# Effect of Athermal Solvency Conditions and Solvent Size on Intra Molecular Chain Transfer to Polymer in Acrylate Radical Polymerization Through Computational Approach

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# Dedication

I would like to dedicate this work to my Parents

# *ACKNOWLEDGEMENTS*

*First of all, thanks to Almighty Allah who is the most beneficent and merciful, Who gave me knowledge and power to complete this thesis report successfully. I also offer my greatest and heartiest feelings to our last Holly Prophet Muhammad (S.A.W.W) who is torch for guidance and knowledge for humanity as a whole.*

*I would like to place on record my gratitude to Dr. Nasir M. Ahmed who gives me opportunity to work with him and also provide full support and coordination till the end of project. I appreciate Dr. Uzma Habib for her insightful suggestions and guidance on the computations performed*

*No sophisticated words can express my thanks to my parents for their unconditional love and support. Due to their affection I always felt comfortable in difficult circumstances and it is because of their prayers.*

# Abstract

The influence of solvent as a true thermodynamics medium effect in the free radical solution polymerization of n-butyl acrylate (n-BA) monomer was studied using density functional theory calculations. Three solvent systems which include cyclohexane, cycloheptane and cyclooctane were considered with B3LYP as a hybrid density functional by using 3-21 Basis set. The activation energy of the n-BA monomer was estimated from measurements of monomer conversion to polymer in free radical solution polymerization. Additionally, a conductor-like polarizable continuum model (C-PCM) was applied on the geometries with three different solvents system in propagating monomer chain. This model has a dramatic effect on all the propagation rates. These studies predict that with the increasing size of solvents, there was a decrease in the activation energy, which can follow same energy trend to result in decrease in the extent of chain transfer to polymer (CTP). Probability of CTP relative to propagation analysis were also carried out and molar fraction branching calculation predicts that polymer chains have tendency toward less branching formation via intramolecular chain transfer to polymer in cyclooctane larger solvent system than other two smaller solvents systems of cyclohexane and cycloheptane.

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# Chapter 1

# Introduction

## 1.1 Polymer

Polymer is a large molecule or a macromolecule, which is formed by many small repeating units. Both natural and synthetic polymers are prepared by polymerization of small repeating unit called”monomer”. Polymers have many features that will make this material unique. The large molecular mass produced unique physical properties such as hardness and viscoelasticity. Polymer science and engineering is an interdisciplinary field that encompasses many fields. Polymer is also referred as Macromolecule because of very high molecular weight. Polymer scientist and engineers are developing new ways of reacting monomers to form polymer with improve properties. Polymer reaction engineering is very vast discipline and many properties of polymer depends on the reaction mechanism. Reaction engineering will explain how monomer creates larger molecule and which factors are playing key role in the formation of final polymer. Mechanical properties such as stress, modulus and elongation at the break point are all related with microstructure and fundamental reaction chemistry of polymer [1].

### 1.1.1 n- Butyl Acrylate:

n- Butyl Acrylate is the most widely used acrylate monomer. It is used in the production of polymers and resins for textile, leather finishes, coatings, adhesives, paints, binders and emulsifiers application. It is highly reactive and polymerizes easily when exposes to heat. Therefore proper inhibitors are used in the commercial production of n-butyl acrylate. It is mostly stabilized with hydroquinone. Its odor is released into the environment in fugitive and stack emissions or in wastewater during its production and use.

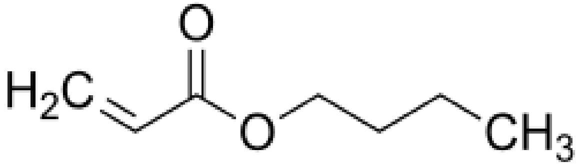


Figure 1.1. Chemical structure of monomer n-Butyl Acrylate [2]

Table 1.1 Properties of nBA [3]

| Polymer | Molecular Weight | Boiling point | Density |
|---|---|---|---|
| n-Butyl Acrylate | 128.17 g/mol | 145$^o$C | 0.89g/mL |

n-BA is clear colorless liquid, has very strong fruity odor and soluble in ethanol, ethyl ester, acetone and slightly soluble in carbon tetrachloride.

## 1.2 Free radical polymerization and solvent role:

Free radical solution polymerization is a widely used process for the commercial production of variety of polymers. It is a multistage complicated process. Determination of rate coefficient of the various elementary reactions is challenging for both computational and experimental researcher. With the development of computer power, advanced numerical methods and computational chemistry has established itself a useful tool for radical polymer field. In literature both experimental [4-8] and theoretical data for a broad range of radically polymerization monomers like ethylene [9-10] (methacrylate type) [11-12], styrene [13] and vinylchloride [14] are available.

Mostly Polymerization is carried out in solution to study the influence of solvent in polymerization. Role of solvent is very crucial in the reaction engineering of polymer. It has been recognized that solvent may effect the reaction kinetics and its influence on reaction kinetics is active research area. Reaction rate coefficient ($k_p$) for styrene and methylmethacrylate (MMA) polymerization have been measured in wide variety of solvent by Olaj et al [15] and changes via solvent were found to vary around 22%. Solvent changes can easily effect the kp value. It also made an impact on hindered rotational modes, hydrogen bonding or electron pair interaction. Variation in solvent size also effects the kp value but to less extend.

Fundamental of CTP for many acrylic monomer are still, lacking as compare to CTP studies of other monomer system. Furthermore, since the more diluted solution $[BA]_0$ $\leq$10% the role of solvents were identical to control the $[P]_{local}/[M]_{local}$ to determine the extent of CTP in CHX solution polymerization. Considering the significance of above solvent effect on $[P]_{local}/[M]_{local}$ for many commercial acrylic polymer, and is literature reflect no identification of any detailed study of CTP in free radical polymerization in different solvents, we became interested in pursuing the more detail studies of the solvent effects. Therefore, in continuation of our efforts to further investigate factors that control the extend of CTP. Project aims to study the free radical solution polymerization of n-BA with three cyclic solvents and explore the extents of CTP in various thermodynamics true solvent, which are mainly differing in term of their sizes, while rest of the properties remain same. The approach to tackle this problem is Computational via Density functional theory.

Mechanism of free radical polymerization reaction has also been studied using Density functional Theory (DFT) method [16-21]. This method was applied for the calculation of rate constant of initiation, propagation, chain transfer and termination reactions [22-24]. DFT was used in studying Alkenes and Acrylate; its rate constant and molecular geometries of various reactions were predicted. Some reactions by this computing tool like chain transfer to monomer [25] and chain transfer to solvent [23] reactions also have been reported.

The solvent molecule effects the stability of transition-state structure of polymer during free radical solution polymerization [26]. Computationally, solvation model, the conductor-like polarized continuum model (CPCM) was applied to explore the effect of solvents with different dielectric constants on the propagation rate coefficients in free-radical polymerization.

In this work we applied following solvents model i.e., self-consistent reaction field (SCRF) and conductor like polarized continuum model (CPCM) to calculate the propagation reactions of n-BA and also compute transition states so that we compare the activation energy of polymer propagation at different solvent conditions. In the continuum (CPCM) model, solute is used to polarize the solvent and this solvent is act as a dielectric mean field. Solute is mostly placed at inner continuum cavity. While the solute in the cavity is defined by self-consistent reaction field (SCRF) method, molecular shape of the cavity is defined by polarizable continuum model (PCM) .

## 1.3 Research Challenges:

We need to explore a solvent that shows variability in terms of their sizes relative to monomer n-Butyl Acrylate (nBA), and at the same time the solvent should behave as a true thermodynamics solvent with athermal characteristics. So, to discover and differentiate between poor and good cyclic solvents with nBA, we started our model with ideal and athermal solvents and use computational tool to define the behavior of propagating monomer chain in different solvent. Finally predict the best solvent with this Polymer system.

## 1.4 Thesis Objective:

- Calculate computationally the influence of different solvents and their pure thermodynamic conditions that effect the chain transfer to polymer (CTP) reaction.
- Major focus will be to investigate intra-molecular CTP in the free radical solution polymerization of n-butyl acrlyate monomer (n-BA)
- Monomer: n-Butyl Acrylate is the most widely used acrylate monomer in industry.
- Project aims to explore the extents of CTP in various thermodynamics true solvent, which are mainly differing in term of their sizes, while rest of the properties remain same.
- Present project is the 1st such attempt to understand the size effect of solvent to the best of our knowledge.

## 1.5 Project Scope:

n-Butylacrylate (nBA) is widely used acrylate monomer. It is used in paint, adhesive, coating and many water paint industries. Butyl acrylate is also used as a feedstock for the synthesis of many chemicals because it undergoes rapid addition reaction with organic and inorganic compound. By controlling the chain transfer to polymer (CTP), properties like molecular weight distribution, degree of polymerization, viscosity, density and optical properties of polymer can be estimated. To avoid the experimental challenges computational tool is used to consider the research with new vision. Now a day, research and development (R&D) in computational sector is improving and become the first choice to tackle the problem. It is used in wide variety of discipline and industries including aerospace, power, manufacturing, polymer processing, petroleum exploration and astrophysics.

# Chapter 2

# Theoretical Development

## 2.1 Background:

Reaction Mechanism in free radical polymerization process is successfully investigated using quantum computational chemistry [27]. Styrene has been explored using Density functional theory (DFT) calculation. It uses 6-31G basis set and B3LYP hybrid density functional [28]. Free radical polymerization of Alkene and propagation of methyl methacrylate [29] have been studied using B3LYP hybrid functional. Application of quantum computing is very essential in formation mechanism of radical and its propagation. It is also very successful in studying the free radical polymerization process. Computational study using DFT is less intensive than other wave function based model that's why it is used to study the chain transfer reaction in polymerization.

Primary reactions of free radical polymerization like initiation, propagation and termination has been reported at low and elevated temperature [30-31]. On the other hand, there are some secondary reactions i.e., backbiting, short chain branching, chain transfer to solvent, polymer and monomer also receive equal importance in predicting the properties of polymer. Propagating chain polymer size decreases, when chain transfer reaction is favorable then propagation. The effect cause premature termination of chain and decreasing the molecular weight of polymer. During free radical polymerization chain transfer to polymer has been experimentally studied using monomer n-butyl acrylate in 1998 [32]. NMR and viscosity results of n-butyl acrylate clearly depicts that both intermolecular and intramolecular chain transfer chain transfer reaction occur and decrease the molecular weight of polymer. In 2009, [33] paper has been reported that contained both experimental and theoretical calculation for chain transfer to polymer of n-butyl acrylate. It showed mathematical calculation of molar fraction branches and experimental results of branching using both atomic transfer radical polymerization and free radical polymerization. It concluded that polymer formed using free radical polymerization have more branching than atom transfer radical polymerization.

In 2009, research paper related to chain transfer to polymer and branching in controlled radical polymerization of n butyl acrylate has been reported [34]. Author investigated chain transfer behavior of butyl acrylate monomer via NMR spectroscopy and compared the branching result with controlled polymerization and conventional polymerization. The mol % branches reduced significantly in controlled polymerization as compare to convention free radical polymerizations. In conventional free radical polymerization, the distribution of radical concentration is broad and their always is present a significant properties of short chain radical, where as in controlled radical polymerization the distribution is narrow.

Bar Dee Starch in 2010 [35] applied DFT and used B3LYP and other electronic functional to study the solvent effect in free radical polymerization. He studied the influence of water in the propagation of acryl amid and methacylamid. Activation energy and transition state has been estimated using computational technique.

DFT method with four Basis has been applied on ethyl acrylate, methyl acrylate and n-butyl acrylate monomer and studied its chain transfer reaction using GAMES software. This study indicated that activation energy of reactant conversion to product has less or minimum effect on chain length. Moreover, in chain transfer to polymer reaction, energy barrier shows similar trend in all selected monomer i.e., methyl acrylate, ethyl acrylate, and butyl acrylates [36].

## 2.2 Chain Transfer Reactions

Size of propagating polymer chain decreases as a result of chain transfer (chain breaking) reaction, It effects the degree of polymerization and also reduced the molecular weight of end polymer due to premature termination of reaction. There are many kinds of transfer reactions i.e., chain transfer to polymer, chain transfer to solvent and chain transfer to monomer. We will discuss only chain transfer to polymer, it occurs by two ways: via intramolecular chain transfer to polymer and by intermolecular chain transfer to polymer. Radical or active site is formed as a result of chain transfer reaction and we get branched polymer as our end polymer. Long chain branched polymer is formed as a consequence of intermolecular chain transfer to polymer. In case of intramolecular chain transfer to polymer backbiting of polymer chain estimate, the type of branching in final polymer. By this chain transfer to polymer reaction, we can control the properties of polymer like molecular weight. Solvent is considered as a chain transferring agent to control and estimate the properties of polymer. It is added deliberately to achieve the specific required properties especially, molecular weight.

## 2.3 Ab Initio Molecular Orbital Theory

The primary role of this ab initio molecular orbital theory is to solve the many body stationary Schrodinger equation. Equation is:

$$Hy = Ey$$ Equation 2.1

Where ψ is the wave function, E is the energy of electron that depends on configuration of nuclei and H is the Hamiltonian.

Wave function can be estimated using single electron function. This single electron function is a product of spatial orbital and single electron function. Basis function is used to define the geometry of spatial orbital. Exact solution of Eigen value problem will come if we have infinite basis set. A basis set is used to determine the shape of orbital

The problem in application of wave equation is related to Eigen value problem whose exact solution can be feasible if we process infinite basis sets. A basis set is combination of several basis functions to determine the shape of the orbital.

$$H = E_{kinetic} + E_{potential} + E_{coulomb}$$ Equation 2.2

Where H is Hamiltonian operator is calculated using kinetic energy of electrons and nuclei and by Coulomb interaction between electron-electron, nucleus- nucleus and electron-nucleus. To make this calculation simpler and easier different model has been applied. In Born-Oppenheimer approximation said that the motion of electron should be considered and neglect the motion of nucleus because of size. Now the final equation after this approximation is:

$$H_e \Psi_e (r_i, R_i) = H_e \Psi_e (r_i, R_i)$$ Equation 2.3

In this equation ri represents the coordinates of electron while where Ri depicts the coordinates of nuclei. Above equation can be solved via different computational technique and different geometries of polymer can be achieved. Activation energy, frequency factor and transition state geometry can be obtained by applying second derivative of wave function to the above equation.

In case of free radical polymerization initiation, propagation and termination are the most practical steps in this addition polymerization. Rate of reaction is depending on temperature and chain length, in case of industrial production there are more than one monomer and determination of accurate value of rate constant is very challenging step to tackle, such as in case of emulsion and copolymerization finding the accurate solution is unsuccessful. Quantum computational is used to find out the rate of individual addition on active polymer chain, without any model or assumptions. While, more accuracy demands high scale environment, accurate procedure, high level simulation, and cost effective computation. However, it is not practical to gather all features in one system however continuous improvement in this computational field soon establishing an accurate tool for radical polymerization.

## 2.4. Transition State Theory

This theory is applied to find out and estimate the kinetic parameter of the reaction [40, 46]. It contained following assumptions for simple and accurate results. Transition states is considered as in statistical equilibrium state, classical motion is involved in this state and space and surface is defined in such a way that reactant cross the surface reaches to product without any re-crossing of the surface. Following equation is used:

$$k_p = A\exp(\frac{E_a}{RT}) \qquad \text{Equation 2.4}$$

Where k is the rate constant at constant temperature, A is frequency factor or Arrhenius pre-exponential factor, Ea is activation energy require to convert reactant to product, R is gas constant and T is temperature.

## 2.5 Quantum Computation:

Kinetic parameter of reaction system has been investigated using this quantum computational approach [37-40]. Lowest or ground state of molecular geometry has been find out easily using this computational technique. Lowest energy state cannot determine using experimental approach. Schrodinger wave equation for many body system is solved using some model (theory+ basis set) has been used to predict the wave function and energy of system. Transition state geometry, initial geometry, product geometry enthalpy and energy barrier information can be derived using this quantum approach.

Reaction mechanism and kinetic models for explaining free radical polymerization has been better estimated using quantum computational approach. In case of alkyl acrylate free radical polymerization mechanism such as propagation and self-initiating monomer reaction has been explained using density functional theory and wave based classical model [41]. Density function theory (DFT) is ground state technique. It uses exchange correlation function and it is used to define the accuracy of system. High level wave function is involved in determine the transition state and accuracy is neglected in this case. However, molecular geometry is predicted with more accuracy [42]. Accuracy of transition state in DFT has been increased by the introduction of modern exchange correlation function such as M06 [43]. Polymer propagation reaction and chain transfer to polymer reactions were investigated and calculate the kinetic parameters for lower computational cost and with good [44]. For larger system this DFT is more reliable that classical wave-based model because of practical reliability [45]. Thermodynamics and kinetic parameter were estimated by applying certain models, theory and functionals. Functional exchange-correlation function is considered as a functional [46,47]. Hartree-Fock exchange correlation functionals combined with generalized gradient density, meta generalized gradient density and local gradient density functional to reduce cost and increase the accuracy. These combinations of functionals are collectively as hybrid density functionals most commonly used is B3LYP, B3 exchange function and LYP is correlation functional and it is generalized gradient density functional. Chain transfer reaction require high computational cost and large polymer formed in free radical polymerization require specific selection of hybrid density functional with electronic structure. More accuracy on transition states can be determined using M06-2X Meta gradient density functional [48-51]. Alkyl acrylate propagation rate constant were estimated using DFT analysis.

