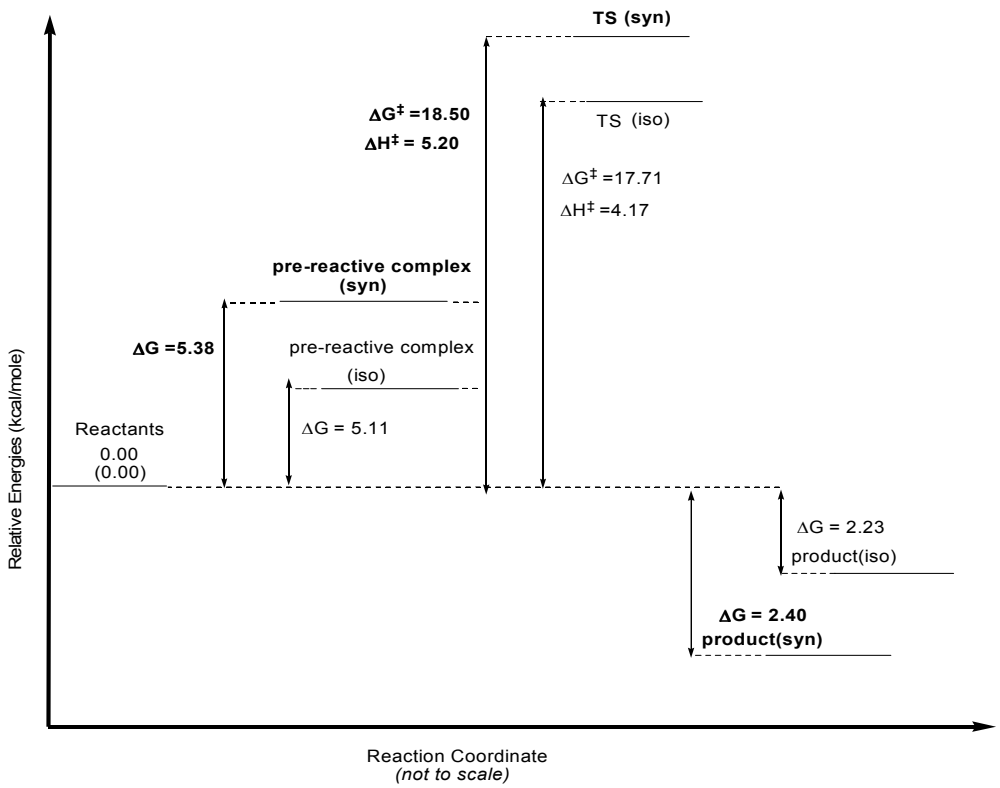


Figure 3.8 : Reaction profiles for DMAAm-ts-iso-1 and DMAAm-ts-syn-1 additions in gas phase.

3.2.2 With tartrates

Different tartrate molecules (diethyl L-tartrate, diisopropyl L-tartrate and di-n-butyl L-tartrate) were used as a syndiotacticity inducer in free radical polymerization of DMAAm in toluene at temperatures ranging from 0°C to -80°C by Hirano et al [9]. In the experimental study [9], it was proposed that there exists a complex formation between tartrate molecules and the monomeric species through hydrogen bonding interaction between the carbonyl oxygen of the DMAAm monomer and the hydroxyl hydrogen of the tartrate. This complex formation effects the favorable addition of the monomer to the propogating chain and turns the situation in favor of r dyad formation. Three possible complexes were proposed to form between the monomer and the tartrate (Figure 3.9).

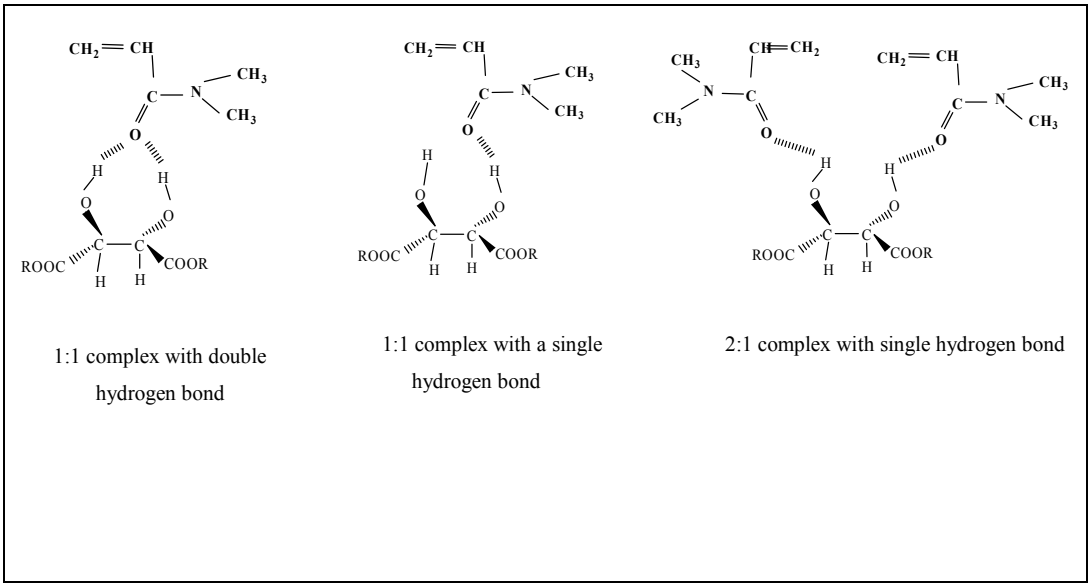
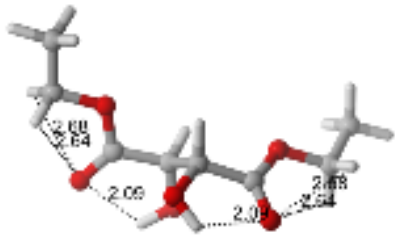
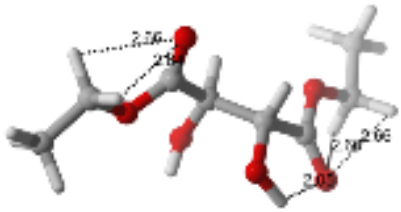


Figure 3.9 : Possible complex formations of DMAAm and tartrate.

According to the reaction stoichiometry, 2:1 complex of tartrate and the monomer was excluded. Among the two 1:1 complex structures, the one with double hydrogen bonds was assumed to be energetically favorable because the two hydroxyl hydrogens would prefer to make two hydrogen bonds rather than the complex structure with one H-bonding. In the favorable 1:1 structure, hydroxyl groups are located on the same side in the tartrate conformation so that formation of two hydrogen bondings is allowed.

In our study, to show the effect of tartrates on the stereoregularity of the polymer chain, conformational analysis of tartrate and tartrate-monomer complexes were done. In Table 3.5, the two most stable conformers of ethyltartare are shown.

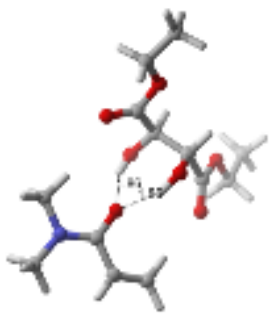
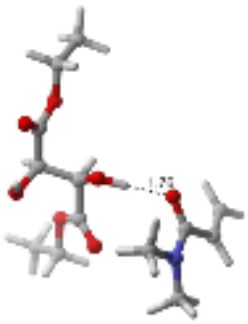
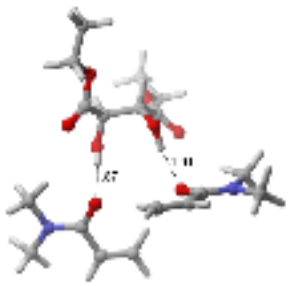
Table 3.5: Relative Electronic (in paranthesis) and Gibbs Free Energies at 25 °C of the two lowest energy tartrate conformers (given in kcal/mole).

