การสร้างแบบจำลองโมเลกุลของพอลิเอทิลีน พอลิพรอพิลีน และบล็อคโคพอลิเมอร์ของเอทิลีน/พรอพิลีน

นายสุรเกียรติ คำตา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2547

ISBN 974-17-6192-9

MOLECULAR MODELING OF POLYETHYLENE, POLYPROPYLENE AND ETHYLENE-PROPYLENE BLOCK COPOLYMER

Mr. Surakiat Kumta

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2004
ISBN 974-17-6192-9

Thesis Title	MOLECULAR MODELING OF POLYETHYLENE, POLYPROPYLENE AND ETHYLENE-PROPYLENE BLOCK COPOLYMER
By	Surakiat Kumta
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Vudhichai Parasuk, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

…………………………………………………Dean of the Faculty of Science
(Professor Piamsak Menasveta, Ph.D.)

THESIS COMMITTEE

……………………………………………………….Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

……………………………………………………….Thesis Advisor
(Associate Professor Vudhichai Parasuk, Ph.D.)

……………………………………………………….Member
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

……………………………………………………….Member
(Assistant Professor Vipavee P. Hoven, Ph.D.)

……………………………………………………….Member
(Somsak Tonmunphean, Ph.D.)

สุรเกียรติ คำตา : การสร้างแบบจำลองโมเลกุลของพอลิเอทิลีน พอลิพรอพิลีน และบล็อคโคพอลิเมอร์ของเอทิลีน/พรอพิลีน (MOLECULAR MODELING OF POLYETHYLENE POLYPROPYLENE AND ETHYLENE-PROPYLENE BLOCK COPOLYMER) อ.ที่ปรึกษา : รศ.ดร.วุฒิชัย พาราสุข, 94 หน้า. ISBN 974-17-6192-9.

งานวิจัยนี้ได้ทำการศึกษาถึงโครงสร้างของพอลิเอทิลีน (พีอี) พอลิพรอพิลีน (พีพี) และเอทิลีน-พรอพิลีนบล็อคโคพอลิเมอร์ (อีพีเอ็ม) ที่ 3 อุณหภูมิได้แก่ อุณหภูมิศูนย์องศาสัมบูรณ์ อุณหภูมิเปลี่ยนสถานะคล้ายแก้ว และอุณหภูมิหลอมเหลวผลึก โดยใช้วิธีการคำนวณระเบียบโมเลกุลาร์ไดนามิกส์ซิมุเลชัน ด้วยโมดูลดิสคอพเวอร์ ในโปรแกรมสำเร็จรูปซีเรียส2 และใช้สนามแรงเป็นแบบ PCFF เพื่อทำการคำนวณแบบจำลองโมเลกุลของพอลิเมอร์ขนาด 1 สายโซ่ และ 2 สายโซ่รวมทั้งแบบจำลองพอลิเมอร์ที่เป็นมัดด้วย โดยพิจารณาที่ความยาวสายโซ่เป็น 5, 10, 100 และ 500 ตามลำดับ โครงสร้างเริ่มต้นของพอลิเมอร์ได้มาจากโครงสร้างเอ็กซเรย์ของพอลิเอทิลีนและพอลิพรอพิลีน ซึ่งจากการศึกษาพบว่า ทั้งแบบจำลองโมเลกุล 1 และ 2 สายโซ่ที่มีความยาวเป็น 500 หน่วยซ้ำเป็นตัวแทนที่ดีในการศึกษาพอลิเมอร์ในทุกอุณหภูมิ และจากการศึกษาโครงรูปพบว่า ที่อุณหภูมิสูงคืออุณหภูมิหลอมเหลวผลึก โครงรูปของพอลิเมอร์ทุกชนิดมีแนวโน้มที่จะเกิดการเกี่ยวพันกัน และเกิดการม้วนเป็นก้อนกลมได้ดีกว่าที่อุณหภูมิอื่นๆ นอกจากนี้ยังพบว่าพอลิเอทิลีนและเอทิลีน-พรอพิลีนโคพอลิเมอร์ น่าจะเกิดการจัดเรียงตัวของสายโซ่แล้วเกิดเป็นโครงสร้างที่มีระเบียบได้ง่ายกว่าพอลิพรอพิลีน ผลการทดลองดังกล่าวมีความสอดคล้องกับผลการคำนวณพื้นที่ผิวต่อปริมาตรของพอลิเมอร์ ซึ่งค่าพื้นที่ผิวต่อปริมาตรที่ต่ำกว่าแสดงถึงความสามารถในการจัดเรียงตัวเพื่อให้เกิดความเป็นระเบียบของสายโซ่พอลิเมอร์ โดยพื้นที่ผิวต่อปริมาตรของพอลิเอทิลีนมีค่าต่ำกว่าพื้นที่ผิวต่อปริมาตรของพอลิพรอพิลีน สำหรับโครงสร้างที่เป็นมัดของพอลิเมอร์จำนวน 10 สายโซ่ แต่ละสายโซ่ยาว 50 หน่วยของแบบจำลองพอลิเอทิลีนและพอลิพรอพิลีน จะสังเกตเห็นโครงสร้างที่อุณหภูมิเปลี่ยนสถานะคล้ายแก้ว และอุณหภูมิหลอมเหลวผลึกแตกต่างจากโครงสร้างที่อุณหภูมิศูนย์องศาสัมบูรณ์เล็กน้อย นั่นคือไม่สามารถสังเกตเห็นการม้วนงอและการเกี่ยวพันกันของสายโซ่ได้อย่างชัดเจน ซึ่งอาจเป็นผลมาจากความยาวของแต่ละสายโซ่ 50 หน่วยนั้นสั้นเกินไป ดังนั้นเราจึงสรุปได้ว่าแบบจำลองโมเลกุลแบบ 2 สายโซ่ เป็นตัวแทนที่ดีที่สุดในการศึกษาพอลิเมอร์ในทุกอุณหภูมิ และนอกจากนี้ยังพบว่าแรงอันตรกิริยาระหว่างสายโซ่พอลิเมอร์ของพอลิเอทิลีนและพอลิพรอพิลีน ให้ค่าพลังงานจากแรงเฉือนค่อนข้างคงที่ และในกรณีพอลิพรอพิลีนต้องใช้พลังงานของแรงเฉือนมากกว่าพอลิเอทิลีน ซึ่งผลที่ได้จากการคำนวณมีความสอดคล้องกับผลที่ได้จากการทดลอง