Self-initiating reaction require less usage of thermal initiator such as peroxide [52]. Properties achieved in the end polymer by this method is discussed in literature [53]. Experimental technique didn’t cover the initiation reaction mechanism, study using NMR and Mass spectroscopy have been reported [54]. While combination of quantum computation with experimental equipment MALDI has been used to study the self-initiating reaction mechanism of alkyl acrylate in detail [55]. Chromatography and pulse laser polymerization has been used to study the reaction mechanism for chain transfer to polymer for alkyl acrylate [56]. High temperature polymerization of n-butyl acrylate at 70°C has been carried out using pulse laser polymerization and propagation reaction has been estimated at frequency of 500 hertz [57]. Analytical techniques were applied to investigate the intramolecular and intermolecular chain transfer to polymer in n-butyl acrylate but the technique didn't determine the kinetic parameter at 70°C

Thermodynamics and kinetic parameter of n-butyl acrylate were investigated using mechanical modeling. This modeling is referred as macroscopic and used to estimate the kinetic parameter such as rate constant, chain transfer to polymer, transition states and activation energy for self-initiating monomer [58]. This model is in revised form known as first principle method and it is better than semi empirical method that require some experimental result for the computational analysis [59]. Accuracy depends on individual reaction mechanism and exchange-correlation functional. It is used for high temperature polymerization calculation for n-butyl acrylate [60,61]. This model is referred as mechanical mechanistic model. There is other model that is also used in n-butyl acrylate calculation is based on method of moments, its modeling rate is 10 equations and not consider the number of monomer added on active center. It is more accurate than previous model.

We applied first principle model throughout our computational calculation, although both models have been used in past for the analysis of n-butyl acrylate [62-64].

## 2.6 Free Radical Polymerization:

Polymerization that initiate with an active or radical center is known as Free Radical Polymerization. In this type of polymerization, polymer grows by the addition of monomer in their radical canters. After the addition of each monomer molecule the radical center shifted to a new chain end. This is how chain length increases.

It is extensively used method for the polymerization. It is also commercially and industrial used procedure for the formation of polymer from small unit called monomer. It is considered as best and useful way for the production of polymer, by generation of radical center. Free radical polymerization is widely used method for the industrial production of polymer. Almost, 1 Billion ton polymer per year produced by this way. It represents 54 % synthetic polymer production. Now a day, many other polymerizations technique that is devised from free radical polymerization is industrially applicable. Controlled and living radical polymerization is one of the best examples of this application. Free radical has been known for more than 70 years. Its reaction mechanism include the process mechanism, proper understanding of kinetics and chemistry of basic reaction involved, with the determination of the corresponding absolute rate constants, the structure, and concentrations of the growing species, as well as a correlation of the structure of the involved reagents and their reactivates. A multitude of monomers can be used in radical polymerization.

Free-radical solution polymerization has its application in many industrial and research areas. By this process acrylic resin is commercially produces and it is used in paint, coating and adhesive industry. Now a day many Environment hazards are involved with usage of polymer materials. In order to surpass this tighter environmental regulation, polymerization method has moving toward higher temperature and lower solvent level. Properties of final polymer coil formed by free radical polymerization is effected by many reaction such as chain transfer to polymer, thermal initiation and branching plays a vital in controlling the molecular structure and polymerization rate of polymer. Many research works has been done on the chain transfer to polymer (CTP) in conventional free-radical polymerization (FRP) of ethylene and vinyl acetate, and gives rise to short- and long-chain branches via intra- and inter-molecular processes, respectively.

In common with other type of chain polymerization and reaction can be divided into three separate stages: initiation, propagation, termination.

## 2.7 Mechanism

### 1 Initiation

Polymerization starts with the step called initiation. Initiator adds in the system. Most prominent example of initiator are molecule like benzoyl peroxide (BPO) or 2,2'-azo-bis-isobutyrylnitrile (AIBN). Main reason for its selection as an initiator is its ability to decompose and generate free radical. Mostly by heating thermal decomposition occur and it breaks and generates free radical, by heating strong triple bond of Nitrogen –N (N2) formed. Double bond of Nitrogen N=N breaks into AIBN and form triple bond of nitrogen.

These unpaired electrons in the molecule are referred as free radicals.

It is generally a 2-step reaction:

1. Generation of a radical (1st step)
2. Chain Reaction initiation (2nd step)

**2 Propagation**

In propagation step chain further grow by the successive addition of monomer in the radical centre. In an initiation step chain initiate by the generation of radical centre, then monomer addition in the propagation step can lead the further propagation of chain. Macro-radical is formed in this step because most of the monomer is consumed by addition into polymer chain and big radical formed sometime referred as polymer radical. During propagation step nearly, 99% of the Polymer produced. Two steps are involved in this propagation step:

1. Successive addition of monomers to the reactive radical center
2. Polymerization at its peak, nearly 99% of monomer consumed in this step

**3 Termination**

These Polymer-Radicals that formed during propagation step are unstable. It tries to stabilize itself by finding a way to pair with some other radical without generation of new radical center. This is how this polymerization terminates and chain reaction will become stable.

There are many ways to terminate the free radical polymerization. The simplest way is to growing chain with radical coupled with each other and become stable. Coupling is basically defined as the process in which two unpaired electron joins and become paired and new chemical bond formed that joins the respective chains. Coupling is considered as one of the main types of termination reaction. Basically, it is the final step of a chain-growth polymerization.

The termination step can take place in two ways:

1. Disproportionation
2. Coupling

## 2.8 Kinetics:

In order to get proper understanding of Mechanism in free radical polymerization, Kinetics study is very important and informative to determine the rate as a function of various variables such as influence of monomer concentration and type of initiator. By applying steady state concentration, equation of kinetics has been derived. According to steady state condition, the propagation rate $R_p$ = overall polymerization rate $R_{overall.}$

So, applying steady state we can write as:

$$R_p = R_{overall} = (d(M))/dx) = kp\,[M][P^*]$$

[M] is monomer concentration

and [P*] is steady-state radical concentrations.

### 2.8.1 Average Degree of Polymerization:

The term Average kinetic chain length of polymer is defined as the step to initiate the polymer chain, by fulfilling its requirement of average number of monomer polymerize per radical. It is denoted by "*v* ". Mathematically,

$$v = R_p/R_i = R_p/R_t$$

When there is no side reaction then this average kinetic chain length "*v* " is directly related to average degree of polymerization. Degree of polymerization is denoted by, $x_n$ this parameter is totally depends on termination mechanism, i.e.

i) If disproportion is the mechanism of termination, then degree of polymerization is related with average kinetic chain length as $x_n = v$

ii) If coupling is the mechanism of termination, then $x_n = 2v$

### 2.8.2 Kinetics of step 1: Initiation

If AIBN is considered as initiator then this AIBN break into 2 radical centers as:

$$I \rightarrow 2R^*(k_d)$$

Rate of formation of active center is:

$$R_i = 2fk_d[I] \qquad \text{Equation 2.5}$$

- $k_d$ is rate constant for decomposition of initiator molecule,
- f, is initiator efficiency, it is formed by primary radical R* fraction to successfully initiate polymerization,
- Since, two radical are formed from 1 initiator molecule. That's why factor 2 is in equation.

### 2.8.3 Kinetics of Step 2: Propagation

Propagation steps where we calculate the amount of monomer consumed, so its reaction is related as:

$$d[M]/dt=kp[M]([M_1^* M]+[M^{*2}]+[M^{*3}]....[M_j])$$

$$d[M]/dt=kp[M]([M_1^*]+[M^{*2}]+[M^{*3}]....[M_j^*])$$

So [M*] is considered as concentration of all radical species then

$$-(d[M]/dt)=k_p[M]\ [M^*]- \qquad \text{Equation 2.6}$$

### 2.8.4 Kinetics of Step 3: Termination

Termination can be represented by:

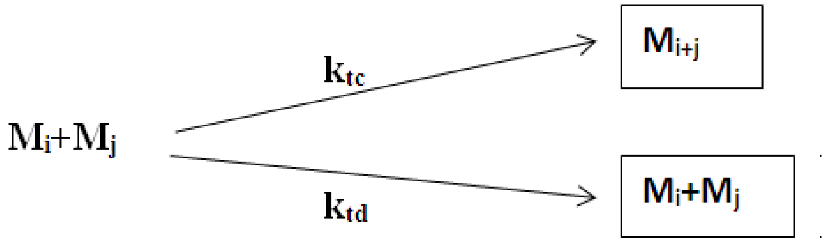


**Figure 2.1** Schematic of termination reaction

Therefore, $k_{tc}$ and $k_{td}$are the rate constants for coupling and disproportionation, respectively. Thus overall rate can be written as:

$$-d[M]/dt=2k_{tc}[M^*][M^*]+2k_{td}[M^*][M^*]$$

Use of total concentration [M*] of radical species arises between two growing chain of any length is consumed by each termination reaction:

Above Equation is simplified as:

$$-(d[M]/dt)=2kt[M^*]^2 \qquad \text{Equation 2.7}$$

Where $k_t$ is the overall rate constant for termination and is given by:

$$k_t = k_{tc} = k_{td}$$

## 2.9 Steady State Concentration Case:

Equation for steady states equation is:

$$dR/dt = -(d[M])/dt)$$

Solution of initiation and termination equations (2.1 and 2.3) gives [24]:

$$R_i = 2k_t[M^*]^2$$

According to steady state condition the total concentrations of all radical species are given by:

$$[M] = \sqrt{(R_i)/2kt}$$

$R_p$, is considered as rate of polymerization, we can calculate the rate of polymerization by taking value of total concentration from above equation and putting in Equation 2.2. So final equation we get as:

$$R_p = -(d[M]/dt)$$

By further simplification we can write as:

$$Rp = \frac{(k_p)}{2^{1/2} k_t^{1/2}} R_i^{1/2} [M]$$

Above equation indicate that rate of polymerization $R_p$ is directly proportional to total concentration [M] and it shows 1st order dependence

## 2.10 Chain Transfer to Polymer (CTP)

Highly branched polymers with some specific properties are formed as a result of chain transfer to polymer (CTP). CTP occur by free radical polymerization. Polyethylene is produced by free radical polymerization at high pressure and temperature. CTP is well observed as by this polymerization in polyethylene [65]. In case of free radical polymerization of n-Butyl Acrylate chain transfer to polymer is well established it involves abstraction of hydrogen atoms from backbone tertiary C-H bonds. N- Butyl Acrylate shows high branching by free radical polymerization has been previously observed. Either the propagation reaction or chain transfer reaction occur is totally depends upon extent of chain transfer to polymer in free radical polymerization of given monomer. In case of all acrylate radical polymerization some reasonable and basic principle should be applicable [66] Our system contains n-Butyl Acrylates n-BA as a principle monomer because of its considerable interest and largely used acrylate monomer also shows maximum extents of Chain transfer to polymer in conventional Free radical polymerization.

The primary reactions of chain transfer are:

$$P_n \rightarrow Q_n \qquad \text{(Backbiting)}$$

$$P_n + D_m \rightarrow D_n + Q_m \qquad \text{(Chain Transfer to polymer)}$$

Where $P_n$ is secondary radical with chain length n
Occurrence of backbiting can lead tertiary radical $Q_n$
$D_n$ $D_m$ are dead polymer chain having length n and m

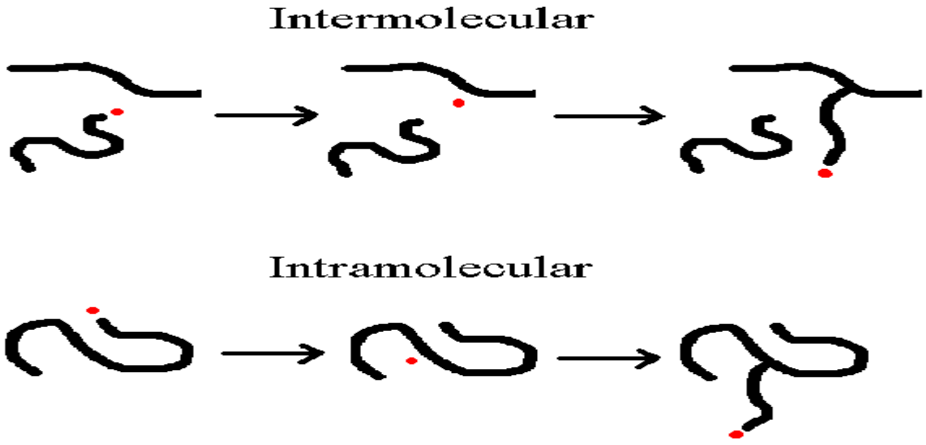


Figure 2.2. Schematic representation of the inter-molecular and intra-molecular CTP during the free-radical polymerization reactions.

The key objective of the present thesis is to study the extent of chain transfer to polymer in free radical solution polymerization of n-Butyl Acrylate with three different solvents. Solvent vary in term of their sizes, selected solvents are cyclohexane ($C_6H_{12}$), cycloheptane ($C_7H_{14}$) and cyclooctane ($C_8H_{16}$). Resulting polymer formed by intramolecular or intermolecular chain transfer to polymer shows same chemical structure NMR analysis cannot distinguish between these two events [66] Nevertheless, by carrying out solution polymerizations at constant monomer concentration and equal conversion of n-BA with three different solvents the probability of both intramolecular and intermolecular chain transfer to polymer can be varied in a controlled way, We can find out the key role of these two process at different monomer concentration. When the concentration of monomer is less then intramolecular CTP plays its part while in case of high concentration intermolecular CTP is prominent. That's why solution polymerization has been considered and low concentration of monomer is selected because at low concentration the total polymer concentration is very less that's why interamolecular is favored and probability of intermolecular CTP is very less. Increasing solvent from cyclohexane to cyclooctane has been considered because it is considered as good solvent with n-BA and very less effect the polymer system. Second reason is its low transfer constant. A low value for solvent $C_{\mathrm{trS}}$ is important, because it nullify the complication arises from Chain transfer to solvent [66].

Two types of reactions are likely to occur when polymerization of n-Butyl Acrylate is performed. In first case intramolcular CTP and in other case intermolecular CTP occur. In first case polymer chain backbit its own chain and we called its intramolecular and in other case the active center of polymer chain target the dead end of other polymer chain. So radical center is transferred to dead end it is called as intermolecular CTP.

Several explanations has been explained about the short chain radical, that undergoes only intramolecular CTP in less concentration. In conventional Free radical polymerization, there is more affinity of chain transfer to polymer because there is broad distribution of radical concentration. In this case short range of radical is always present, [66] whereas in other case like controlled radical polymerization, the affinity of chain transfer is less because less and very narrow distribution of radical concentration is available. Also, very less proportion of short-chain radicals is present in controlled living polymerization. So, it concludes that free radical polymerization shows more branching than controlled radical polymerization under similar working condition. The acrylate monomer that shows branching during free radical polymerization also shows same trend as mentioned above.

Typical reaction mechanism of acrylate monomer includes:

- Initiation
- Propagation
- Backbiting
- Re initiation
- Termination

## 2.11 Intramolecular Chain Transfer:

In case of free radical polymerization of nBA the probability of intramolecular chain transfer to polymer is high because of less monomer concentration and solution polymerization. Intramolecular CTP has been more favored and more consideration type of polymerization because of newly developed reaction path and available tool for characterization.

It is also referred as backbiting; In case of ethylene, it is well described. Formation of six- membered carbon ring and hydrogen abstraction has been explained. This pictorial has depicts the intramolecular reaction and represent backbiting of carbon atom.