	
(0.0) 0.0	(1.14) 1.24

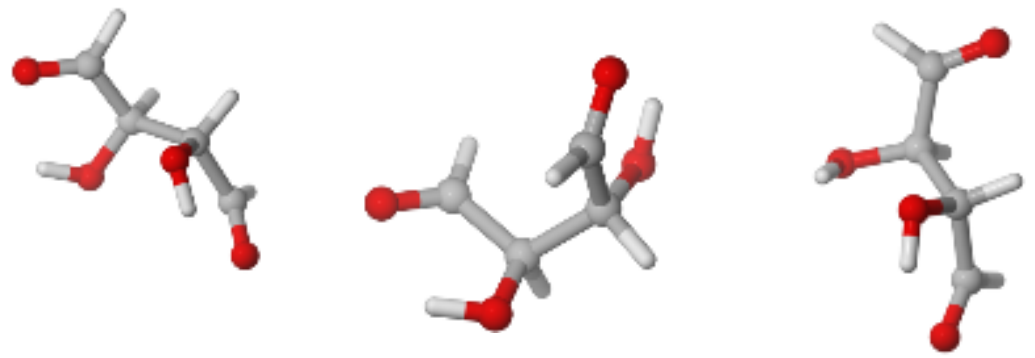
In the lowest energy conformer, there are two hydroxyl groups located on the same side with two intramolecular hydrogen bondings that provide an extra stabilization to this conformer. This result is in agreement with the predictions of the experimental work [9] and also other works conducted by Polavarapu [36] and Buffetau [37].

From the minimum energy conformer of ethyltartrate, monomer-tartrate complexes are modelled. The minimum energy structures for possible complexes are shown in Table 3.6.

Table 3.6: Relative Gibbs Free Energies at 25 °C and Electronic Energies (in paranthesis) of monomer and tartrate complexes (given in kcal/mole).

		
0.0 (0.61) Model A	0.74 (2.58) Model B	8.08 (0.00) Model C

Model C is slightly more favorable (0.61 kcal/mole) than model A and model B in terms of electronic energy but when entropy effects are included, model A is more favorable in terms of Gibbs Free Energy. One monomer and two tartrates coming together to form a complex by two hydrogen bonds between the tartrates and the monomer is entropically unfavored, thus, this is reflected in higher Gibbs Free Energy value of that complex. Polymerization reaction propagates as tartrate molecules form complexes with monomeric units. Thus, Model A and the radical form of model A are considered in modelling the propagation reaction of free radical polymerization in the presence of tartrates. At this stage, due to the necessity of saving time and computer resources, a model of ethyltartrate has been used in calculations, where $-OCH_2CH_3$ parts has been replaced with a proton. The minimization was done in a way that the critical points (e.g. hydrogen bonds) of the geometries were kept still. The most stable three conformers of model tartrate molecules are depicted in Figure 3.10.



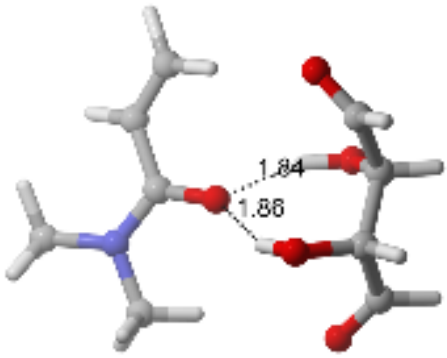
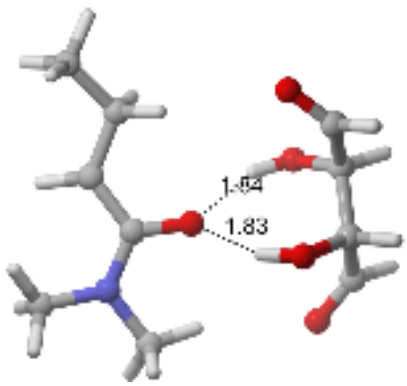
Tartrate1	Tartrate2	Tartrate3
0.14 (0.00)	0.00 (0.18)	0.33 (0.34)

Figure 3.10 : Relative Gibbs Free Energies (in paranthesis) and Electronic Energies of minimized ethyltartrates (given in kcal/mole).

In the ethyltartrate, the –OH groups are anti to each other, thus the monomer and the tartrate complex is formed from DMAAm-s-cis and Tartrate 1 where -OH groups are anti to each other (Table 3.7).

The most favorable iso and syn additions are obtained from DMAAm_complex and DMAAm_rad_complex (given in Table 3.8).

Table 3.7: The minimized A complex.

	
DMAAm_complex	DMAAm_rad_complex

Syndiotactic addition is favored over isotactic addition in the free radical polymerization DMAAm in the presence of tartrates as seen in reaction profiles obtained with DMAAm-ts-complex-syn1 and DMAAm-ts-complex-iso1 in Figure 3.11.

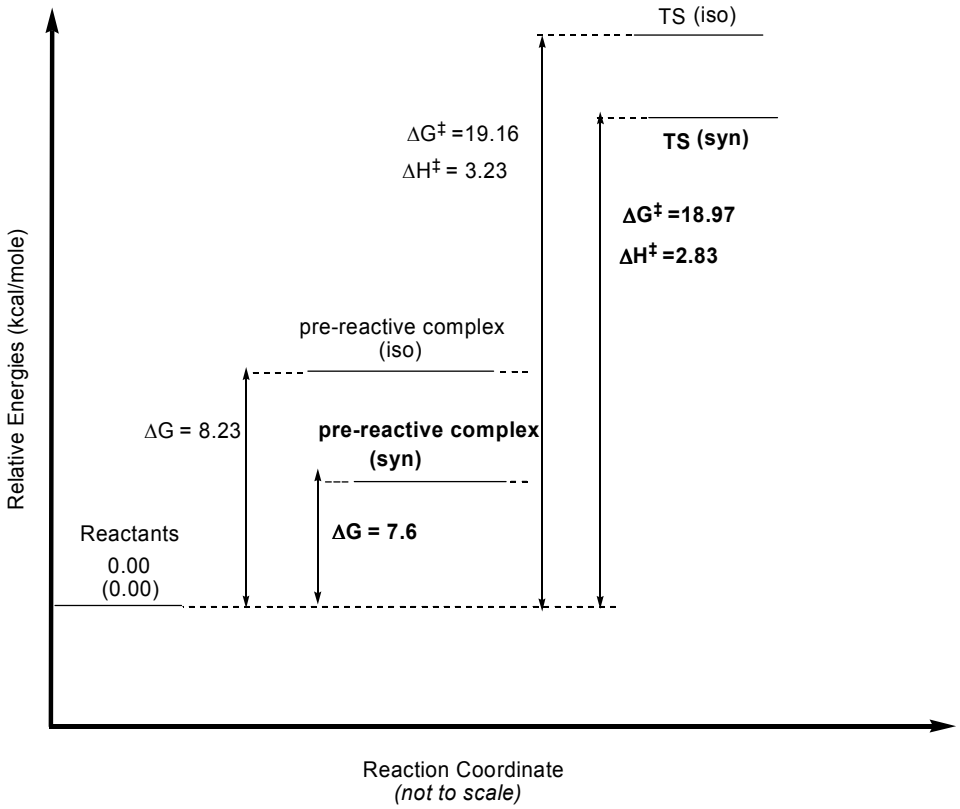
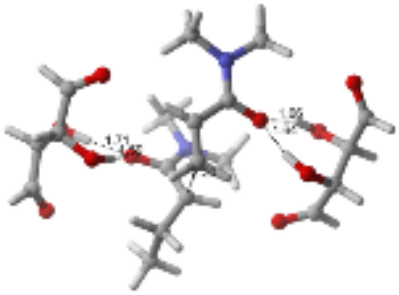
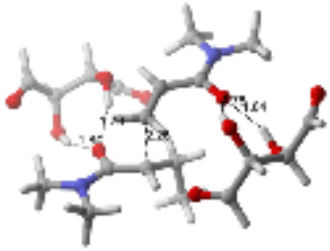
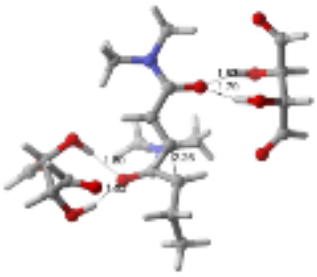
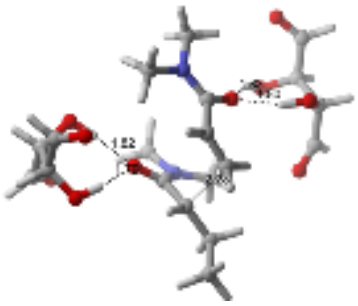
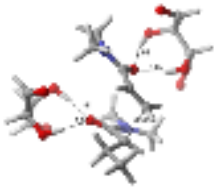


Figure 3.11 : Reaction profiles of DMAAm-ts-complex-syn1 and DMAAm-ts-complex-iso1.