สาขาวิชา…ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์….. ลายมือชื่อนิสิต…………………………………………

ปีการศึกษา………………..2547…………………. ลายมือชื่ออาจารย์ที่ปรึกษา……………………………

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม………………………..

 # # 4472468423 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: polyethylene, polypropylene, ethylene-propylene copolymer, glass transition temperature, molecular dynamic simulation, force field.

SURAKIAT KUMTA : MOLECULAR MODELING OF POLYETHYLENE POLYPROPYLENE AND ETHYLENE-PROPYLENE BLOCK COPOLYMER. THESIS ADVISOR: ASSOC. PROF. VUDHICHAI PARASUK, Ph. D. 94 pp., ISBN 974-17-6192-9

Structures of polyethylene (PE), isotactic polypropylene (iPP), and ethylene-propylene block copolymer (EPM) at 3 temperatures i.e. 0 K, glass transition temperature (T_g), and melting temperature (T_m) were investigated. Molecular Dynamics (MD) Simulations were carried out by the Discover module in the Cerius2 program for single chain polymers, double chain polymers as well as bundle polymers using PCFF molecular mechanics force field. Models with various number of repeating units of N=5, 10, 100, and 500 were applied. The starting geometries of these models were taken from the X-ray structures of PE and PP. It was suggested both of single chain and double chain polymers that the model with N=500 is the best representative of polymer at all temperatures. The conformation of all polymer models tends to be more entangle and turns into globule at high temperature, T_m. It was found that PE and EPM seem to orientate their long chains into ordered domain more easily than PP. These results correspond to the calculation data of surface area/polymer volume, in which lower value related to the formation of locally ordered structure. It was indicated that such value of PE was less than one of PP. For 10 chains with 50 repeating units per chain of PE and PP bundle models, structures at T_g and T_m are slightly deviated from the structure at 0 K, i.e., folding and entanglement are not observed. Probably, the chain length of 50 is too short. We then conclude that the double chain could be the best representative model of polymer at all temperatures. From the energies of chain – chain interaction, it can be observed that the shear energies of PE and PP are almost constant and PP has larger shear strength than PE, these results are agreed with the experimental data.

Field of study...Petrochemistry and Polymer Science… Student’s signature………..................
Academic year……………...2004……………………. Advisor’s signature…………………..
Co-advisor’s signature……………….