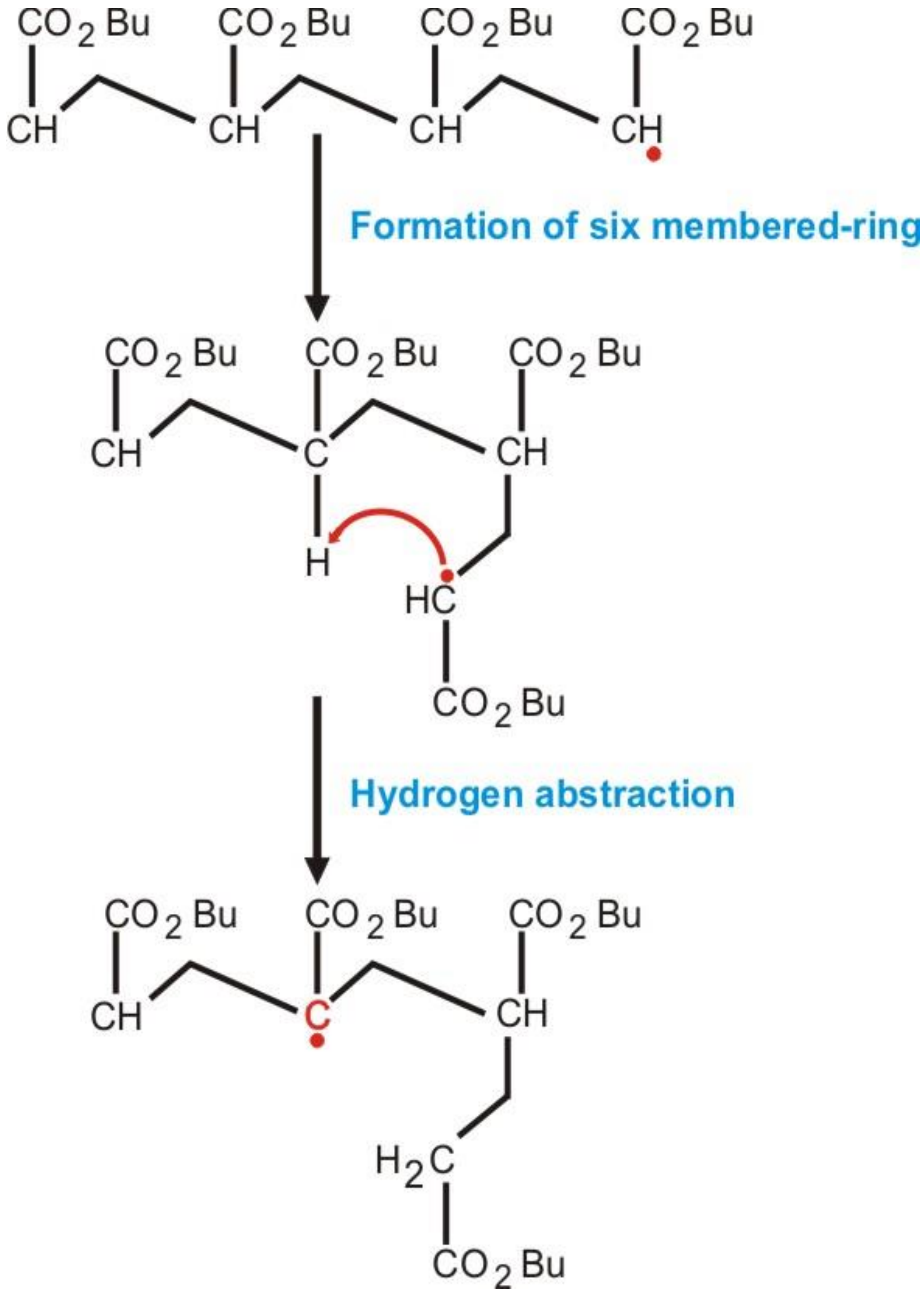


Figure 2.3. Schematic of intramolecular chain transfer reaction

## 2.12 Solution Polymerization

In Industry, solution polymerization is mostly used for the commercial production of polymer. During this process monomer is dissolved in a solvent, that is not reactive and only contain catalyst for polymerization.

Polymer formed by this reaction is also soluble in the solvent and also heat ejects from the system is absorbed by the solvent, and ultimately the reaction rate is reduced. Furthermore, the reaction product (resulting polymer) viscosity and concentration of monomer are reduced. When the desired Polymer with specific properties is formed, excess solvent has removed to keep the properties constant. Therefore, this type of polymerization has many application areas some are varnish and adhesive where the solvent quantity and presence is required.

# Chapter 3

# Computational Model

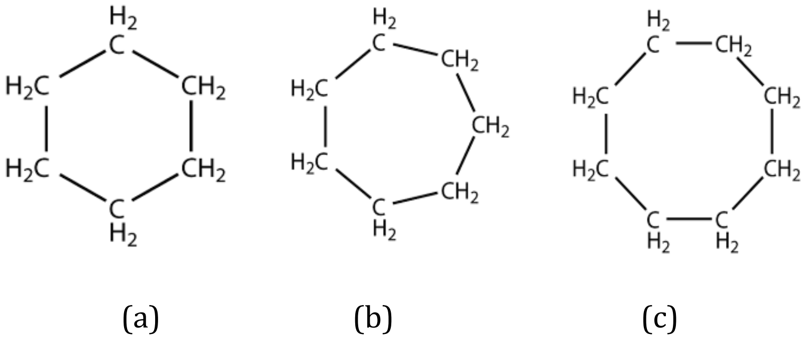
All computations in this project were performed using Gaussian 09 software. This study specifically focused on the free radical solution polymerizations of nBA with three cyclic solvents that are different from each other in term of their sizes. This chapter will describe the feasibility and miscibility of polymer butyl acrylate with three solvents. Some detail about computational approach that is used in drawing and optimization all including transition state geometries of polymer coil in three different solvents is also explained.

## 3.1 Materials and Methods:

Monomer n-BA is polymerizing with three cyclic solvents. These solvents are:

- Cyclohexane ($C_6H_{12}$)
- Cycloheptane ($C_7H_{14}$)
- Cyclooctane ($C_8H_{16}$)

The structures of these solvents, selected on the basis of their sizes are shown in Figure 3.1. All other interactions are assumed to be absent i.e., ΔH=0. Solvents are true solvents only size effect will be considered



(a) (b) (c)

Figure 3.1. Schematic of (a) cyclohexane (b) cycloheptane (c) cyclooctane [67-69]

Table 3.1. Materials used during polymerization.

| No | Monomer | Solvent | Polymerization | Temperature |
|---|---|---|---|---|
| 1. | n-butyl acrylate | cyclohexane<br>cycloheptane<br>cyclooctane | Free Radical Solution Polymerization | $25^0$C/298K |

Table 3.2. Properties of solvent in polymerization of nBA [70]

| Properties | Cyclohexane ($C_6H_{12}$) | Cycloheptane ($C_7H_{14}$) | Cyclooctane ($C_8H_{16}$) |
|---|---|---|---|
| Molar mass | $84.16 gmol^{-1}$ | $98.16 gmol^{-1}$ | $112.21 gmol^{-1}$ |
| Boiling point | $80.74^0$C | $118^0$C | $149^0$C |
| Density | 0.7781g/ml | $0.811 g/cm^3$ | $0.834 g/cm^3$ |

## 3.2 Feasibility of Reaction:

**Solubility Parameter:**

Solubility Parameter is widely used to assess polymer- solvent interaction. It is defined as

$$\delta=\left(\frac{\Delta E}{V}\right)^{1/2} \qquad \text{Equation 3.1}$$

Where ΔE is the cohesive Energy and V is molar Volume

We can relate the relation between polymer and solvent as:

1. A good solvent for a given amorphous polymer is one whose solubility parameter δs is equal to or close to the solubility parameter for the polymer, δp, i.e., δp=δs. This is an agreement with the general rule that like dissolve like and that chemical structure similarities favor solubility.
2. As the difference between δp and δs become larger the solvent becomes poorer

The solubility Parameter approaches can be extended to the prediction of polymer-solvent miscibility and it requires the knowledge of δ value for the solvent and polymer. An estimation of δ from a known structure of polymer repeats unit can be made [71]. These estimations lead to an approximate guide to the polymer solvent miscibility. In these estimation procedures the contribution to the cohesive energy ($E_{coh}$), of various group present in the polymer repeat unit are considered. Such group contribution methods are based on data for small molecules. Table 3.2 summarizes the contribution of some important structural group to $E_{coh}$ with molar volume. Using values from Table 3.2 and putting in Equation 3.1 solubility parameter of PBA and three selected solvents i.e cyclohexane, cycloheptane and cyclooctane were calculated. The difference (δp- δs) were also calculated for PBA with three solvents. The results are summarized in Table 3.3.

Table 3.3. Group contributions to cohesive energy, $E_{coh}$, and Molar Volume, $V_M$ [72]

| **Group** | **$E_{coh}$ (298K)/Jmol$^{-1}$** | **$V_M$ (298K)/cm$^3$mol$^{-1}$** |
|---|---|---|
| $-CH_3-$ | 9640 | 33.5 |
| $-CH_2-$ | 4190 | 16.1 |
| -CH- | 420 | -1.0 |
| -C- | -5580 | -19.2 |
| -COO- | 13410 | 18 |

. Polymer Butyl acrylate Solubility Parameter δp=18.70 $J^{1/2}cm^{-3/2}$

Table 3.4. Estimated Solubility parameter for three solvents and δp-δs values

| **Solvent** | **Solubility Parameter (δs) $J^{1/2}cm^{-3/2}$** | **(δp-δs) $J^{1/2}cm^{-3/2}$** |
|---|---|---|
| cyclohexane | 16.132 | 2.568 |
| cycloheptane | 16.132 | 2.568 |
| cyclooctance | 16.132 | 2.568 |

Results show that all three solvents interact equally well with the polymer. They are not excellent solvents because δp-δs values show that it is neither zero nor very close to it. Result shows that Polymerization in suggested three solvents is feasible and literature also shows that polymerization occur in these solvents.

## 3.3 Free Energy of Mixing:

In order to check thermodynamic criteria for solubility of Polymer in solvent free energy of mixing $\Delta G_M$ is used. Two substances are mutually soluble if, at least $\Delta G_M$ is negative.

$$\Delta G_M = \Delta H_M - T\Delta S_M \qquad \text{Equation 3.2}$$

Where $\Delta H_M$ is enthalpy of mixing and $\Delta S_M$ is entropy of mixing.

As $\Delta S_M$ has generally positive value and also $\Delta H_M$ has limited positive value below which polymerization is possible.

Flory Huggins lattice theory for the predicts the relation for polymer solution [44] i.e.,

$$\Delta G_M = \Delta H_M - T\Delta S_M = nRT[\frac{\varphi}{x}\ln\varphi + (1-\varphi)\ln(1-\varphi) + \chi\varphi(1-\varphi)] \qquad \text{Equation 3.3}$$

Where $\Delta H_M$ and $T\Delta S_M$ can also be further modified as

$$\Delta H_M = nRT\chi\varphi(1-\varphi)$$

$$TS_M = nRT[\frac{\varphi}{x}\ln\varphi + (1-\varphi)\ln(1-\varphi)]$$

φ = Volume fraction of polymer

(1-φ) = volume fraction of solvent

χ = Flory Huggins interaction parameter

And x = degree of Polymerization

### 3.3.1 Athermal Solvency Condition:

The effect of solvent on Polymer chain configuration depends on the difference between polymer-polymer, polymer-solvent and solvent-solvent interaction. The simplest case where all interactions are identical, the coil will not have preference for more or fewer segment-segment contact and it will behave as a regular self-avoiding walk. Such a solvent is called Athermal solvent, as there will be no heat of mixing. A situation occur where polymer refer as ideal chain similar to ideal gas model. The probability of finding a chain is very easy by Gaussian distribution. Such a condition is also known as theta condition.

Polymer solvent interaction is more favorable then polymer-polymer contacts then coil will tend to promote such trend by expanding the more. This is a proper evidence of liking of polymer chain to solvent.

Now according to our assumption we are dealing with athermal condition where enthalpy of mixing is zero. So, we can write as $\Delta H_M = 0$ in Equation 3.3 [73]

$$\Delta G_M = 0 - T\Delta S_M = nRT[\frac{\varphi}{x}\ln\varphi + (1-\varphi)\ln(1-\varphi) + 0]$$

$$\Delta G_M = -T\Delta S_M = -nRT[\frac{\varphi}{x}\ln\varphi + (1-\varphi)\ln(1-\varphi)] \qquad \text{Equation 3.4}$$

At constant temperature and degree of polymerization only controlling parameter is available are volume fraction of solvent and polymer. Equation 3.4 clearly shows that we get negative value of free energy of mixing $\Delta G_M$. It also shows that polymerization is feasible under athermal solvency condition.

## 3.4 Computational Model:

Density Functional Theory (DFT) has been used to study the free radical polymerization mechanism i.e., propagation reaction in n-butyl acrylate. DFT is in principle and exact ground state technique. The accuracy of DFT depends on exchange correlation function. Generally, it is used to predict the molecular geometry and energy barrier with accuracy.

Software package of Gaussian 09 [74] is used on the supercomputer to compute the propagation of monomer (nBA) and investigate the role of solvents.

### 3.4.1. Density Functional Theory:

In general, DFT is defined as a method of obtaining an approximate solution to the Schrodinger equation of a many-body system. In quantum mechanics Schrodinger Equation is used to describe the energy of a given system.

Mathematically it is written as:

$$H\Psi = E\Psi$$

Where H is a Hamiltonian describe the Dynamic of a molecule.

E is Energy and $\Psi$ is a wave function of a single molecule.

Hamiltonian contains the Kinetic and Potential energy of a single molecule.

**Single Molecule to Polymer Chain (Schrodinger Equation for Polymer Chain):**

- Hamiltonian describes the dynamics of whole chain.
- Ψ represent the wave function of whole system.
- Ψ contain the wave function of all molecule in a chain.

We faces following computational challenges:

1) Mathematical equation that completely describe the dynamics of single molecule
2) Generalize that equation to the set of non-solvable system of equations, which describes the chain of molecule.
3) Computational techniques and approximations are used to simplify the equations to get the solution.

**Hartree-Fock Approximation:**

Electron correlations are completely negligible for electron of opposite spin but taken into account for electron of parallel spin

By using Hartree Fock the final Energy is in the form of:

$$E_{HF} = V + < hp > + 1/2 < Pj(P) > - 1/2 < PK[P] >$$

V= Nuclear repulsive Energy

[P] Density Matrix

<hp> one electron energy (Kinetic + Potential)

1/2<Pj(P)>The classical coulomb repulsion of the electrons.

-1/2<PK[P]>The exchange quantum energy

**Density Functional Theory:**

We can further simplify our model using Kohn Sham Equation. Exchange quantum (HF) for a single determinant is replaced by a more general expression, the exchange-correlation functional

$$E_{KS} = V + < hp > + 1/2 < Pj(P) > E_x[P] + E_c[P]$$

$E_X$[P] is the exchange functional, and $E_C$[P] is the correlation functional

Exchange Function is considered as effect occurs because of electron of same spin. Correlation function effect explains how the movement of one electron influenced by the presence of all other electron. Gaussian 09 software supports hybrid density Function i.e., B3LYP in this software.

Density functional theory is successfully applied to study the free radical polymerization reaction. It is also used to identification of transition state geometry that is unable to analyze in experimentation.

## 3.5 Gaussian 09

Gaussian 09 software is used for computational analysis [74]. It is used worldwide for modeling and simulation by chemists, materials engineers, physicists and scientists. Gaussian 09 contain scientific modeling feature and it is impossible to add artificial limitation and calculation in it. It is different from previous version because it produces complete, reliable and accurate models.

It is very simple and easy tool of calculation even a difficult system is computed easily and automated.

It gives us complete control on data and calculation. Also, it provides flexibility in data handling and easy to use option. Results obtained from computational analysis are natural and intuitive graphical form.

We used this software for following analysis:

1. Gauss view (GUI) was used to develop the optimized/transition state geometry of polymer coil. (GUI is graphical user interface for Gaussian 09)
2. Calculate the activation energy of polymer coil
3. Study the solvation by considering the role of different solvent

**Geometrical Parameter:**

All geometries were optimized using Gaussian 09 with the hybrid density functional B3LYP [75] and the 3-21G basis set [76-78]. The reaction starts by the decomposition of initiator 2,2'-azo-bis-isobutyrylnitrile (AIBN). It was selected as an initiator because it easily decomposed and generates free radical. Triple bond of Nitrogen is formed by the breakage of double bond of Nitrogen- N (N2) in AIBN initiator. After that one free radical attacks the monomer and Polymerization started. Frequency calculation proved transition states to have exactly one imaginary frequency with the correct transition vector. This starting active butyl acrylate was then further utilized for generation of polymer coil. Single point energies were computed with the B3LYP functional and the Stuttgart-Dresden effective core potential basis set (SDD) [79-80] augmented by polarization functions for all atoms except H ($\zeta$ =0.600, 1.154, and 0.864 for C, O, and N respectively). Self-consistent reaction field (SCRF) computations were performed on the optimized geometries to model the solvent surrounding the active site by a conductor like polarizable continuum method (CPCM) [81] as implemented in Gaussian 09 [82-83].

## 3.6 Supercomputer:

Supercomputer has been used for computing as Gaussian 09 software package is installed on it. It is available at Research Center for Modeling and Simulation, NUST, Pakistan.