Table 3.8: Relative Electronic Energy, Enthalpy (in italics) and Gibbs Free Energies (in paranthesis) at 25 °C of iso and syn additions in the presence of model tartrate (given in kcal/mole) and diheadral angles *(θ)* of the main chain (-CH_2 - CH - CH_2 – CH-).

SYN ADDITION	**ISO ADDITION**
	
DMAAm-ts-complex-syn1 0.00 (0.00) *0.00* *(θ = -152.97°)*	DMAAm-ts-complex-iso1 0.34 (0.18) *0.40* *(θ = 23°)*
 DMAAm-ts-complex-syn2 0.19 (0.99) *0.25* *(θ = -140.31°)*	 DMAAm-ts-complex-iso2 3.78 (4.06) *3.65* *(θ = 174°)*
 DMAAm-ts-complex-syn3 1.54 (2.01) *1.35* *(θ = -64°)*	

Syn addition is more favored than the iso when tartrates are present in the reaction system. The m/r dyads ratios are found to be 37/63 at -80°C in toluene in the experimental study [9]. Without the tartrate, in the syn addition, the $CON(CH_3)_2$ groups are trans to each other whereas in the isotactic addition, gauche to each other. In the presence of tartrates, the backbone of the polymer does not change in the syn addition because the anti conformation of the backbone of the polymer chain let the tartrates approache to the substituents from the monomer and radical side enable the formation of double hydrogen bonding between the tartrates and monomeric species. In the iso addition, the $CON(CH_3)_2$ groups are synperiplanar (23°) to each other. The gauche orientation of the bacbone in the presence of tartrates do not reveal a sterically free geometry as shown in Fig.3.13. The tartrate groups cause steric hindrance at such a conformation depicted in Figure 3.13. So the methyl group is located in such a manner that tartrates have enough free space to approach and interacts with the substituents' oxygens. The comparison of electronic energy and gibbs free energy of the DMAAm-ts-complex-iso1 and the gauche version (Figure 3.12) of the backbone of this transition structure is given in Table 3.9.

Table 3.9: Comparison of the DMAAm-complex-iso-ts1 and DMAAm-complex-iso-gauche (given in kcal/mole).

	Electronic Energy	**Gibbs Free Energy**
DMAAm-complex-ts-iso1	0.00	0.00
DMAAm-complex-iso-gauche	3.76	4.74

Hydrogen bonding is an important interaction and many times utilized to achieve the control of stereospecifity of acrylamide derivative monomers free radical polymerizations [5,38-45].

The stereospecificity in free radical polymerization of various monomers in the presence or absence of added additives was reported to be induced with conformational limitation near the propagating chain –end through H-bonding

interaction or by the steric repulsion of the monomer binding near the propagating chain end.

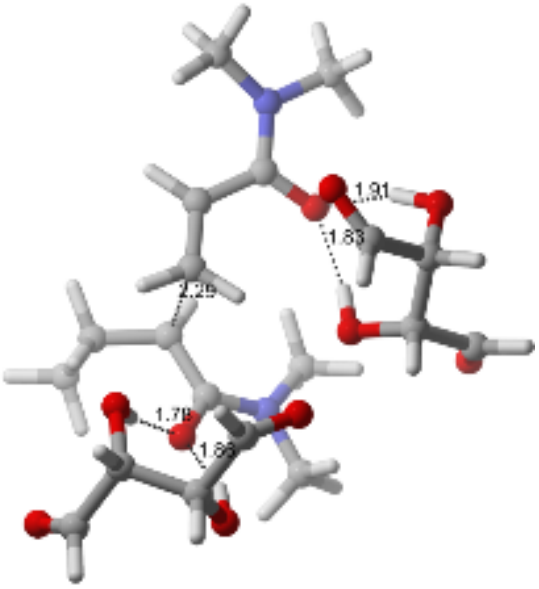


Figure 3.12 : The transition structure of DMAAm-complex-iso-gauche.

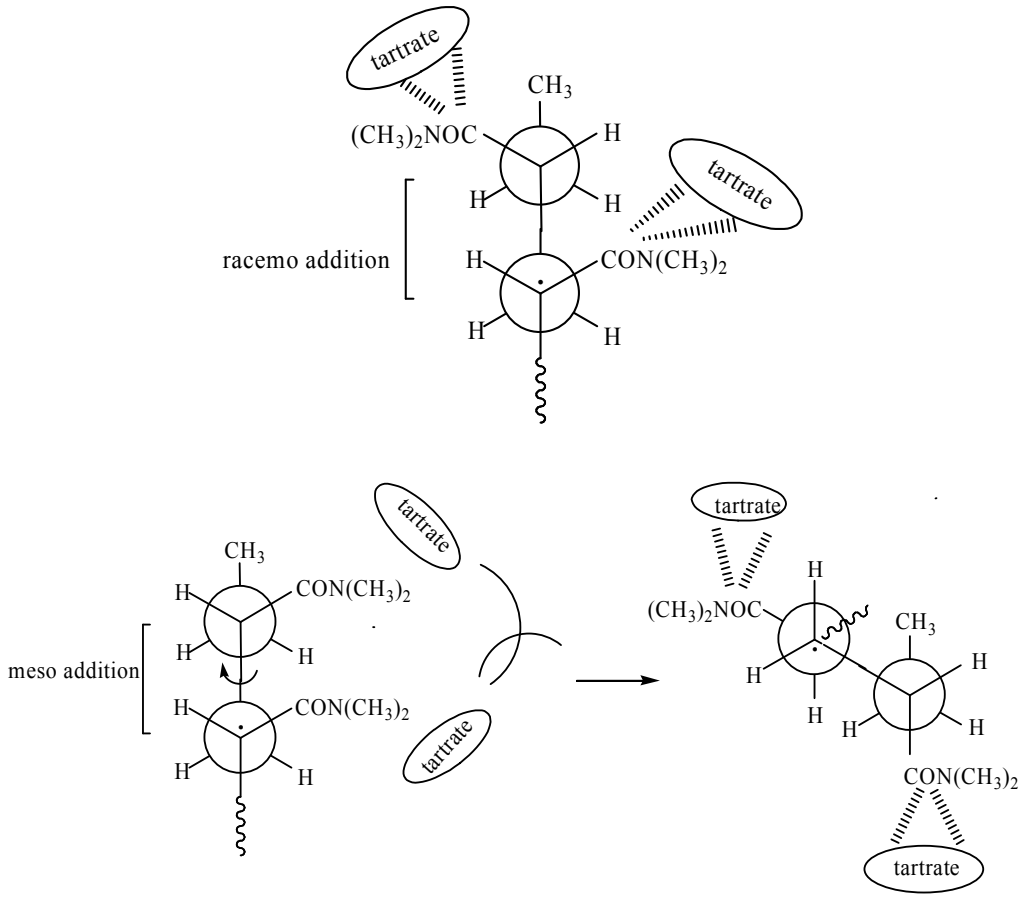
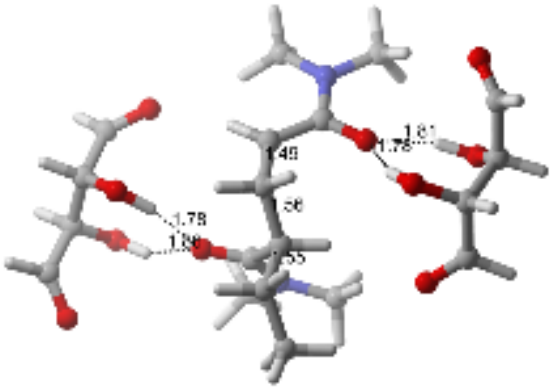


Figure 3.13 : Tartrate effect on the conformation of the main chain of poly(N,N-dimethylacrylamide).