ACKNOWLEDGEMENT

I would like to express my sincerest gratitude to my thesis advisor Assoc. Prof. Dr. Vudhichai Parasuk. as well as Assoc. Prof. Dr. Supot Hannongbua, Dr. Tawun Remsungnen and Dr. Chinapong Kitiyakornnupong for their guidance, kindness, suggestions, supports and also aids in my writing and discussion in this thesis. In addition, I thank the thesis committee for their valuable suggestions and attention.

I would like to thank the Department of Chemistry, Faculty of Science and the Graduate School, Chulalongkorn University for providing the basic facilities and financial support.

Finally, I would like to express much appreciation to my family members for their encouragement and supports to make my study successful.

CONTENTS

Pages

LIST OF FIGURES

Pages

Pages

Pages

LIST OF TABLES

Pages

Pages

CHAPTER I
INTRODUCTION

1.1 Polymer

Polymers are macromolecules built up by linking together of a large number of much smaller molecules. The small molecule which is combined with each other to form polymer is termed “monomer”, and the reaction by which they were combined is termed “polymerization”. There may be hundreds, thousands, tens of thousands, or more monomers linked together in a polymer molecule.

1.2 Physical State

1.2.1Crystalline and Amorphous Behavior

Most polymers show simultaneously the characteristics of both crystalline solids and highly viscous liquids. The terms crystalline and amorphous are used to indicate the ordered and unordered polymer regions, respectively. Different polymers show different degrees of crystalline behavior. Lamellar crystal phase is demonstrated the equilibrium properties and diffusion behavior different from amorphous disorder phase.(1) The term semicrystalline is used to refer to polymers that are partially crystalline. Completely crystalline polymers are rarely encountered.

The fringed-micelle theory, developed in the 1930s, considers polymers to consist of small-sized, ordered crystalline regions termed crystallites imbedded in an unordered, amorphous polymer matrix. Polymer molecules are considered to pass through several different crystalline regions with crystallites being formed when extended chain segments from different polymer chains are precisely aligned together and undergo crystallization. Each polymer chain can contribute ordered segments to several crystallites. The segments of the chain in between the crystallites make up the unordered amorphous matrix.

The folded chain lamella theory arose in the last 1950s when polymer single crystals in the form of thin platelets termed lamella were grown from polymer solutions. The polymer molecules are presumed to fold back and forth on themselves in an accordion-like manner in the process of crystallization. In the chain folded lamella of polymer crystallinity less than 100 % crystallinity is attributed to defects in the chain folding process. The defects may be imperfect folds, irregularities in packing, chain entanglements, loose chain ends, dislocations, occluded impurities, or numerous other imperfections.

Folded chain lamella represent the morphology not only for single crystals grown from solution but also polymers crystallized from the melt which is how almost all commercial and other synthetic polymers are obtained. Melt crystallized polymers have the most prominent structural feature of polymer crystals, the chains are oriented perpendicular to the lamella face so that chain folding must occur. The polymer chains can be slightly rotated from their corresponding orientations in the bulk structure were confined to the first three molecular layers (approximately 10 A°) at the surface.(2) Chain folding is maximum for polymers crystallized slowly near the crystalline melting temperature. However, crystal structure of polymer, such as orthorhombic polyethylene crystal, can be also destroyed under atomic collision.(3)

1.2.2 Thermal Transitions

Long chain polymers tend to resist changes in bond angles along their backbones and the separation of the individual atoms. The extent of molecular mobility will be temperature dependent. At temperatures close to the absolute zero, a solid polymer will have very little thermal energy and its molecular chain will be stationary. As temperature increased, the acquired thermal energy is shared by all the possible modes of molecular motions. A rotation around a C-C bond requires only a low potential threshold and is consistent with the concept of free volume activation requiring small energy.(4) Polymeric materials are characterized by two major types of transition temperatures, the crystalline melting temperature T_m and the glass transition temperature T_g. The crystalline melting temperature is the melting temperature of the crystalline domains of a polymer sample. The glass transition temperature is the temperature at which the amorphous domains of a polymer take on the characteristic properties of the glassy state-brittleness, stiffness, and rigidity.

The difference between the two thermal transitions can be understood more clearly by considering the changes that occur in a liquid polymer as it is cooled. The transitional, rotational, and vibrational energies of the polymer molecules decrease on cooling. When the total energies of the molecules have fallen to the point where the translational and rotational energies are essentially zero, crystallization is possible. If certain symmetry requirements are met, the molecules are able to pack into an ordered, lattice arrangement and crystallization occurs. The temperature at which this occurs is T_m. However, not all polymers meet the necessary symmetry requirements for crystallization. If the symmetry requirements are not met, crystallization does not take place, but the energies of the molecules continue to decrease as the temperature decreases. A temperature is finally reached the T_g at which long range motions of the polymer chains stop. Long range motion, also referred to as segmental motion, refers to the motion of a segment of a polymer chain by the concerted rotation of bonds at the ends of the segment.