Figure 3.2. Supercomputer at RCMS, NUST [84]

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Table 3.5: Specification of Supercomputer [84]

| **Specification:** | **Super computing** |
|---|---|
| Total Number of Nodes | 34 |
| Number of Processing Cores | 272 |
| Total Memory | 1.312TB |
| Operating System | CentOS Linux 6.5 |
| Interconnects | Infiniband Switch |
| Storage | 22TB |
| Performance | 132 Teraflops |

## 3.7 Free Radical Polymerization:

We used computational tool to investigate the propagation of polymer via free radical polymerization process. Polymerization that starts with an active center is called free radical polymerization.

**Initiation Reaction:**

Active center is generated by the initiator 2,2'-azo-bis-isobutyrylnitrile (AIBN). It decomposes into two radical one of the radical attacks the monomer and polymerization process starts.

**Propagation Reaction:**

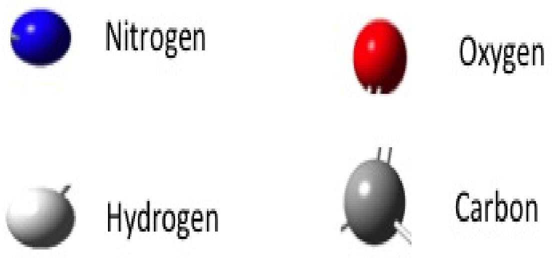
Polymer coil of different size were developed using Gauss view GUI and optimized its energy and optimization using Gaussian 09 to conclude that either the polymerization occur or not. But the results clearly elaborate the polymerization occur. Following are the geometries of coil with different monomer unit.

2-Unit Monomer Chain

3-Unit Monomer Chain

4-Unit Monomer Chain

5-Unit Monomer Chain



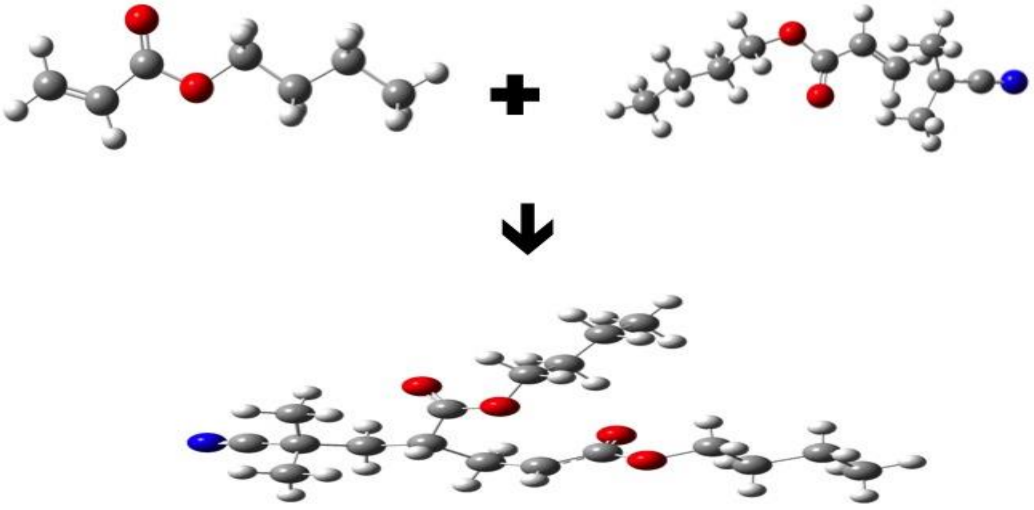


Figure 3.3. Formation of 2-Unit Monomer Chain.

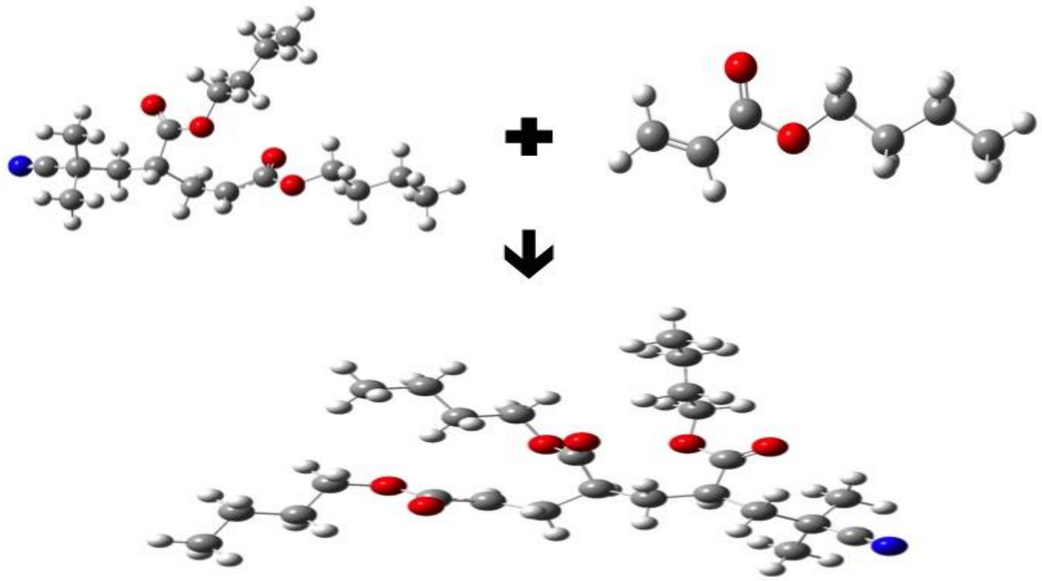


Figure 3.4. Formation of 3-Unit Monomer Chain

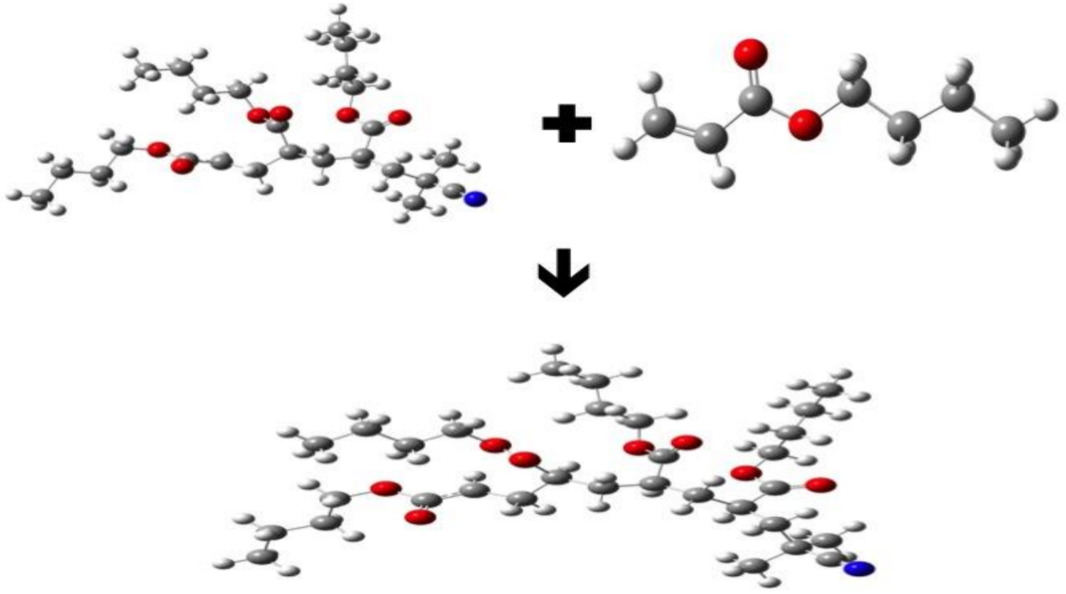


Figure 3.5. Formation of 4-Unit Monomer Chain

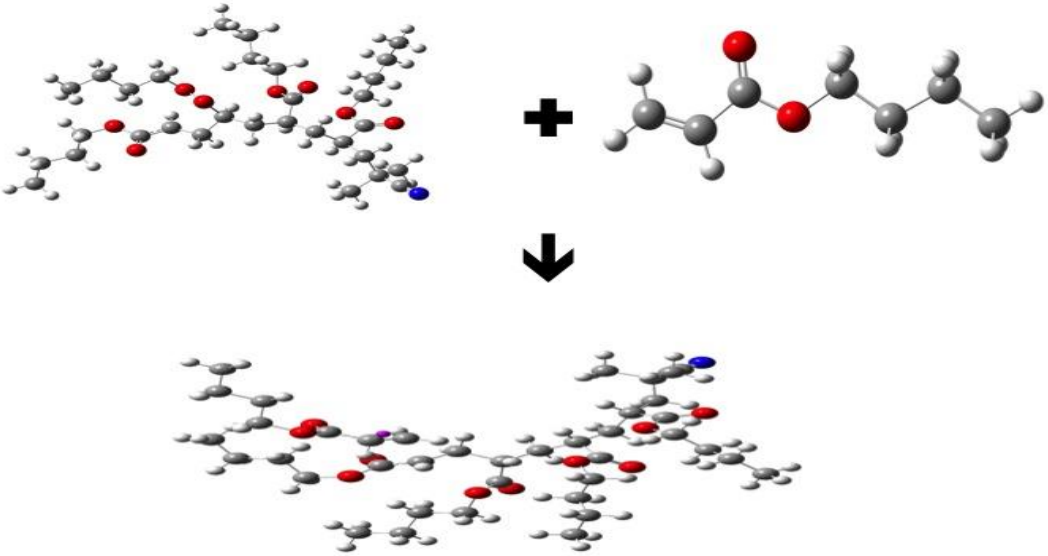


Figure 3.6. Formation of 5-Unit Monomer Chain

## 3.7 Computational Calculation:

The thermodynamics and kinetic parameter of propagating polymer chain of n-BA are calculated using DFT approach. All geometrical parameter were discussed in previous section. We use Gaussian 09 software package for all computation.

Arrhenius equation is also used for further calculation of frequency factor (A):

$$k_p = A\exp(-E_a/RT)$$

Where $E_a$ is activation energy,

$k_p$ is the rate of propagation

R is Gas constant

T is temperature

We started our computational approach with the formation of polymer via free radical polymerization. Transition state geometry were computed then estimate the behavior of solvents by applying Arrhenius relation.

# Chapter 4

# Results and Discussions

Different results obtained from the computational analysis will be discussed in this chapter. The computed results of optimization and single point energy of polymer coil will be presented in the 1st part of the chapter. The 2nd Part contains the role of cyclic solvents ($C_6H_{12}$, $C_7H_{14}$ and $C_8H_{16}$) in the activation energy of monomer conversion to polymer. Chapter also discusses the variables of Arrhenius equation to differentiate the solvent behavior. Some comparison of results with literature is also discusses in this chapter.

## 4.1 Stability of Polymer chain:

Density functional Theory (DFT) has been used to study the free radical polymerization reaction. First step is to draw the polymer coil and optimize it to lowest energy state so that further computational analysis will be performed. We started our chain from monomer to 5-Unit monomer chain. Firstly, we computed the optimization then calculate the single point energy. Polymer coil of different size were developed using Gauss view (GUI). Formation of polymer coil by free radical polymer has been discussed in Chapter 3.

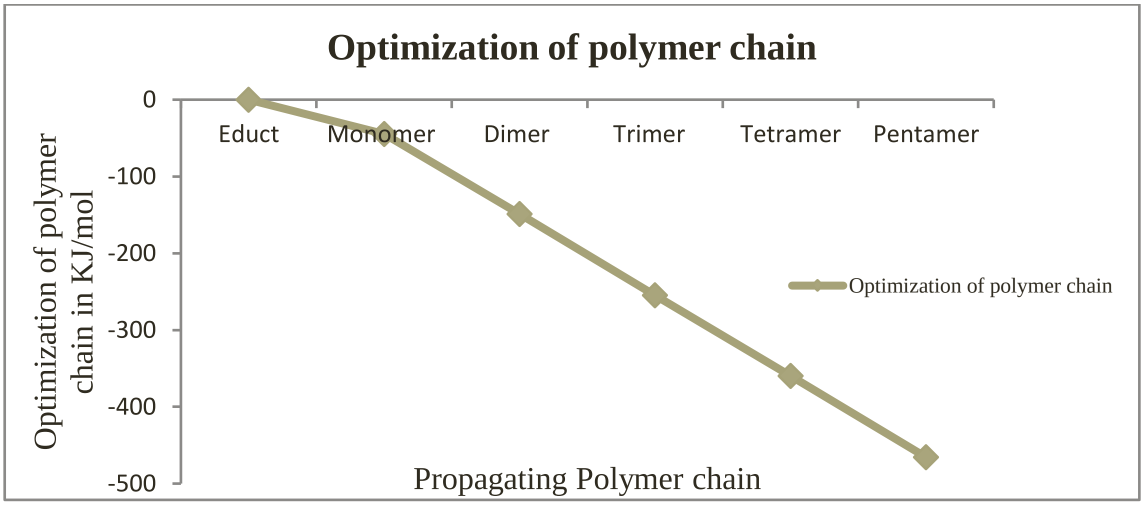


Figure 4.1. Computation results of optimization of Polymer coil

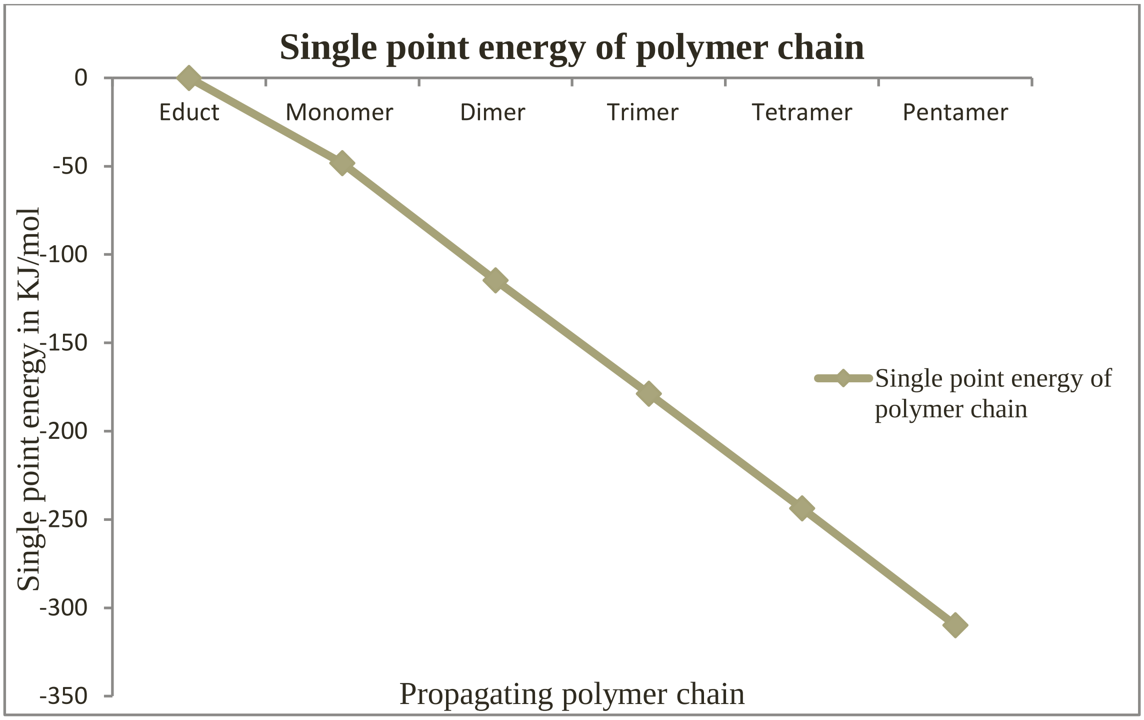


Figure 4.2. Computation results of single point energy of polymer coil

Single Point Energy is basically the potential energy required to convert reactant to product. From the result it clearly estimated that approximately same amount of energy is required for all conversion. For example: monomer conversion to dimer and dimer conversion to trimer required equal amount of energy.

## 4.2 Role of Solvent:

### 4.2.1 Computational studies of Polymer Geometry:

To understand the influence of solvent in free radical solution polymerization of n-BA, different sizes of polymer coil geometries and transition states were computed using B3LYP/3-21G electronic structure at Gaussian 09 software. Solvation of polymer chain was studied by considering solvents cyclohexane $C_6H_{12}$ then cycloheptane $C_7H_{14}$ and finally cyclooctane $C_8H_{16}$.