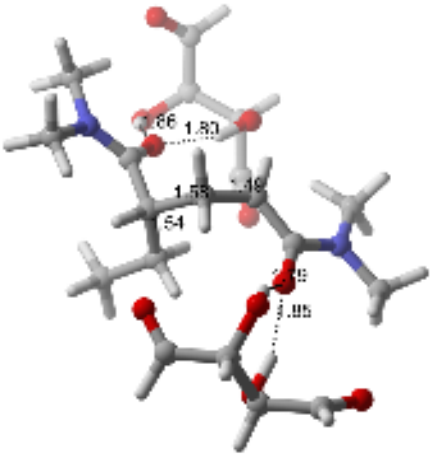
In our study, the effect of stereospecifity inducer (tartrate) on the propogation step of N,N-dimethylacrylamide free radical polymerization through hydrogen bonding is reported and reproduced.

The competative polymeric propagating radicals in reaction medium are shown in Figure 3.14 and the results of our calculations are summarized and compared with experimental results in Table 3.10.

Our results reproduce the experimental results [9] and gives the same trend that the polymer chain propagation assumes syn addition more favorable than the iso addition in terms of enthalpy of activation.



DMAAm-complex-syn-product



DMAAm-complex-iso-product

Figure 3.14 : Two competative dimeric propagating radical in free radical polymerization of DMAAm in the presence of tartrate.

Table 3.10: Activation parameters for propagation reaction in free radical polymerization of DMAAm in the presence of tartrates.

	Experimental Results [9]	**Our Results (25 °C)**
Added Agent	L-EtTar	Model Tartrate
$\Delta H^{\ddagger}_{i} - \Delta H^{\ddagger}_{s}$	0.71±0.03 (kcal/mol)	0.40 (kcal/mol)
$\Delta S^{\ddagger}_{i} - \Delta S^{\ddagger}_{s}$	2.27±0.14 (cal/mol K)	0.74(cal/mol K)

3.2.3 Temperature effect on stereoregularity of the polymer chain in the absence of tartrates

In the absence of tartrates, it is found that the m dyad content of the polymer chain inreases with decreasing temperature. It was reported that m/r ratio equals to 62/38 at 0 °C and 73/27 at -80 °C in the experimental study [9].

The calculations in this study (Table 3.11, second column) shows that Gibbs Free Energy difference between isotactic and syndiotactic dimeric chains increases slightly as temperature decrease from 0°C to -80°C. This data supports the experimental results that declare an inverse relationship between the temperature and m dyad content of the polymer chain.

3.2.4 Temperature effect on stereoregularity of the polymer chain in the presence of tartrates

To evaluate the temperature effect on stereospecific radical polymerization of DMAAm in the presence of tartrates, frequency calculations at 0°, -20° -40°, -60° and -80° C were performed with the most stable iso and syn transition structures to get the Gibbs Free Energies of the species. The results are summarized in Table 3.12.

The syndiotacticity that is induced by tartrate increases as temperature decreases which can be seen from the change in Gibbs Free Energy values in Table 3.12.

Table 3.11: Experimental [9] m/r values and our corresponding results of relative Gibbs Free Energy differences of m and r dyads (absence of tartrates).

Temperature (°C)	**$\Delta(G_{iso} - G_{syn})$ (kcal/mole)**	**Experimental m/r values**
0	-0.80	62/38
-20	-0.82	64/36
-40	-0.84	66/34
-60	-0.85	70/30
-80	-0.87	73/27

Table 3.12: Gibbs Energy difference of the iso and syn addition modes in the presence of tartrates at different temperatures (experimental values are taken considering the L-EtTar as stereospecificity inducer).

Temperature (°C)	**$\Delta(G_{iso} - G_{syn})$ (kcal/mole)**	**Experimental [9] m/r values**
0	0.19	46/54
-20	0.21	43/57
-40	0.23	40/60
-60	0.24	37/63
-80	0.26	37/63

3.2.5 Solvent effect on stereoregularity of poly(DMAAm) obtained with free radical polymerization

Most of the radical polymerization reactions are carried out in a solvent. Using solvent in the reaction medium brings advantages such as control of heat removal and viscosity of the reaction mixture; but an appropriate solvent selection is a crucial point as it may bring some undesired outcomes as well. For example, chain transfer to solvent may cause a decrease in molecular weight of polymers which directly effects the mechanical properties of the final product.

Solvent effects can be understood by exploring the reaction kinetics as it changes the propagation rate constants of polymerization reactions especially in the case of water soluble monomers. For instance, acrylic acid [46] and acrylamides [47] show large variations with use of various solvents depending on the polarity and the nature of the intermolecular interactions that is formed between the monomer and the solvent.

Solvent effect on the stereospecificity of the radical polymerization is also known from experiments [9,48] and quantum chemical studies [49]. Many specific solvents have been found to allow stereospecific radical polymerizations via various interactions with monomers [7].

In an experimental work [10], solvent effect on tacticity of DMAAm was investigated explicitly. Various solvents were used including toluene, THF, fluoroalcohols, 2-propanol, methanol and water at different temperatures with different monomer and initiator ratios. A relationship between the solvent polarity and the tacticity was obtained in that work.

In this work, the role of the solvent on the tacticity of free radical polymerization of DMAAm was investigated by running Single Point Energy calculations in various solvents.

Our results show that although the energy difference is small, it is still good enough to show that as the solvent polarity increases, the possibility of formation of iso and syn products come closer to each other. This can be attributed to the fact that electrostatic effects are often much less important for species placed in a solvent with a high dielectric constant than they are in the gas phase [21].

The electronic energy difference between the iso and syn additions in toluene, chloroform, THF and 2-Proponal can be seen from Table 3.13.

The experimental study [10] also supports our findings which indicates the decrease of isotacticty (m dyad content) as solvent polarity increases as can be seen from Table 3.13.

Table 3.13: Single point energy calculation results for DMAAm polymerization in various solvents (Monomer/Initiator ratios and iniator type are same in all cases).

Solvent	**$\Delta E_{iso\text{-}syn}$ (kcal/mole)**	**Dielectric Constants of the Solvents**	**Temperature (°C)**	**Experimental [9] m/r ratio**
Toluene	-0.40	2.38	-80	73/27
Chloroform	-0.23	4.81	-60	70/30
THF	-0.09	7.5	-78	62/38
2-Propanol	-0.02	18	-78	57/43

3.3 N-methyl-N-phenylacrylamide (MphAAm)

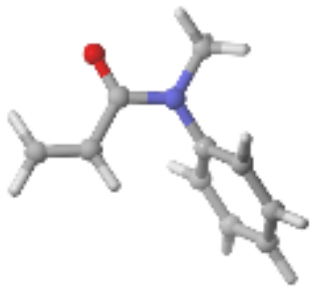
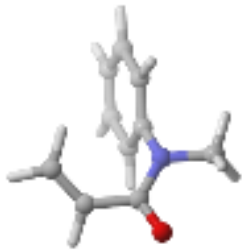
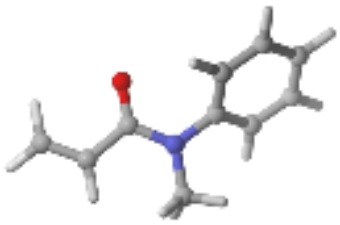
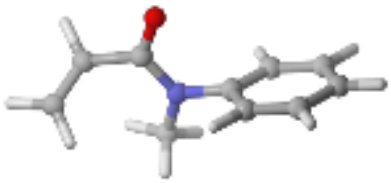
In an experimental work [8] free radical polymerization of MphAAm was conducted in toluene at temperatures between 0 °C and -80 °C. The difference between the activation parameters for isotactic and syndiotactic propagations are shown in Table 3.14.

Table 3.14: Experimental [8] activation parameters (Enthalpy and Entropy) for stereospecific free radical polymerization of MphAAm.

Solvent	**$\Delta H^{\ddagger}_{i} - \Delta H^{\ddagger}_{s}$ (kcal/mol)**	**$\Delta S^{\ddagger}_{i} - \Delta S^{\ddagger}_{s}$ (cal/mol)**	**Experimental m/r dyad ratio (-80 °C)**
Toluene	0.39±0.06	-0.31±0.26	24/76

Four different MphAAm monomers (Table 3.15) and MphAAm monomeric radicals (Table 3.16) are located by running conformer searches.