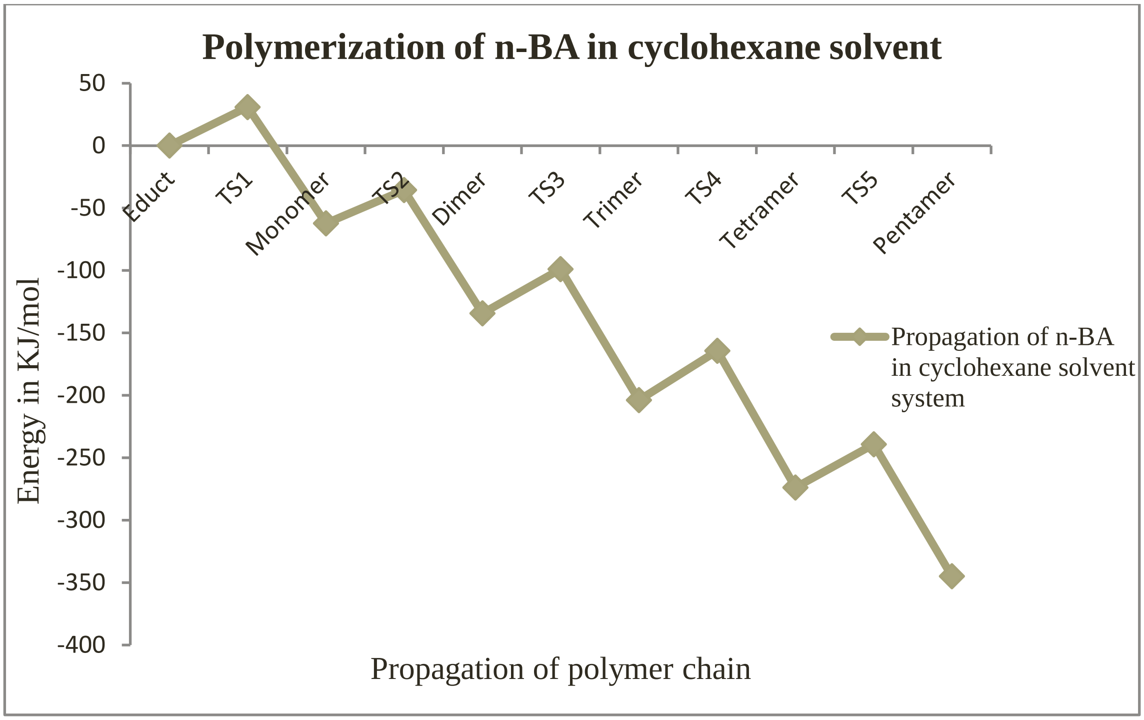


Figure 4.3. Computational results of energy for transition state and propagating polymer chain in cyclohexane solvent system

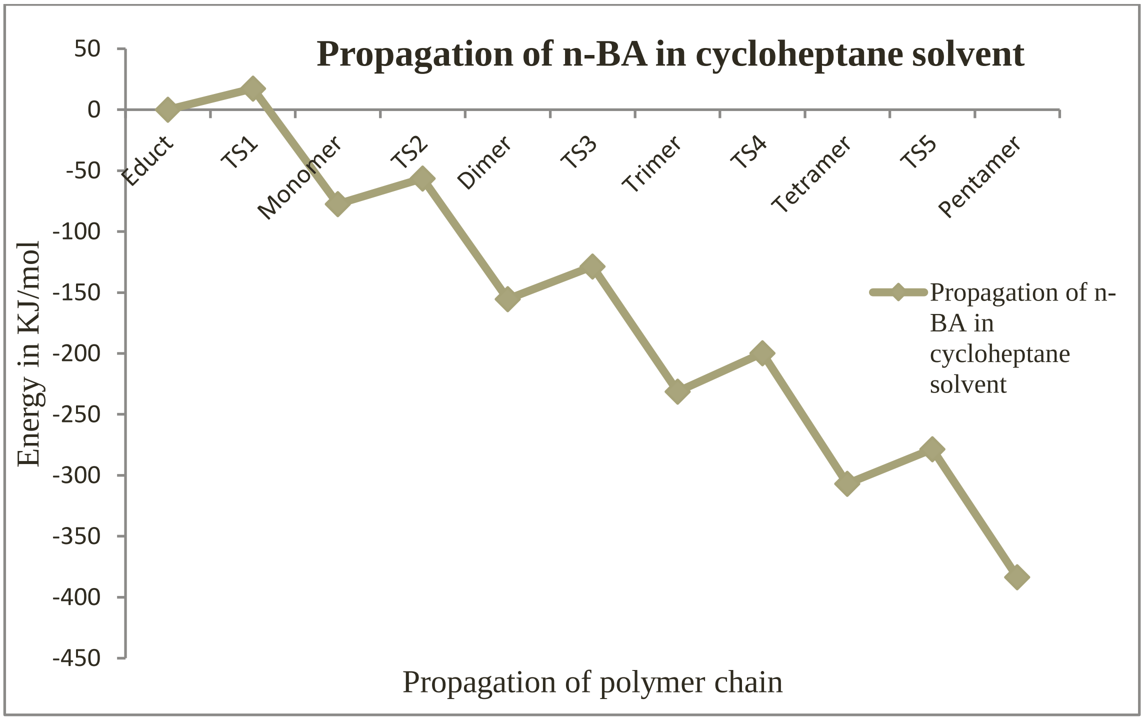


Figure 4.4. Computational results of energy for the transition state and propagating polymer chain in cycloheptane solvent system

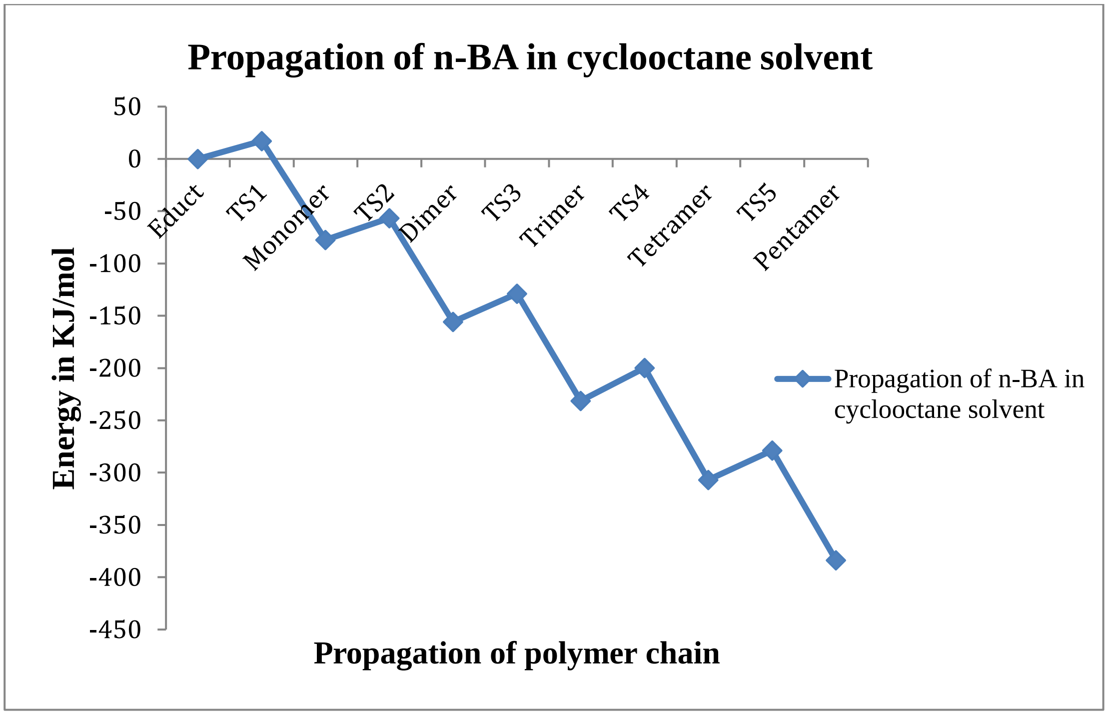


Figure 4.5. Computational results of energy for the transition state and propagating polymer chain in cyclooctane solvent system

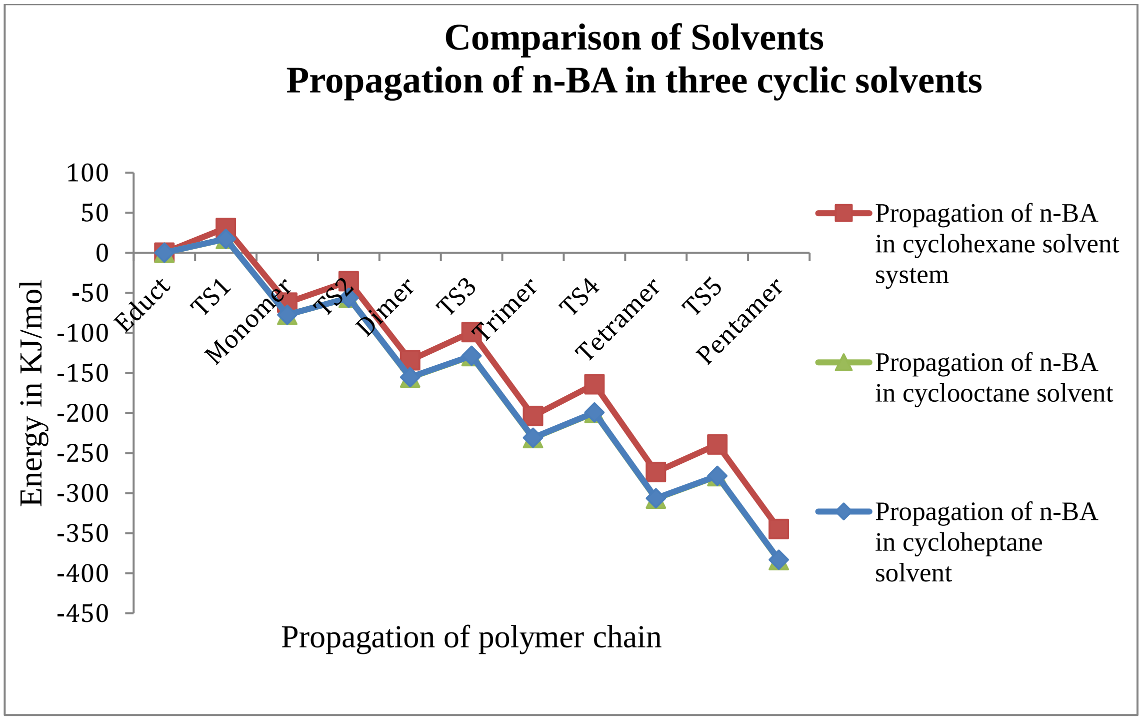


Figure 4.6. Comparison of solvents in the propagation of polymer chain

Figure 4.3. Figure 4.4. and Figure 4.5. shows the computed results of polymer chain geometries and transition states in three cyclic solvents. Figure 4.6. depicts the comparison of computed results. Computed results of propagating polymer chain indicates that more activation energy is required to convert reactant to product when solvent $C_6H_{12}$ is used than other two solvents ($C_7H_{14}$ and $C_8H_{16}$). Results will be explained in details in next section.

## 4.3 Estimation of Activation Energy in propagation of polymer chain:

The polymer chain of n-BA was propagated using free radical polymerization. The activation energy of the n-BA are estimated from measurements of monomer conversion to polymer in free radical solution polymerization. Activation energy is the minimum energy required to form the polymer chain. In this work different sizes of chain were propagated at 298K to estimate the Arrhenius Parameter (A) and Activation energy ($E_A$). Temperature is selected as room temperature because at higher temperature depropagation of polymer chain become a significant complicating factor [85].

Activation Energy $E_A$ and frequency factor A has been calculated by keeping $k_p$ constant at specific temperature. $k_p$ is temperature dependent property, It is taken from the literature [86].Value of $k_p$ in our analysis is 15,832 $Lmol^{-1}sec^{-1}$.

### 4.3.1 Monomer Conversion to Dimer:

Transition state of dimer is confirmed by single imaginary frequency, which is equal to -330.490 $cm^{-1}$. It is also the required transition states

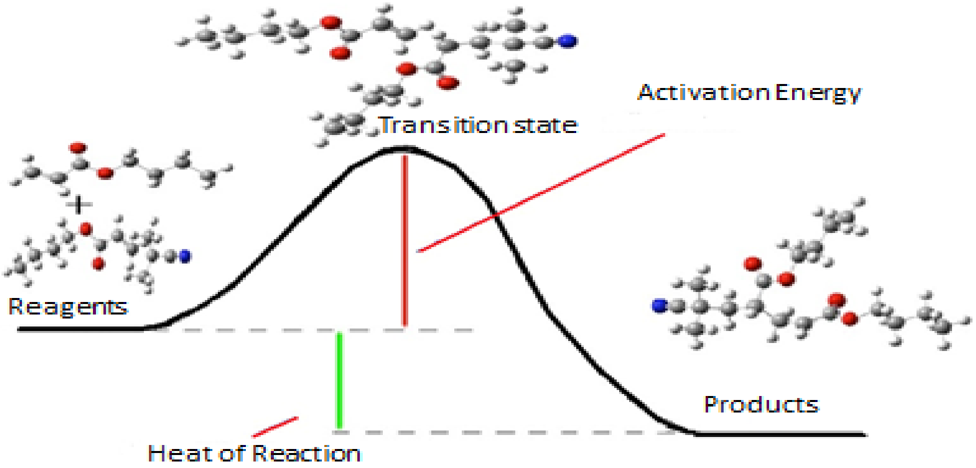


Figure 4.7. Energy diagram for monomer conversion to dimer

Table 4.1 Calculated results of activation energy, heat of reaction and frequency factor of monomer conversion to Dimer

| **Solvent** | **Activation Energy (KJ/mol)** | **Heat of reaction (KJ/mol)** | **Frequency factor (A) Lmol$^{-1}$sec$^{-1}$** |
|---|---|---|---|
| **Cyclohexane** | 26.78 | -73.64 | 7.54E+08 |
| **Cycloheptane** | 20.98 | -78.24 | 7.68E+07 |
| **Cyclooctane** | 20.98 | -78.24 | 7.52E+07 |

### 4.3.2 Dimer Conversion to Trimer:

Transition state of trimer is confirmed by single imaginary frequency, which is equal to -319.090 $cm^{-1}$. It is also the required transition states

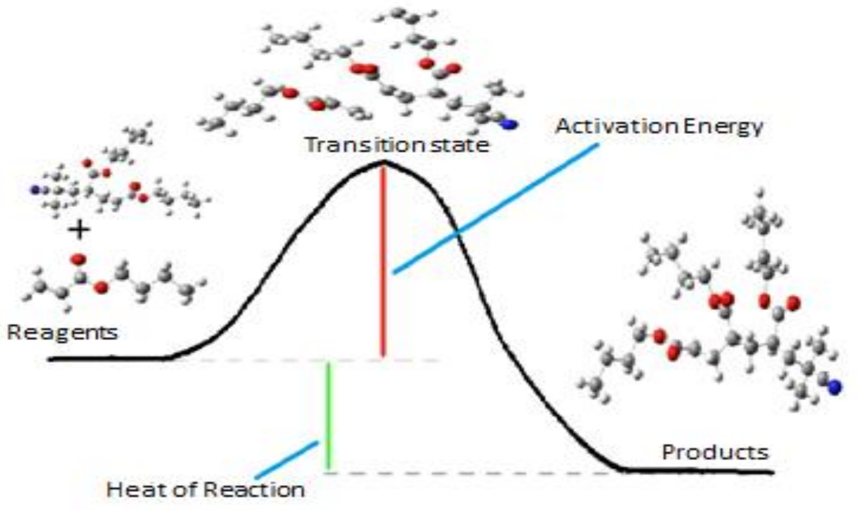


Figure 4.8. Energy diagram for dimer conversion to trimer

Table 4.2. Calculated results of activation energy, heat of reaction and frequency factor of dimer conversion to trimer

| **Solvent** | **Activation Energy (Kcal/mol)** | **Heat of reaction (Kcal/mol)** | **Frequency factor (A) $Lmol^{-1}sec^{-1}$** |
|---|---|---|---|
| **Cyclohexane** | 35.15 | -69.45 | 2.21E+10 |
| **Cycloheptane** | 26.78 | -75.73 | 7.45E+08 |
| **Cyclooctane** | 26.78 | -75.73 | 7.21E+08 |

### 4.3.3 Trimer Conversion to Tetramer:

Transition state of tetramer is confirmed by single imaginary frequency, which is equal to -359.210 $cm^{-1}$. It is also the required transition states

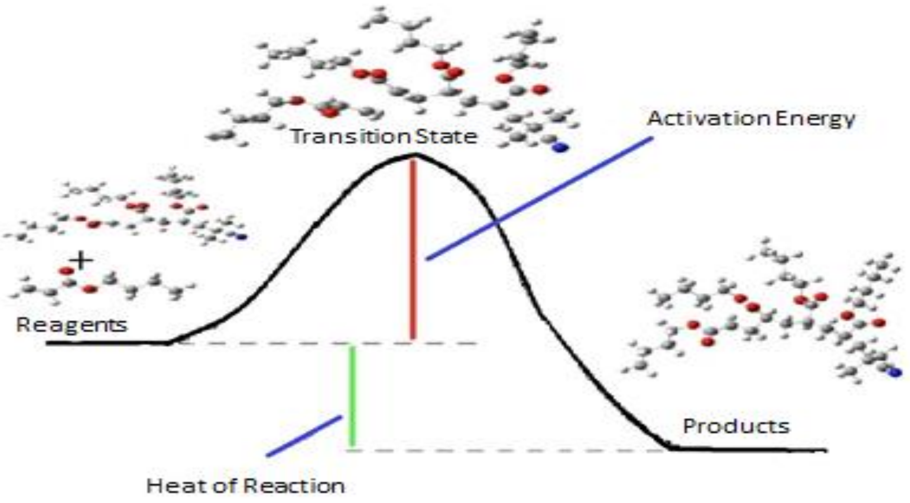


Figure 4.9. Energy diagram for monomer conversion to dimer

Table 4.3 Calculated results of activation energy, heat of reaction and frequency factor of trimer conversion to tetramer

| **Solvent** | **Activation Energy (Kcal/mol)** | **Heat of reaction (Kcal/mol)** | **Frequency factor (A) $Lmol^{-1}sec^{-1}$** |
|---|---|---|---|
| **Cyclohexane** | 39.33 | -70.29 | 1.20E+11 |
| **Cycloheptane** | 31.38 | -75.73 | 5.10E+09 |
| **Cyclooctane** | 31.38 | -75.73 | 4.94E+09 |

### 4.3.4 Tetramer conversion to Pentamer:

Transition state of pentamer is confirmed by single imaginary frequency, which is equal to -372.187 $cm^{-1}$. It is also the required transition states

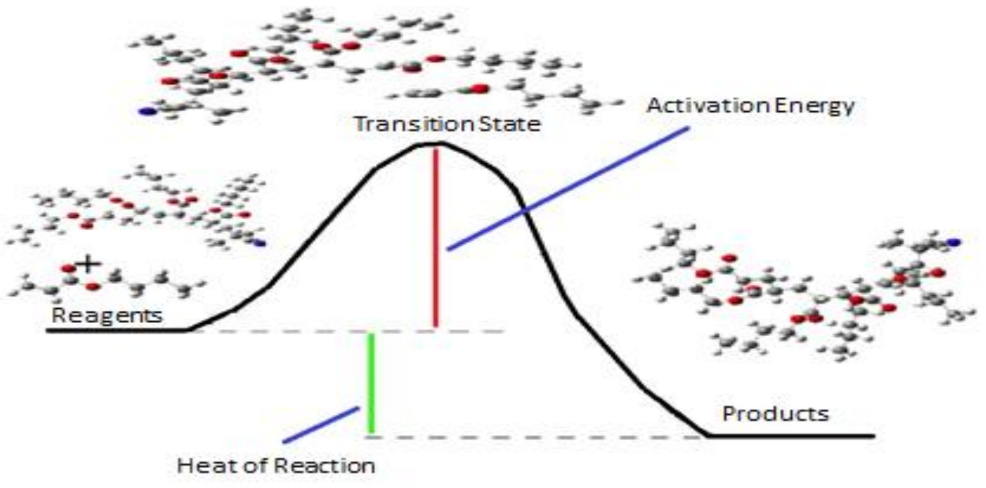


Figure 4.10. Energy diagram for tetramer conversion to pentamer

Table 4.4 Calculated results of activation energy, heat of reaction and frequency factor of tetramer conversion to Pentamer

| **Solvent** | **Activation Energy (Kcal/mol)** | **Heat of reaction (Kcal/mol)** | **Frequency factor (A) $Lmol^{-1}sec^{-1}$** |
|---|---|---|---|
| **Cyclohexane** | 34.72 | -71.13 | 1.87E+10 |
| **Cycloheptane** | 28.45 | -76.57 | 1.38E+09 |
| **Cyclooctane** | 28.03 | -76.99 | 1.35E+09 |

Figure 4.7 to Figure 4.10. shows the propagation of polymer chain. Polymer chains of different sizes were investigated and Table 4.1 to Table 4.4 shows the results of activation energy, heat of reaction and frequency factor. At each length of polymer chain transition states and energy of reactant and product were computed and results indicate that less amount of activation energy is required to convert reactant into product when we use cyclooctane ($C_8H_{16}$) as a solvent in the polymerization of n-BA. Moreover, energy barrier was lower when we used $C_8H_{16}$ than other two solvents cyclohexane and cycloheptane ($C_6H_{12}$ and $C_8H_{16}$). Frequency factor and heat release also strengthen our results of activation energy. We performed all our computational at 298K. According to literature study activation energy of bulk polymerization of n-BA using pulse laser polymerization [PLP-SEC] at high temperature was reported [87-88] and it is 16KJ/mol. In our case our estimated values of activation energy in solution polymerization of n-BA with three cyclic solvents (cyclohexane, cycloheptane and cyclooctane) are 34KJ/mol, 28.45KJ/mol and 28.03KJ/mol respectively.

Table 4.5 Comparison of kinetic parameter of present work with Literature results

| **Monomer/Polymerization** | **Frequency factor (lnA) $Lmol^{-1}sec^{-1}$** | **Activation energy KJ/Mol** | **Technique** | **Reference** |
|---|---|---|---|---|
| n-BA/Bulk polymerization | 2.24E+7 | 17.9KJ/mol | PLP-SEC | Asua et al. 2004 [87-88] |
| n-BA/ solution polymerization with $C_6H_{12}$ | 1.87 E+10 | 34KJ/mol | DFT/ Computational | Present work |
| n-BA/ solution polymerization with $C_7H_{14}$ | 1.38E+9 | 28.4KJ/mol | DFT/ Computational | Present work |
| n-BA/ solution polymerization with $C_8H_{16}$ | 1.35E+9 | 28.0KJ/mol | DFT/ Computational | Present work |

We have calculated the transition states and they are confirmed by having the single imaginary frequency, required frequency for the propagation of polymer chain. We have applied implicit solvent model that is solvent is considered as a continuous medium having average properties of real solvents surrounding the polymer chain. Polymer chain is polarizing by the solvent present around the chain and solvent produces reaction potential. This reaction potential effects the propagation of polymer chain and its interaction with polymer chain is represented by Hamiltonian. Conductor like polarized continuum model (CPCM) is an implicit solvent model that based on dielectric constant is applied in our research to study the solvent effect in the polymerization of n-BA. We have found the pattern of propagation of polymer chain in solvents is:

Cyclooctane > Cycloheptane > Cyclohexane.

Propagation of polymer chain in cyclooctane is most feasible than other two solvents. All three selected solvents have very close values of dielectric constant and shows equal miscibility in polymer solution. So, only size play its role in the propagation step. The size of cyclooctane is larger than other two solvents, so less cyclooctane solvents come around the coil than other two cases. That is why, solvents as a transferring agent are in less quantity in polymerization of n-butyl acrylate in cyclooctane solvent system and participate more in propagation step than other two cyclohexane and cycloheptane solvents solvent.

Results clearly suggest that polymer chain in cyclic solvents cyclohexane and cycloheptane showed more intensity toward some side reactions than cyclooctane. Because of our computational condition intramolecular chain transfer to polymer is most favorable reaction when the solvent didn’t encourage the propagation of polymer chain. So, in order to calculate the affinity of polymer chain toward side reaction, investigation will be required to find out the probability of chain transfer to polymer and molar fraction branches calculation. We will discuss this in next chapter

# Chapter 5

# Mathematical Model

Both the qualitative and quantitative approaches were used to investigate branching. Mathematical model has been used to find out the extent of branching and correlation in polybutyl acrylate with three cyclic solvents. Computational techniques were discussed in previous chapter. Now we discuss Mathematical Models, probability analysis for correlating the extent of Branching and Molar fraction branching for the estimation of branching.

This chapter also discusses the results obtained from these analyses.

First, Probability relation and its controlling parameter will be discussed. Then, branching calculation in nBA with three cyclic solvent using Molar Fraction Branches

## 5.1 Mathematical Approach:

Two mathematical approaches were used for estimation of branching:

- Probability Analysis
- Molar Fraction Branches

### 5.1.1 Probability Analysis of Chain transfer to Polymer:

The simple kinetics equation, which defines the probability of CTP relative to propagation reaction, is given by [32]:

$$P_{trp} = \frac{k_{trp}[P]}{k_{trp}[P] + k_p[M]} \qquad \text{Equation 5.1}$$

We can also write this equation as

$$P_{trP} = \frac{(\frac{k_{trp}}{k_p})(\frac{[P]}{[M]})}{\frac{k_{trp}[P]}{k_p[M]} + 1} \qquad \text{Equation 5.2}$$

Where $k_{trp}$ and $k_p$ are the rate-coefficient for the CTP and propagation, and [P] and [M] are concentrations of the local polymer repeat unit C-H bond and monomer concentration respectively.

The Probability relation is qualitatively an agreement with the prediction of CTP to explain the observation that how the size of solvent effects the Chain transfer to Polymer.

Probability Relation of Equation 5.1 indicate that there are two factors that control the extent of CTP i.e., rate coefficient ratio $k_{trp}/k_p$ ratio and the concentration [P]/[M] ratio. Simple probability relation will cover all the desired parameters. Equation 5.2 mentioned Probability relation to describe the probability of Chain Transfer to polymer relative to propagation

This equation contains two controlling factors:

- $k_{trp}/k_p$ and
- [P]/[M]

Both Parameter will equally importance in maintaining the probability relation, we will discuss separately how it is helpful in finding the probability trend in chain transfer behavior of Polymer.

**Role of $k_{trp}/k_p$:**

Rate coefficient of a monomer depends on number of factors such as steric, polar and electronic. Due to complexities involved during free-radical polymerization, the influence of these factors to control free radical polymerization is far from understanding [32]. Monomer is constant in this system only solvent changes its size from cyclohexane to cycloocatnce so above-mentioned factors become constant. It is not possible to assign the trend of $k_p$ at same temperature. In general $k_p$ value increases with the size of ester group, however if size of this ester group changes it effect pre-exponential factor, A, to the activation energy $\Delta E$ or to both quantities.

In case of constant monomer, rate coefficient of propagation and chain transfer strongly depends on temperature. If the temperature is constant then this ratio is constant.

**Role of [P]/[M]**

If the solvent interact differently than the ratio of [P]/[M] around the domain of propagating radical chain can be different. If due to preferential binding of constituent by the polymer in the multicomponent system in dilute solutions, then the solvent composition with in the domain of polymer molecules greatly different from its size in volume elements of solution that remain unaffected by the force effect the segment of molecule. Therefore, monomer distribution as well as dimension of polymer coil influences the ratio of [P]/[M].

At constant temperature and degree of Polymerization this ratio is written as $[P]_{local}/[M]_{local}$. A useful approach to get information about relative distribution of solvent, monomer and repeat unit C-H is through analysis of the volume of solvents and expansion values of the polymer coil. Volume of monomer nBA is 114.9cm$^3$/mol.

Table 5.1. Estimated volume of solvent [32]

| **No** | **Solvents** | **Volume cm$^3$/mol** |
|---|---|---|
| 1. | cyclohexane | 96.9 |
| 2. | cycloheptane | 112.7 |
| 3. | cyclooctane | 128.8 |

$[P]_{local}$ is constant in all three systems because monomer is constant and $[M]_{local}$ is the only factor in the equation that control the equation when we change the size of solvent.

First, Polymerization of nBA have been performed in the presence of cyclohexane solvent. In this case, volume of solvent is smaller than monomer. So, more solvents molecule will be in the vicinity of coil of PBA. Since, the monomer is less in the coil, the absence of monomer enhances the probability of chain transfer to polymer reaction rather than propagation reaction.

Second, there was a competition between the solvent cycloheptane and monomer molecule because their sizes were comparable. In this case Polymer coil also contain more solvent molecule because smaller size molecule than monomer.

In case of cyclooctane the size of solvent was larger than the monomer. So, more monomer molecule in the vicinity of polymer chain that is why probability of Propagation reaction is more than CTP and branching reactions.

### 5.1.2. Molar Fraction Branches:

Molar fraction Branches are determined by the balance between Chain transfer to polymer and Propagation reaction [34].

Assume that each CTP will form one branch. Mathematically at particular instant Molar fraction branches" fbr" is given as [34]:

$$fbr^{*}=\frac{k_{trp}^{\text{int}er}*[M^{*}]*[P]_{total}+k_{trp}^{\text{int}ra}*[M^{*}]_{norm}*[P]_{coil}}{k_{p}^{norm}[M*]_{norm}*[M]+k_{p}^{tert}[M^{*}]*[M]}$$

$k_{trp}^{Inter}$ and $k_{trp}^{Inter}$ are respectively, rate coefficient of inter and intramolecular CTP, $k_{p}^{norm}$ and $k_{p}^{tert}$ are respectively are rate coefficient of propagation from normal chain radical and from tertiary chain radical that results from CTP. It is assumption that there is no difference between tertiary radical that formed from inter and intra moleculat CTP.

$[M^*]_{normal}$ is concentration of normal chain radical

$[M^*]_{tert}$ is concentration of tertiary backbone radical from CTP.

$[P]_{total}$ is the total concentration of backbone tertiary C-H bond

$[P]_{coil}$ is the mean local concentration backbone tertiary C-H bond

$[P]_{coil}$ is constant so equation become:

$$fbr^{*}=\frac{k_{trp}^{\text{int}er}*[P]_{total}+k_{trp}^{\text{int}ra}}{\{k_{p}^{norm}+k_{p}^{tert}([M*]_{tert}/[M*]_{norm})\}*[M]}$$

Equation 5.3

Applying steady state condition

$$[M^{*}]_{tert}/[M^{*}]_{norm}=\{k_{trp}^{\text{int}er}[P]_{total}+k_{trp}^{*\text{int}ra}\}/k_{trp}^{tert}[M]$$

Applying this above situation in Equation 5.3

$$fbr=(\frac{k_{trp}^{\text{int}er}}{k_{P}^{norm}})*\frac{[P]_{total}}{[M]}+(\frac{k_{trp}^{*\text{int}ra}}{k_{p}^{norm}})*\frac{1}{[M]}$$

Equation 5.4

Equation 5.4 is used in calculating the molar fraction branches, it contains both inter and intramolecular CTP.

We have related the concentration of polymer and monomer from Equation 5.5 and Equation 5.6

$$[P]_{total} = [M]_o * c$$ Equation 5.5

$$[M] = [M]_o * (1 - c)$$ Equation 5.6

Molar fraction branching is a quantitative mathematical approach to measure molar fraction branching. Figure 5.1 is a literature results [89] depicts the Molar fraction branching results for the Polybutyl acrylate (PBA) in cyclohexane solvent. It is important to compare the literature results with computed results with similar conversion and concentrations. Equation 5.4, 5.5 and 5.6 were used to get computed results. Figure 5.1, Figure 5.2. and 5.3 shows remarkable similar trend with similar condition applied.