Table 3.15: Relative Electronic and Gibbs Free Energies (in paranthesis) and Enthalpies (italics) at 25 °C of MphAAm monomer conformers (given in kcal/mole).

 0.0 (0.0) *0.0* MphAAm-s-cis-1	 3.57 (3.60)*3.47* MphAAm-s-tr-1
 3.76 (3.96) *3.81* MphAAm-s-cis-2	 6.43 (5.96)*6.27* MphAAm-s-tr-2

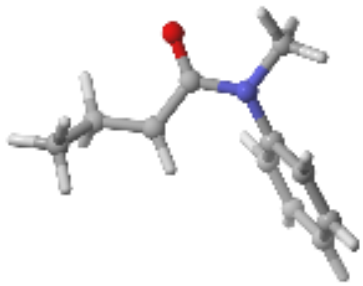
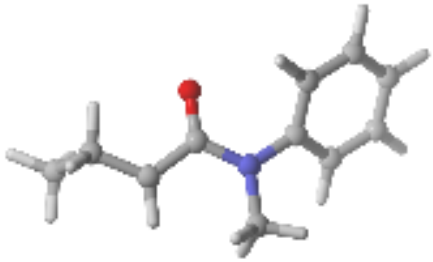
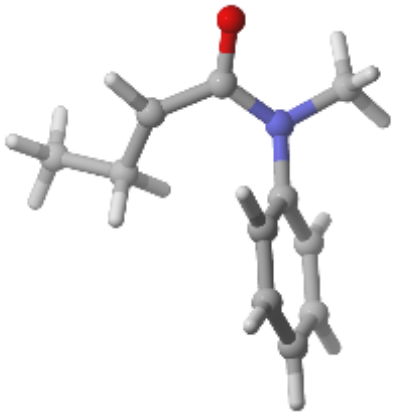
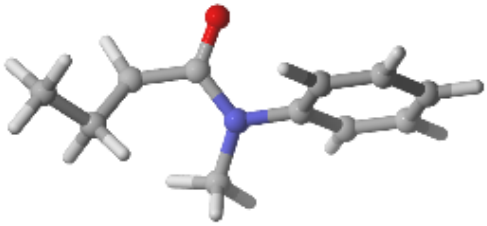
The MphAAm-s-cis-1 has the lowest Electronic Energy, Gibbs Free Energy and Enthalpy as can be seen from Table 3.15.

The radical form of the MphAAm-s-cis-1 monomer conformer is the MphAAm-rad-cis-1 (Table 3.16) and this radical again has the lowest Electronic Energy, Gibbs Free Energy and Enthalpy.

Transition structures are optimized with these four conformers of monomer and monomeric radicals to find the least energetic additions of both iso and syn

configurations. The least two energetics transition state structures for syn and iso additions are depicted in Table 3.17 with relative Electronic Energies, Gibbs Free Energies and Enthalpies.

Table 3.16: Relative Electronic and Gibbs Free Energies (in paranthesis) and Enthalpies (italics) at 25°C of MphAAm monomeric radical conformers (given in kcal/mole).

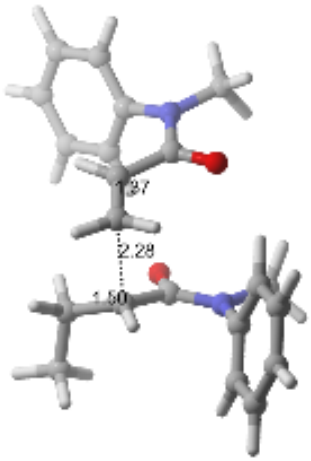
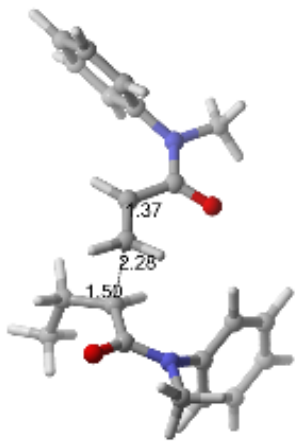
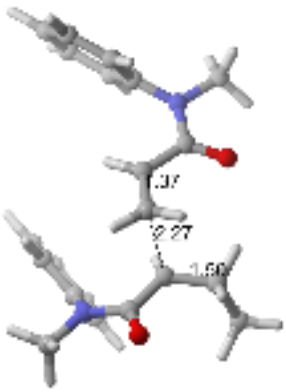
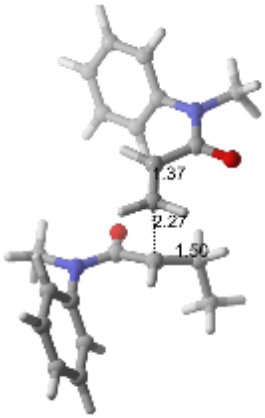
 0.0 (0.0)*0.0* MphAAm-rad-cis-1	 3.28 (3.45)*3.36* MphAAm-rad-cis-2
 3.57 (4.56) *3.52* MphAAm-rad-tr-1	 7.81 (8.09)*7.71* MphAAm-rad-tr-2

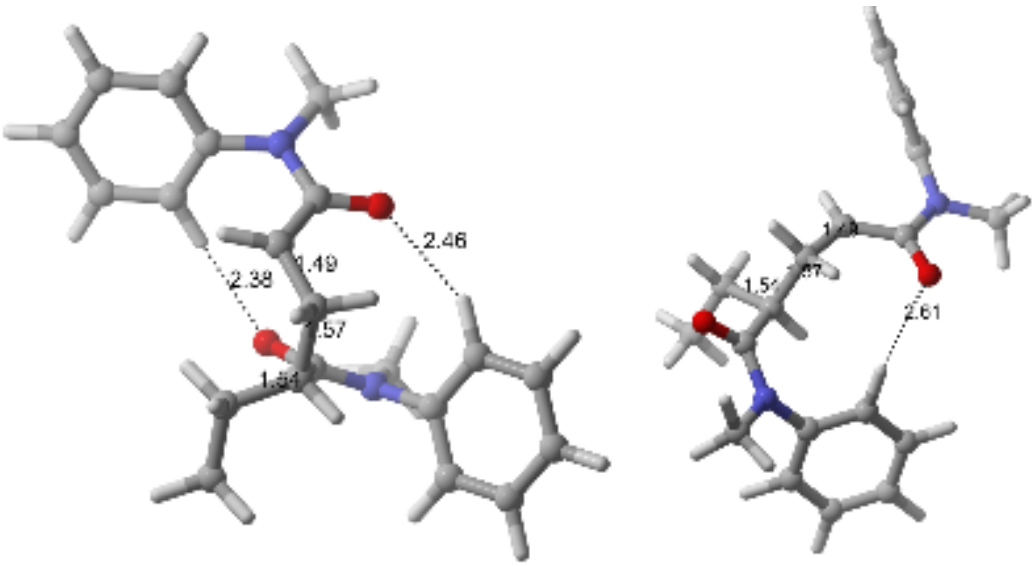
MphAAm-syn-ts1 and MphAAm-iso-ts1 structures both adopt gauche conformation of the backbone. This is due to the repulsions of the bulky phenyl groups of the monomer and the radical in order to prevent overlapping on each other.

The preference of syn addition could be attributed to the extra stabilizing effect of the hydrogen bonding interaction of the monomer's phenyl hydrogen and the oxygen

of the radical which is not present in the iso addition as shown in Figure 3.15. In MphAAm-syn-ts-2, there is no such interaction that lead this structure having higher energy barrier than the former structures.

Table 3.17: Relative Electronic Energies and Gibss Free Energies (in paranthesis), Enthalpies (italics) at 25°C and single point toluene results (italic+bold) of the most stable transition structures for syn and iso addition for MphAAm (given in kcal/mole).

SYN ADDITION	ISO ADDITION
 0.00 (0.00) *0.00* ***0.00*** MphAAm-syn-ts-1	 2.25 (0.11) *2.12* ***1.01*** MphAAm-iso-ts-1
 3.6 (0.61)*3.43* ***1.61*** MphAAm-syn-ts-2	 2.51 (0.64) *2.41* ***1.39*** MphAAm-iso-ts-2



Syn **Iso**

Figure 3.15 : The iso and syn products of dimeric MphAAm chain.