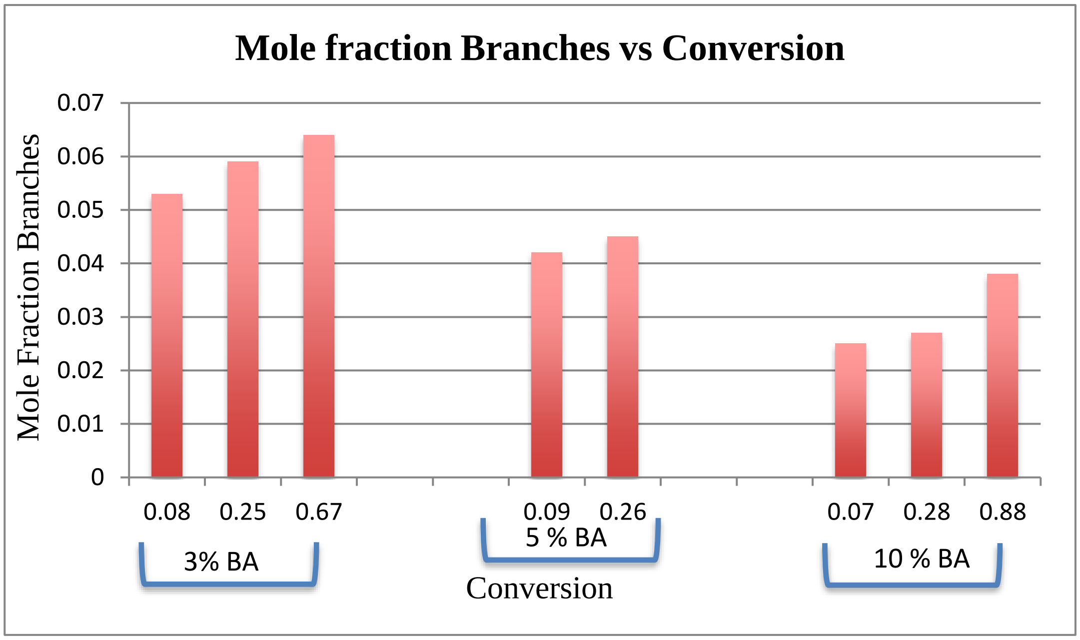


Figure 5.1. Literature result of Molar fraction Branches by NMR spectroscopy [55]

## Computed result:

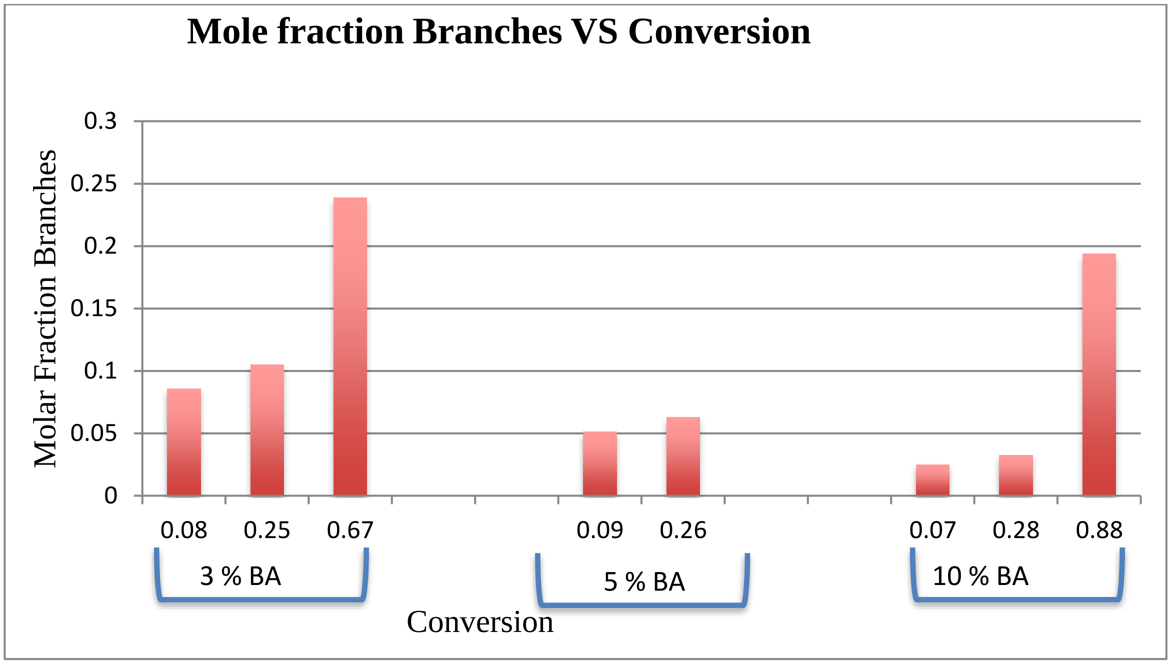


Figure 5.2. Computed results of molar fraction Branches using Equation 5.4

## Computed vs Literature Results

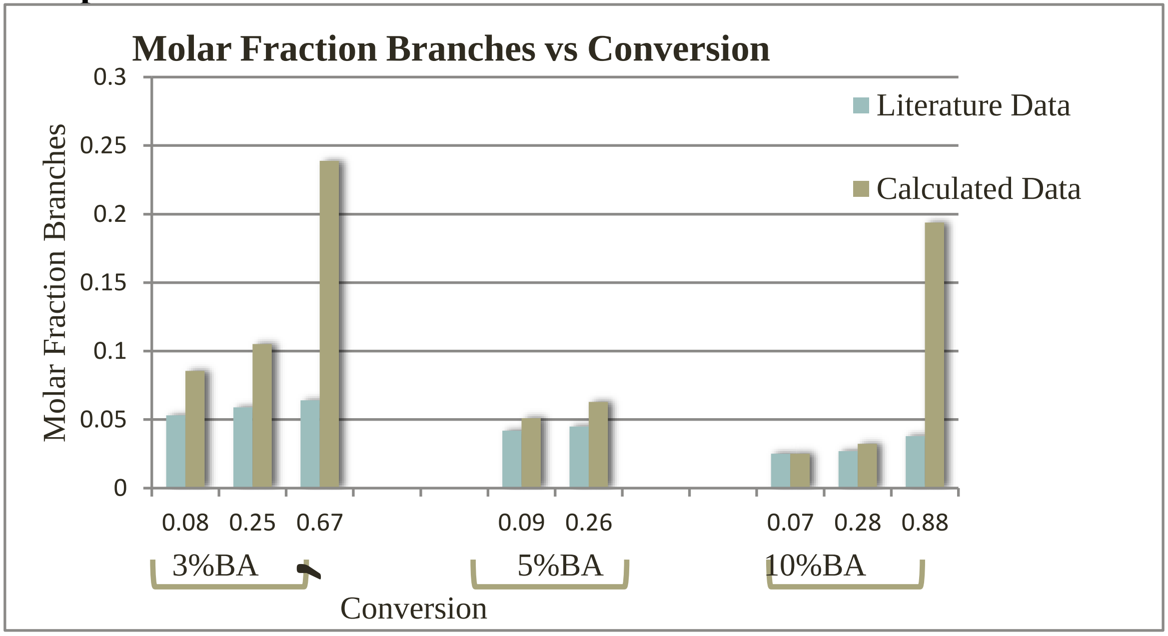


Figure 5.3. Comparison of Literature result (Experimental using NMR) and computed results of Molar fraction branches

## Theoretical Approach on Molar Fraction Branches:

### (Volume of Monomer & Solvent included in relation)

Molar fraction Branches (fbr) shows inverse relation with monomer concentration as shown in Equation 5.4 but fbr is directly related with with solvent concentration. As the solvent concentration increases then molar fraction branches increases. When we consider the volume impact on concentration, then it is inversely related with concentration.

Thus we can relate concentration with volume and it is inverse relation. So it is our purposed Ahmad-Sheraz Model for the determination of molar fraction branches. Now Ahmad-Sheraz model as can be written as:

$$fbr = \frac{V(Monomer)}{V(Solvent)}\{(\frac{k_{trp}^{inter}}{k_P^{norm}})*\frac{[P]_{total}}{[M]}+(\frac{k_{trp}^{*intra}}{k_p^{norm}})*\frac{1}{[M]}\} \qquad \text{Equation 5.7}$$

$$fbr = \frac{V_{mm}}{V_{ms}}\{(\frac{k_{trp}^{inter}}{k_P^{norm}})*\frac{[P]_{total}}{[M]}+(\frac{k_{trp}^{*intra}}{k_p^{norm}})*\frac{1}{[M]}\}$$

Where *V (Monomer)* and *V(Solvent)* are volume of monomer and solvent respectively

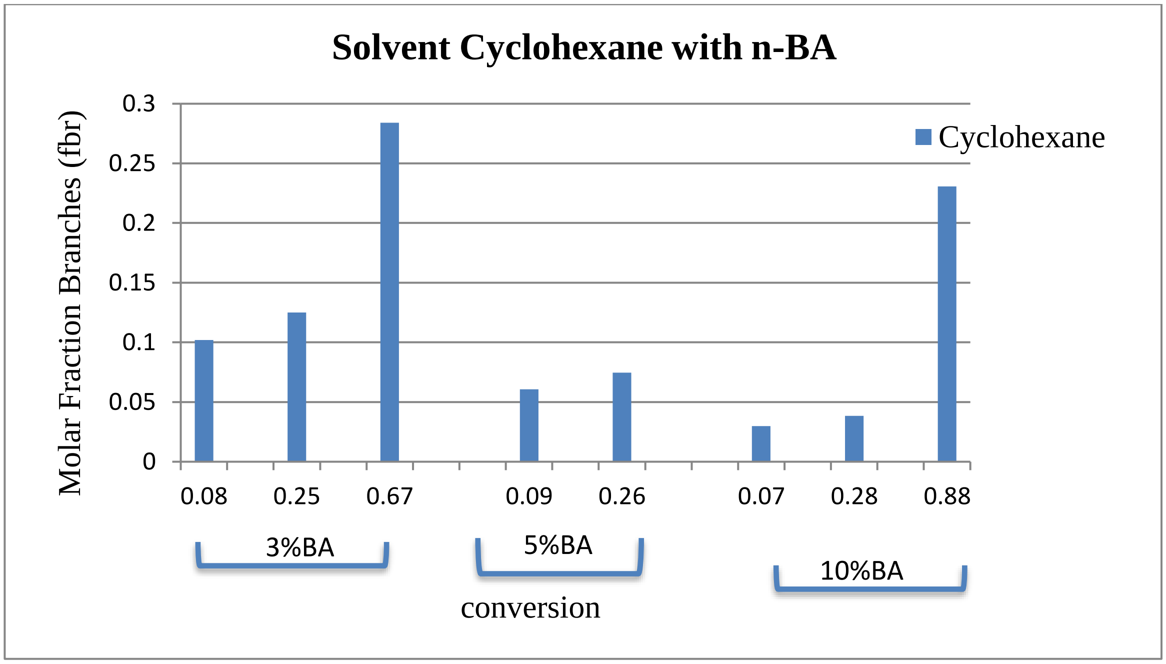


Figure 5.4. Computed result of nBA with cyclohexane solvent

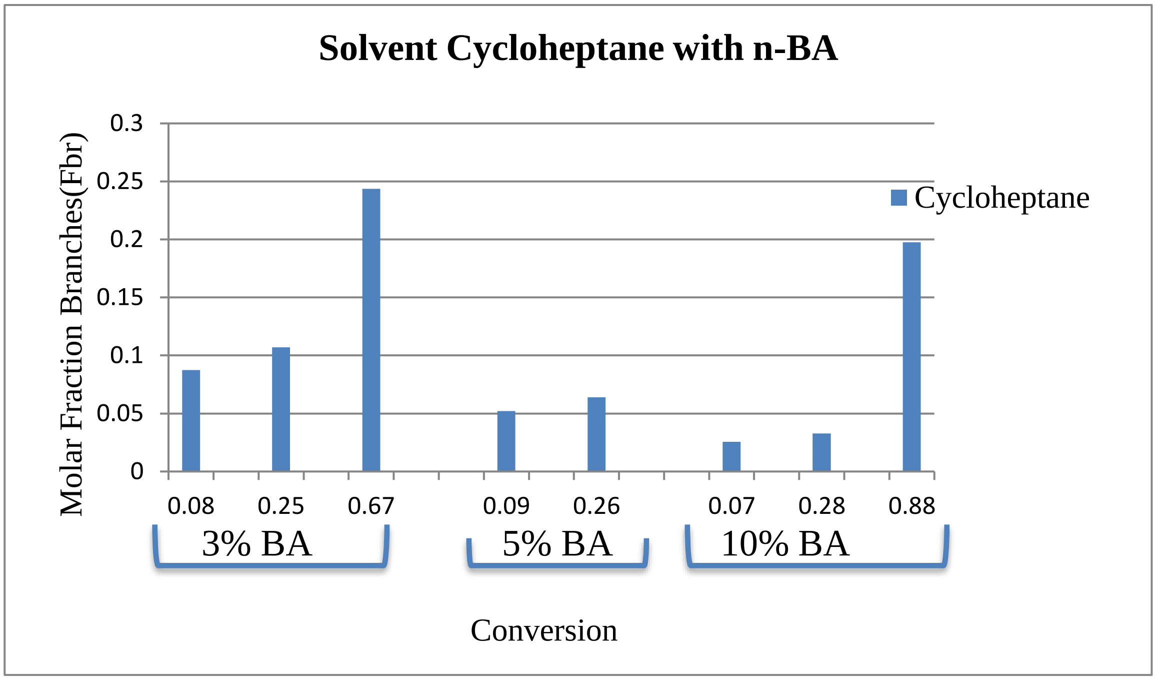


Figure 5.5. Computed result of nBA with cycloheptane solvent

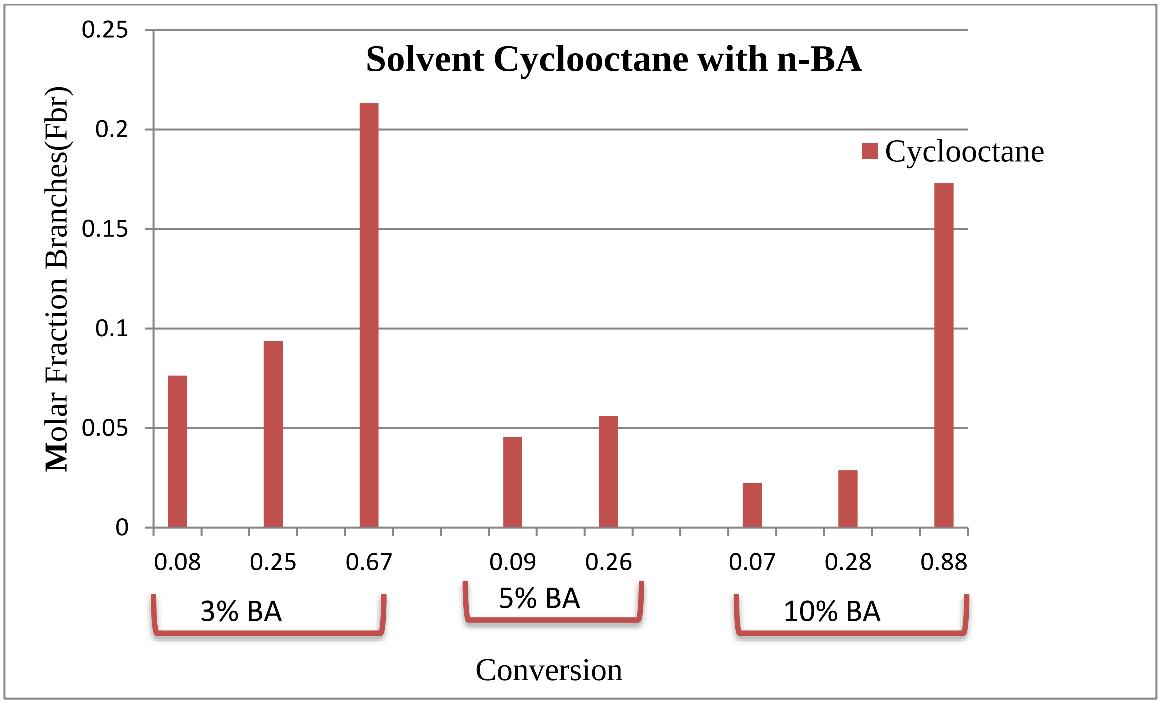


Figure 5.6. Computed result of nBA with cyclooctane solvent

Figure 5.4, Figure 5.5 and Figure 5.6 estimate the molar fraction branching results at 3,5 and 10% BA concentration. Figure 5.7 shows the comparison of molar fraction branches of three solvents i.e., cyclohexane, cycloheptane and cyclooctane. At each conversion and concentration cyclooctane shows less branching value. This model is valid at low conversion value because at high conversion many side reactions occur like diffusion and solubility. These reactions are prominent at high conversion when polymer is reaching toward the termination step.

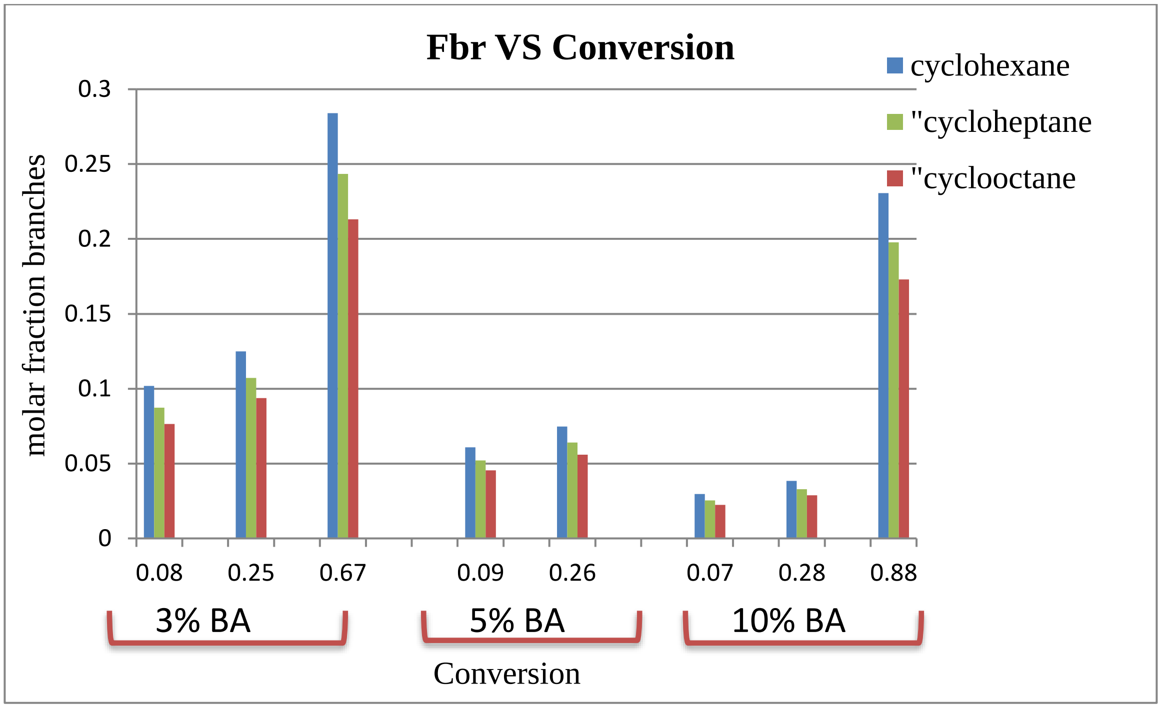


Figure 5.7. Comparison of molar fraction branches results of three solvents with nBA monomer

## 5.2 Solvent concentration around the vicinity of Polymer Coil:

We start our model by assuming that polymer coil, monomer and solvent are spherical in shape [30] in our mathematical model to calculate the concentration of solvent around the vicinity of active polymer coil.

Volume of the polymer coil can be calculated as [32]:

$$V_{coil} = 11.3(\alpha l)^3 (C_{\infty} M / M_o)^{3/2}$$

Where α=expansion parameter, l=length of chain bond, $C_{\infty}$=characteristic ratio,

$M_0$=repeat unit molar mass,

M=molar mass of polymer

Normally it is M=$10^5$ g/mol

Molar mass of polymer depends on the number of repeating unit attached with chain. In our case we will consider only intramolecular chain transfer to polymer as most feasible secondary reaction to be occurred due to the condition adopted. So, intramolecular chain transfer to polymer reaction will take place at low monomer concentration. That is why M=$10^5$ g/mol is considered in this system. Molar volume of solvent and monomer were discussed in section 5.1.1

Table 5.2. Molar Volume of Solvents, Polymer coil and Monomer

| **Molar Volume** | **cm$^3$/mol** |
|---|---|
| Molar Volume of Polymer coil | 23880000 |
| Molar volume of cyclohexane | 96.6 |
| Molar Volume of cycloheptane | 112.7 |
| Molar Volume of cyclooctane | 128.8 |
| Molar Volume of Monomer | 114.9 |

Number of atom inside the polymer coil is approximately equal to number of atom inside the cube of same volume. Formula used:

$$N^3 = V/(8r^3)$$

Now we will discuss solvent effect at different monomer concentrations:

- 1% monomer concentration
- 3% monomer concentration
- 5% monomer concentration
- 10% monomer concentration

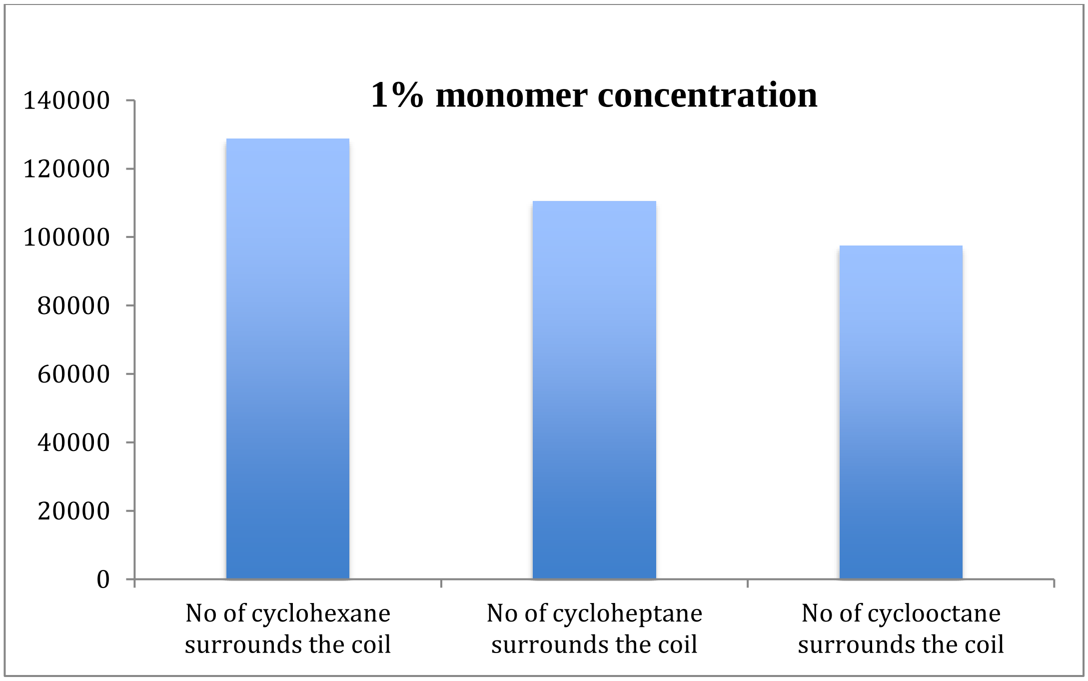


Figure 5.8. Calculated results of solvent concentration around the vicinity of polymer coil at 1% Monomer concentration

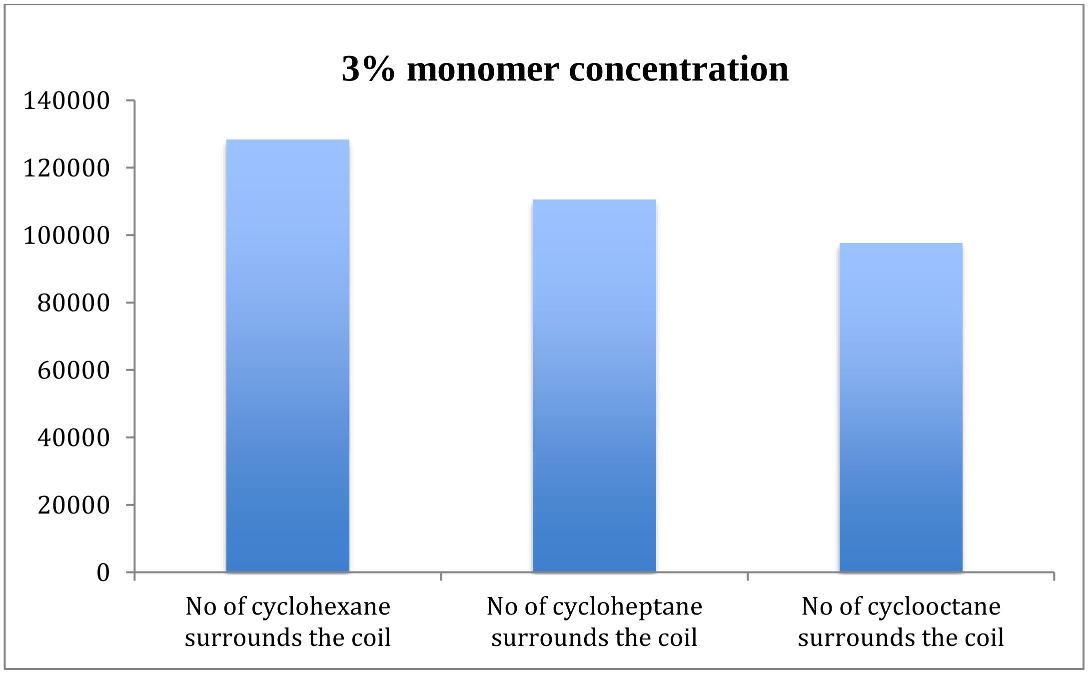


Figure 5.9. Calculated results of solvent concentration around the vicinity of polymer coil at 3% Monomer concentration

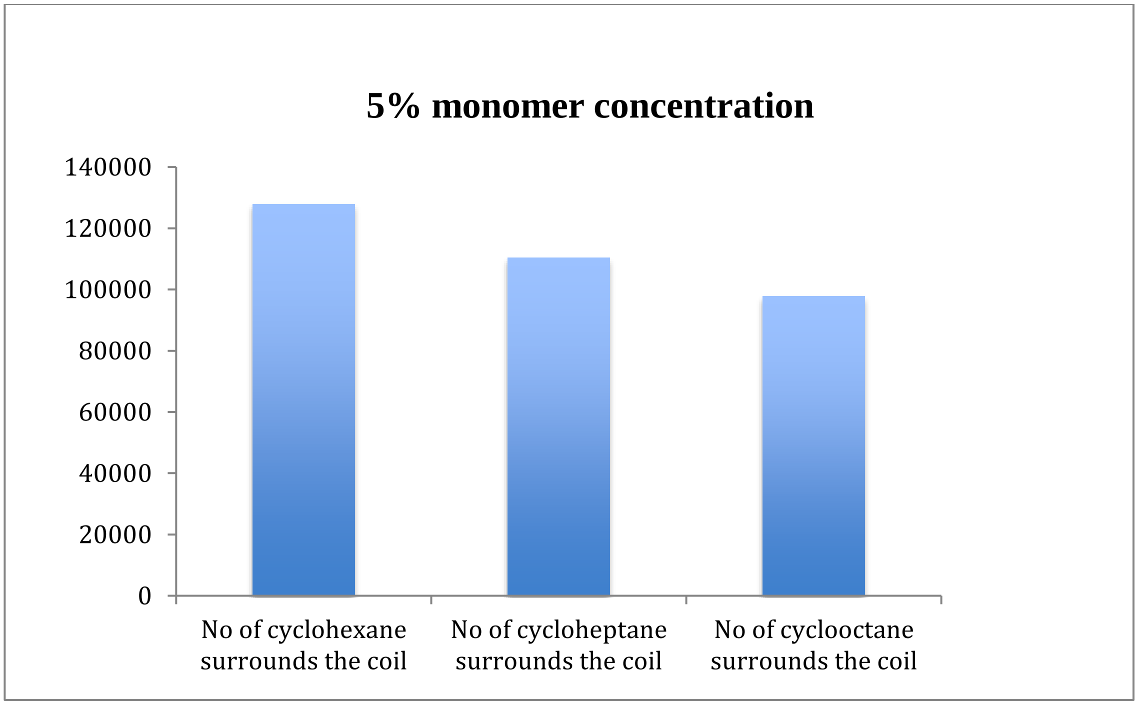


Figure 5.10. Calculated results solvent concentration around the vicinity of polymer coil at 5% Monomer concentration

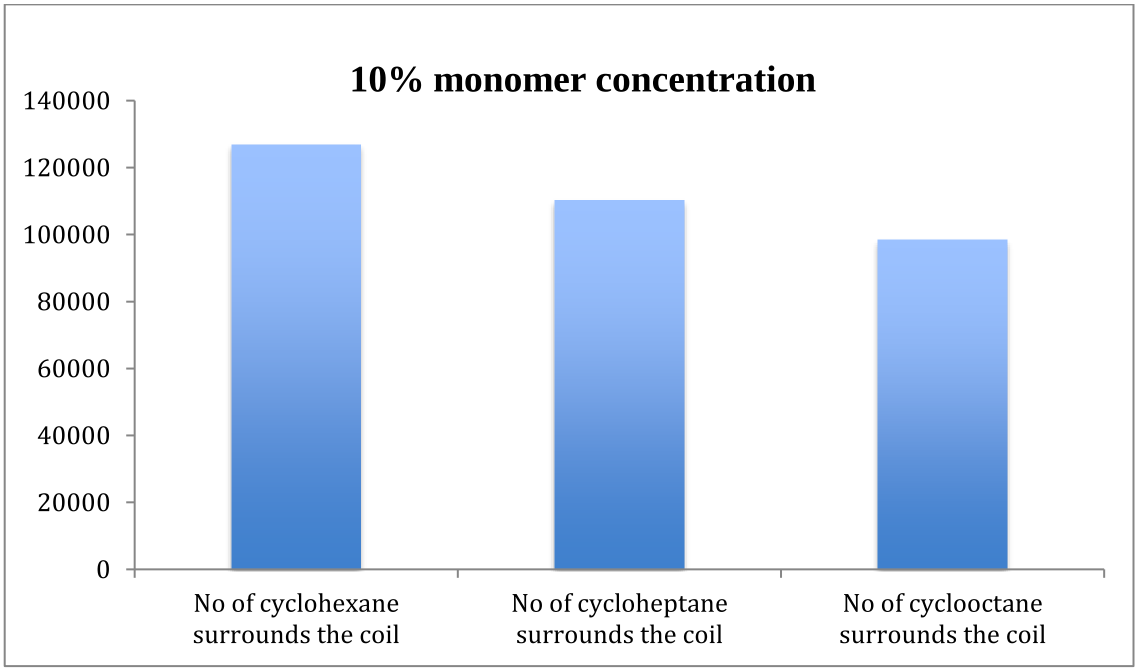


Figure 5.11. Calculated results of solvent concentration around the vicinity of polymer coil at 10% Monomer concentration

Figure 5.8. to Figure 5.11. represents the calculated results of solvent concentration around the vicinity of polymer coil at different monomer concentration. At low concentration of monomer i.e., 1%, 3%, 5% and 10% n-BA, we found that solvent cyclooctane ($C_8H_{16}$) shows least concentration around the polymer coil than other two solvents cycloheptane and cyclooctane ($C_6H_{12}$ and $C_7H_{14}$). Probability of chain transfer to polymer reaction shows dependence on solvent concentration around the vicinity of polymer coil [37]. In this case solvent cyclooctane ($C_8H_{16}$) shows minimum concentration around the propagating polymer chain. That is why propagation reaction is more favorable in this solvent system as compare to chain transfer to polymer. This result cooperates with our previous results of molar fraction branching. That states that molar fraction branching in the polymerization n-BA decreases in cyclooctane solvent system relative to cycloheptane and cyclooctane.

Chain transfer to polymer (CTP) and formation of branching have also been investigated from the calculation of Molar fraction branches. The level of branching formed due to CTP was slightly higher in the polymerization of n-butyl acrylate with cyclohexane solvent system. This suggested that there is possibility of a solvent effect operating as a true medium effect. Differences in solvent power owing to solvent – polymer interaction in three system provided a plausible explanation for the subtle enhancement of branching based on differences in various characteristic in of three solvents as well possible interaction in the $[BA]_{local}$ around the vicinity of the propagation radical chain end.

Solvent surrounding around the vicinity of radical chain at low monomer concentration strengthen the molar fraction branching results, that branching is the only reason of solvent attraction with the polymer coil.

# Chapter 6

# Conclusions and Future Recommendations

## 6.1 Conclusions

### Computational Conclusions

- In the present work, computational study of free radical polymerization of n-butylacrylate (n-BA) was studied using three cyclic solvents cyclohexane, cycloheptane and cyclooctane. These three solvents are thermodynamically equivalent due to their athermal characteristics but differ in terms of their sizes with order that follow Cyclooctane>Cycloheptane>Cyclohexane. Density functional theory with B3LYP as a hybrid density functional using 3-21 Basis set was applied to investigate the propagation rate of n-BA at 298K in the three solvent systems. DFT theory predicted that cyclooctane was most favorable solvent with the monomer n-butyl acrylate because of lower activation energy during the propagation reaction.
- To explore the chain length effect on the kinetic parameter of the propagation reactions, the free radical polymerization model was designed that based on the method of monomer addition at the radical center. Active center was formed by the decomposition of initiator. These studies predict that with the increasing size of solvents, there was a decrease in the activation energy, which can follow same energy trend to result in decrease in the extent of branching in cyclooctane relative to cycloheptane and cyclohexane.

### Mathematical Conclusions

- The molar fraction branching analysis revealed that at similar conversion and concentration of monomer, cyclooctane solvent shows less molar fraction branching than other two solvents. It suggests that as the size of athermal cyclic solvent increases chain transfer to polymer (CTP) and branching decreases and solvent become more stable and energetically more favorable with the formation of less branched polybutyl Acrylate (PBA).

- Mathematical modeling estimates that probability of branching is more in cyclohexane solvents system as compare to cyclooctane.
- The results obtained from computational and mathematical modeling corroborate well and significant in the area of free-radical polymerization. It seems that even athermal solvents can affect the CTP in free radical polymerization reaction. It is concluded that solvent effect are important in many radical polymerization systems, which consequently effect the chain transfer to polymer and hence formation of branching.

## 6.2 Future Recommendations:

- Perform Experimental study in three cyclic solvent systems of cylohexane, cycloheptane and cyclooctane and estimate the solvent effect in polymerization of n-butyl acrylate monomer.
- Study the role of Diffusion and Arrhenius pre exponential coefficient in radical polymerization at variable temperature polymerization.
- Apply higher level of detailed Density Functional Theory to include chain transfer to polymer in the athermal solvency condition to investigate role of solvent.

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