Gas phase calculations show that N-methyl-N-phenylacrylamide free radical polymerization yields product in favor of syndiotactic over isotactic with 2.12 kcal/mol in terms of Enthalpy (Figure 3.16).

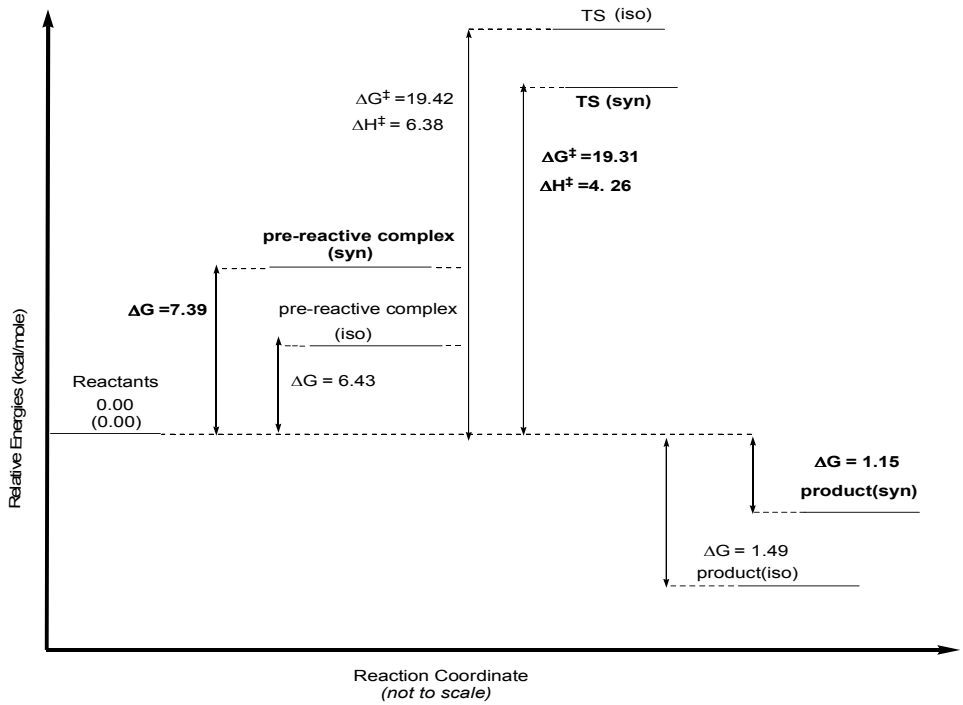


Figure 3.16 : Activation parameters for the competative iso and syn product in free radical polymerization of MphAAm

3.4 N,N-diphenylacrylamide (DPAAm)

Monomer structure is known to effect the stereospecific radical polymerization of vinyl type monomers [29,50,51]. Reactivity of alkenes is highly dependent on the pendant group size and the nature of the substituents due to the steric and polar effects. It was recently shown [8,11] the effect of N-substituent of the monomer on the stereoregularity of free radical polymerization of acrylamides.

N,N-diphenylacrylamide is a good example to see how the bulkiness of a monomer has an influence on constituting a polymer configuration in terms stereoselectivity. Possesing two bulky phenyl groups in the monomer structure, it is expected that the addition mode of this monomer is determined by these phenyl groups on steric hinderance ground.

Free radical polymerization of DPAAm is found to yield highly syndiotactic polymers regardless of the reaction conditions [10,52]. Various solvents including toluene, THF, 2-Propanol, DMF and fluoroalcohols are tested within these experimental works but only a slight difference between the content of r dyad in the polymer was observed when these different solvents are used in the reaction medium especially at high temperatures. Some experimental results [10] for activation parameters (Enthalpy and Entropy) are shown in Table 3.18.

Table 3.18: Experimental [10] activation parameters (Enthalpy and Entropy) for stereospecific free radical polymerization of DPAAm in various solvents at different temperatures.

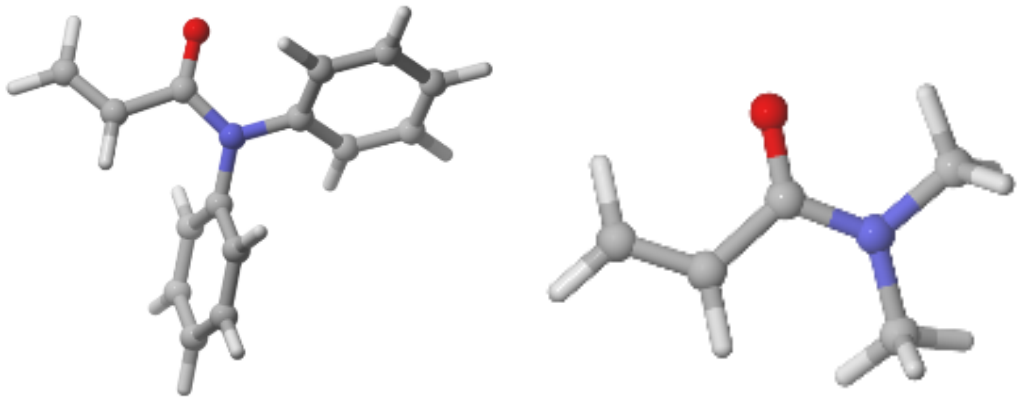
Solvent	**$\Delta S^{\ddagger}_{i} - \Delta S^{\ddagger}_{s}$ (cal/ deg mol)**	**$\Delta H^{\ddagger}_{i} - \Delta H^{\ddagger}_{s}$ (kcal/mol)**	**m/r dyad ratio**
Toluene	-1.2	0.487	13/87 (-78°C) 18/82 (0°C)
DMF	-0.6	0.692	13/87 (-50°C) 20/80 (60°C)
THF	0.2	0.948	9/91 (-78°C) 20/80 (60°C)

It was shown by experiment [9] and our calculations that isotactic polymer is favored in the case of free radical polymerization DMAAm. The difference between these two acrylamide monomers is that methyl groups in DMAAm are replaced by bulky phenyl groups in DPAAm (Figure 3.17).

It seems that the driving force of determining the stereoselective mode of DPAAm monomer is the bulkiness of two phenyl groups attached to the nitrogen atom.

In this work, free radical polymerization of DPAAm is modeled and discussed with the previous experimental findings.

The most stable monomer and monomeric radical were found by conformer search. There are two conformers located; one having the C=O group trans to the C-H and the other cis (Table 3.19).



DPAAm DMAAm

Figure 3.17 : DPAAm and DMAAm monomers.

The propagation reaction is modeled with the DPAAm-rad-trans and DPAAm-rad-cis considering head-to-tail regioselectivity mode. Methyl radical is used to activate the monomer and forms a radical necessary for propagation process.

Two syndiotactic and one isotactic transition state structures could be located on the potential energy surface of the reaction (Table 3.20).

Gas phase calculations show that syndiotacticity is favored over isotacticity in the case of DPAAm polymerization. The energy difference between the least energetic r and m dyads is 1.54 kcal/mole in terms electronic energy and 0.80 in terms of gibbs free energy.

It is clear from the geometries of transition state structures that phenyl groups tend to oriente towards the oxygen atom of the other molecule. The hydrogen bonding interaction plays the crucial role for stabilizing the structures.

In DPAAm-syn-ts1 , phenil group of the monomer is positioned perpendicular to themonomeric unit below which is suitable for formation of a hydrogen bonding between the radical oxygen and phenyl hydrogen. Same interaction exists between the phenyl of the radical and oxygen of the monomer too. This transition state structure is also advantageous over the others in terms of reducing the steric effects between the phenyl groups; especially compared to the DPAAm-syn-ts2 where phenyl groups of each molcule are located on the same side of the planar and close to each others. Reaction profiles of DPAAm-syn-ts1 and DPAAm-iso-ts are obtained and our results are in agreement with experimentally found results such that syndiotactic addition reaction barrier is lower than the iso addition (Figure 3.18).

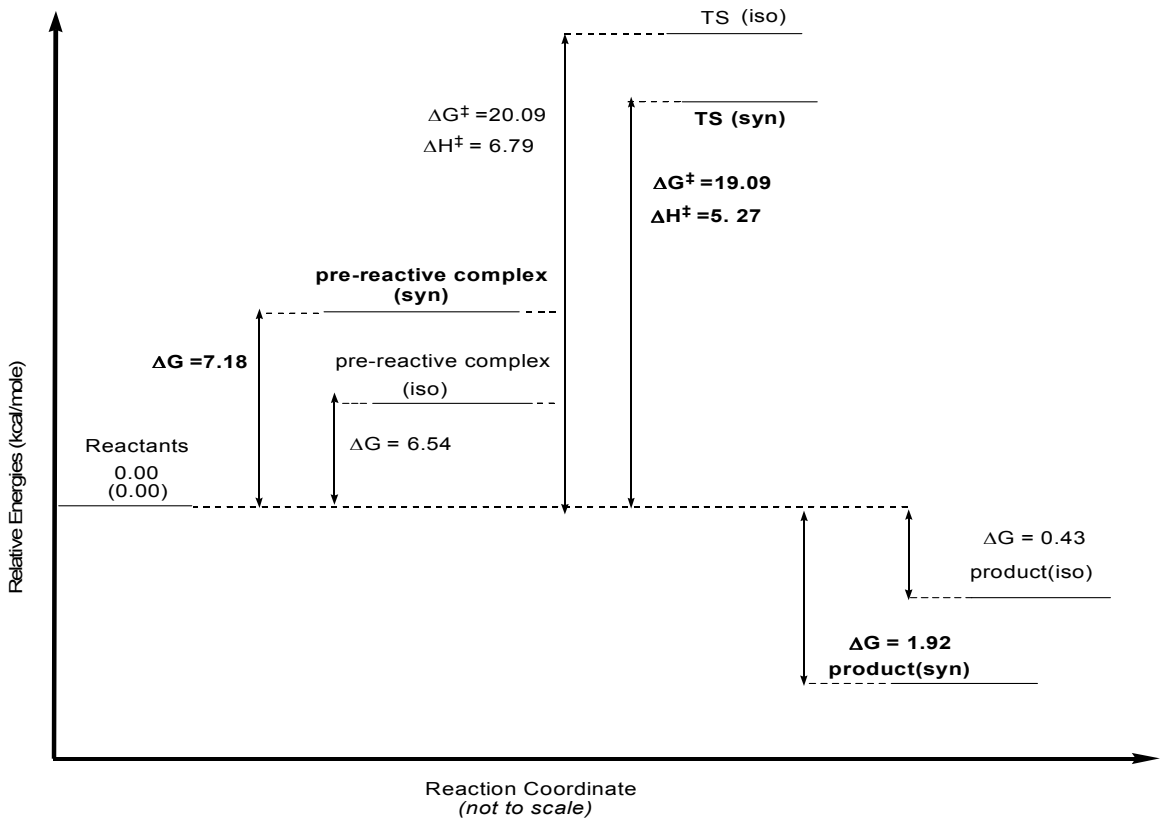


Figure 3.18 : Energy barriers for iso and syn addition in the free radical polymerization of DPAAm in the gas phase.

Table 3.19: Relative Electronic energies , Gibss Free Energies (in paranthesis) and Enthalpies(italics) at 25 °C of DPAAm monomer and DPAAm monomeric radical conformers (given in kcal/mole).

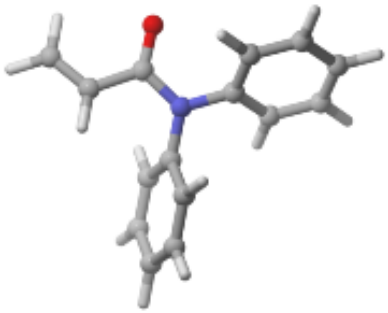
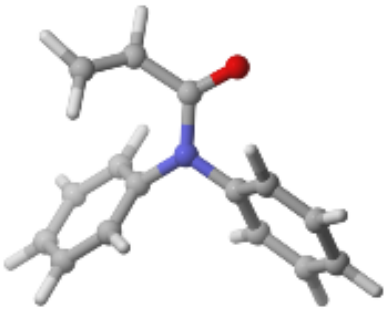
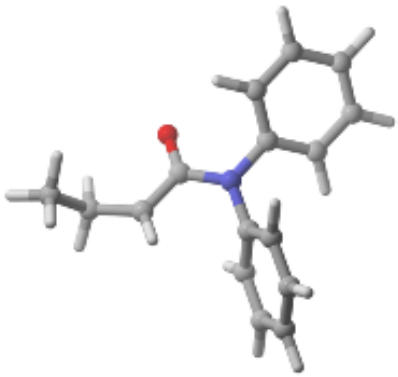
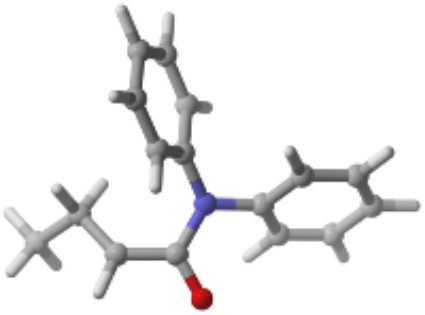
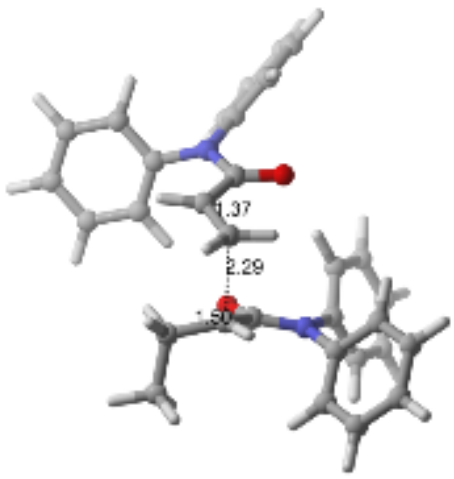
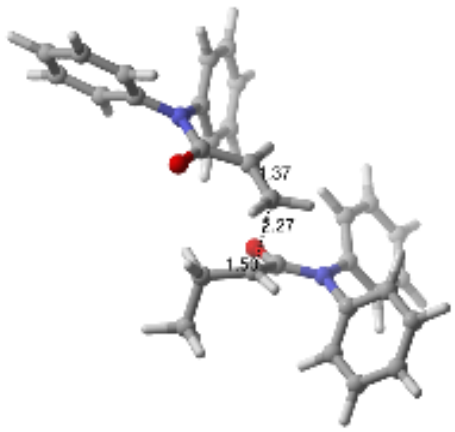
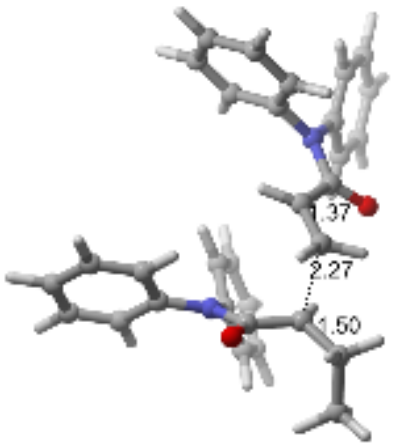
 DPAAm-s-cis 0.00 (0.00) *0.00*	 DPAAm-s-trans 3.54 (3.29) *3.39*
 DPAAm-rad-tr 0.00 (0.00) *0.00*	 DPAAm-rad-cis 3.74 (4.11) *3.61*

Table 3.20: Relative Electronic, Gibbs free energies (in paranthesis) and Enthalpies (italics) at 25 °C of the most stable transition structures for syn and iso addition for DPAAm in the gas phase (given in kcal/mole).

Syn addition	Iso addition
 0.00 (0.00) *0.00* DPAAm-syn-ts1	 1.54 (0.99) *1.52* DPAAm-iso-ts
 1.96 (0.80) *1.84* DPAAm-syn-ts2	

4. CONCLUSION

In this study, the tacticities of free radical polymerization of DMAAm, MphAAm and DPAAm acrylamide monomers are studied with quantum mechanical calculations at the B3LYP/6-31+g(d,p) level and compared with the experimental results. It is shown that the N-substituents play a critical role for the determination of the stereospecificity of the obtained polymer.

As the N-substituents of the acrylamide monomer varies from methyl groups to phenyl groups in the case of DMAAm and DPAAm respectively, the stereospecific addition mode is found to favor m and r dyads respectively. Additionally, in MphAAm case, when one of the methyl group is replaced with a bulkier phenyl group, the same trend is obtained. The tacticity depends on the addition mode of the monomer with respect to the radicalic end group of the polymeric chain. Considering the dimeric propagated chains, it is seen from the calculations that, the determination of the favorable addition modes depend on the intramolecular H-bonding interactions between the monomer and radicals oxygen and hydrogen of the methyl groups. This is attributed to the importance of the stabilizing effect of the hydrogen bonding interactions that lowers the activation barrier of the favorable addition mode which is also related to the conformational limitations between the new coming monomer to the propagated chain.

A general trend of the temperature effect on the tacticity of DMAAm is found which states that lowering the temperature increases the m dyad ratio which causes the polymer chain to have high isotactic sequence.

A relationship between the solvent polarity and stereoregularity of the DMAAm polymerization is also found such that the choice of solvent is an important parameter for the control of tacticity. As the polarity of solvent increases the possibility of formation of iso and syn products come closer to each other.

The stereospecific inducer effect on the DMAAm dimeric chain is investigated and reproduced through hydrogen bonding interaction between the model tartrates and

the reactants. The importance of additives in the reaction medium is evaluated with these calculations because as it is seen in our study, the stereoreospecific addition mode is changed from isotactic to syndiotactic when the reaction is modeled in the absence and the presence of tartrates, respectively. The main reason for such a transition is the steric effect imparted by the tartrate group to meso addition, which is controlled mainly by the hydrogen bonding interactions.

The quantum chemical calculations employed in this study have revealed results that are in qualitative and quantitative accordance with the experiments. It should always be considered that the energy and entropy differences between isotactic and syndiotactic addition modes are very small although they lead to a difference in tacticity and may be within the error range of theories involved in here. Additionally, in this study model calculations have been done such as replacing the polymeric chain by the methyl group in the radicalic monomer. These type of calculations have been utilized successfully in our group and in the literature. If using a model and ignoring the steric effect of the polymer chain insert an error to the system, there will be a cancellation of errors since this error will be present in both isotactic and syndiotactic addition modes. However, to be on the safe side, the difference between the relative isotactic and syndiotactic addition modes that should considered rather than the absolute energies.

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APPENDIX

APPENDIX A.1 : An example for an gaussian input and output geometries (a transition state structure) and an input coordinates:

Input: Output:

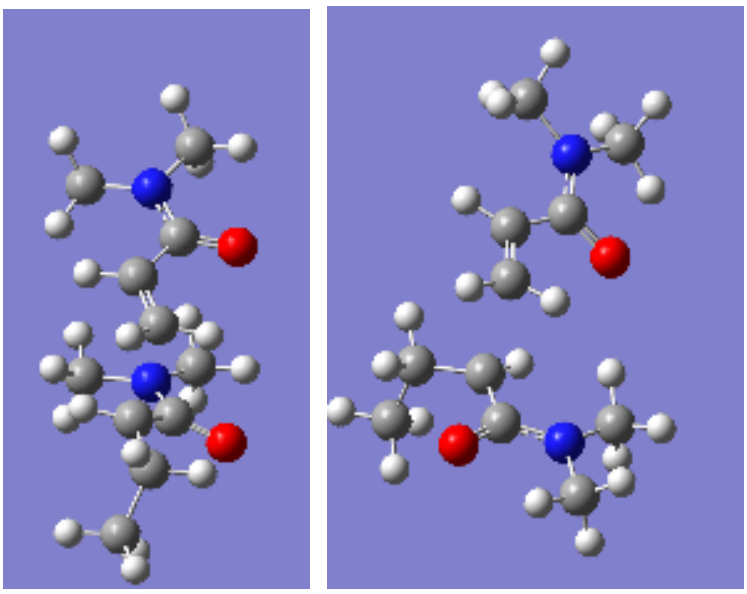

Figure A.1 : An Example for a Gaussian Input and Output Geometry

Input:

```
%mem=2000Mb
%nproc=4
# opt=(calcfc,ts,noeigen) ub3lyp/6-31+g(d,p)

Title Card Required

0 2
 C
 C          1          B1
 O          2          B2    1          A1
 N          2          B3    1          A2    3          D1
```

C	4	B4	2	A3	1	D2	
H	5	B5	4	A4	2	D3	
H	5	B6	4	A5	2	D4	
H	5	B7	4	A6	2	D5	
C	4	B8	2	A7	1	D6	
H	9	B9	4	A8	2	D7	
H	9	B10	4	A9	2	D8	
H	9	B11	4	A10	2	D9	
C	1	B12	2	A11	3	D10	
C	13	B13	1	A12	2	D11	
H	14	B14	13	A13	1	D12	
C	14	B15	13	A14	1	D13	
O	16	B16	14	A15	13	D14	
N	16	B17	14	A16	13	D15	
C	18	B18	16	A17	14	D16	
C	18	B19	16	A18	14	D17	
H	19	B20	18	A19	16	D18	
H	19	B21	18	A20	16	D19	
H	19	B22	18	A21	16	D20	
H	20	B23	18	A22	16	D21	
H	20	B24	18	A23	16	D22	
H	20	B25	18	A24	16	D23	
H	13	B26	1	A25	2	D24	
H	13	B27	1	A26	2	D25	
C	1	B28	2	A27	3	D26	
H	29	B29	1	A28	2	D27	
H	29	B30	1	A29	2	D28	
H	1	B31	2	A30	3	D29	
C	29	B32	1	A31	2	D30	
H	33	B33	29	A32	1	D31	
H	33	B34	29	A33	1	D32	
H	33	B35	29	A34	1	D33	

B1	1.48086329
B2	1.23745337
B3	1.38982588
B4	1.45952010
B5	1.09996749
B6	1.09537850
B7	1.08860514
B8	1.45780465
B9	1.09386034
B10	1.10062560
B11	1.09060457
B12	2.25142103
B13	1.37595544
B14	1.08662598
B15	1.48989907
B16	1.23654318
B17	1.37832270

B18	1.45867796
B19	1.45783059
B20	1.09913784
B21	1.09538719
B22	1.08889260
B23	1.09764611
B24	1.09850397
B25	1.08834497
B26	1.08613881
B27	1.08478647
B28	1.50226121
B29	1.10155817
B30	1.09455637
B31	1.08696976
B32	1.53237593
B33	1.09718154
B34	1.09434644
B35	1.09503934
A1	120.35981299
A2	118.70391836
A3	117.84522821
A4	111.34324720
A5	109.67534120
A6	108.85755588
A7	124.10489643
A8	108.61507009
A9	112.46521622
A10	111.74572172
A11	99.38157736
A12	109.53701703
A13	119.53437947
A14	125.68448698
A15	118.71888015
A16	119.62418270
A17	118.15731032
A18	124.57912013
A19	111.26501093
A20	109.24561320
A21	109.33716627
A22	111.09362291
A23	109.79663714
A24	110.64924880
A25	93.20816704
A26	88.64071148
A27	117.24642859
A28	107.60573119
A29	109.84494307
A30	117.91637042
A31	113.75889610
A32	111.45046991

A33	110.59616145
A34	111.64251891
D1	-177.50945391
D2	165.30006178
D3	98.17052215
D4	-141.76441884
D5	-21.53602896
D6	-34.21000000
D7	161.08813543
D8	-79.56398582
D9	42.93017654
D10	97.91828640
D11	64.03846086
D12	59.11570266
D13	-105.98000000
D14	0.95316080
D15	-176.64000000
D16	175.00369961
D17	-22.69897438
D18	95.17899918
D19	-144.99223203
D20	-24.63445991
D21	125.13811284
D22	-115.47985610
D23	3.94943028
D24	-59.67077262
D25	-175.71013644
D26	-17.71912119
D27	37.80737469
D28	151.44055418
D29	-163.01497935
D30	-83.55000000
D31	58.22945939
D32	178.02868638
D33	-62.47288606

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