Whether a polymer sample exhibits both thermal transitions or only one depends on its morphology. Completely amorphous polymers show only a T_g. A completely crystalline polymer shows only a T_m. Semicrystalline polymers exhibit both the crystalline melting and glass transition temperatures. Changes in properties such as specific volume and heat capacity occur as a polymer undergoes each of the thermal transitions. The melting of a polymer takes place over a wider temperature range than that observed for small organic molecules such as benzoic acid due to the presence of different sized crystalline regions and the more complicated process for melting of large molecules. T_g also occurs over a wide temperature range and is a less well understood process than melting.

The values of T_g and T_m for a polymer affect its mechanical properties at any particular temperature and determine the temperature range in which that polymer can be employed. Polymers with low T_g values usually have low T_m values; high T_g and high T_m values are usually found together. Polymer chains that do not easily undergo bond rotation so as to pass through the glass transition would also be expected to melt with difficulty. This reasonable, since similar considerations of polymer structure are operating in both instances. The two thermal transitions are generally affected in the same manner by the molecular symmetry, structural rigidity, and secondary forces of polymer chains.

High secondary forces (due to high polarity or hydrogen bonding) lead to strong crystalline forces requiring high temperatures for melting. High secondary forces also decrease the mobility of amorphous polymer chains, leading to high T_g. Decreased mobility of polymer chains, increased chain rigidity, and high T_g are found where the chains are substituted with several substituents as in poly(methyl methacrylate) and polytetrafluoroethylene or with bulky substituents as in polystyrene. The T_m values of crystalline polymers produced from such rigid chains would also be high. The effects of substituents are not always easy to understand. The computer simulations is the powerful method that can give a more detailed picture to predict T_g of some polymer.(5)

The rigidity of polymer chains is especially high when there are cyclic structures in the main polymer chains. Polymers such as cellulose have high T_g and T_m values. On the other hand, the highly flexible polysiloxane chain (a consequence of the large size of Si) results in very low values of T_g and T_m.

1.3 Applications

Many polymer properties such as solvent, chemical, gas permeability, and electrical as well as dynamic mechanical behavior(6) are important in determining the use of a specific polymer in a specific application. The prime consideration in determining the general usage of a polymer is its mechanical behavior, that is, its deformation and flow characteristics under stress. The mechanical behavior of a polymer can be characterized by its stress-strain properties. This often involves observing the behavior of a polymer as applies tension stress to it in order to elongate (strain) it to the point where it ruptures (pulls apart). The stress is usually expressed in newtons per square centimeter (N/cm^2) or megapascals (MPa) where 1 MPa = 100 N/cm^2. The strain is the fractional increase in the length of the polymer sample i.e., $\Delta L/L$, where L is the original, unstretched sample length.

Polymers vary widely in their mechanical behavior depending on the degree of crystallinity, degree of crossslinking, and the values of T_g and T_m. High strength and low extensibility are obtained in polymers by having various combinations of high degrees of crystallinity or crosslinking or rigid chains (characterized by high T_g). High extensibility and low strength in polymers are synonymous with low degrees of crystallinity and crosslinking and low T_g values. The temperature limits of utility of a polymer are governed by its T_g and/ or T_m. Strength is lost at or near T_g for an amorphous polymer and at or near T_m for a crystalline polymer.

Different polymers are synthesized to yield various mechanical behaviors by the appropriate combinations of crystallinity, crosslinking, T_g, and T_m. Depending on the particular combination, a specific polymer will be used as a fiber, flexible plastic, rigid plastic, or elastomer (rubber). Commonly encountered articles that typify these uses of polymers are clothing and rope (fiber), packaging films and seat covers (flexible plastic), eyeglass lenses and housings for appliances (rigid plastic), and rubber bands and tires (elastomer).

The differences between fibers, plastics, and elastomers can be seen in the stress-strain plots in figure 1.1.(7) Elastomers are the group of polymers that can easily undergo very large, reversible elongations (≤ 500-1000 %) at relatively low stresses. This requires that the polymer be completely (or almost completely) amorphous with a low glass transition temperature and low secondary forces so as to obtain high polymer chain mobility. Some degree of crosslinking is needed so that the deformation is rapidly and completely reversible (elastic).

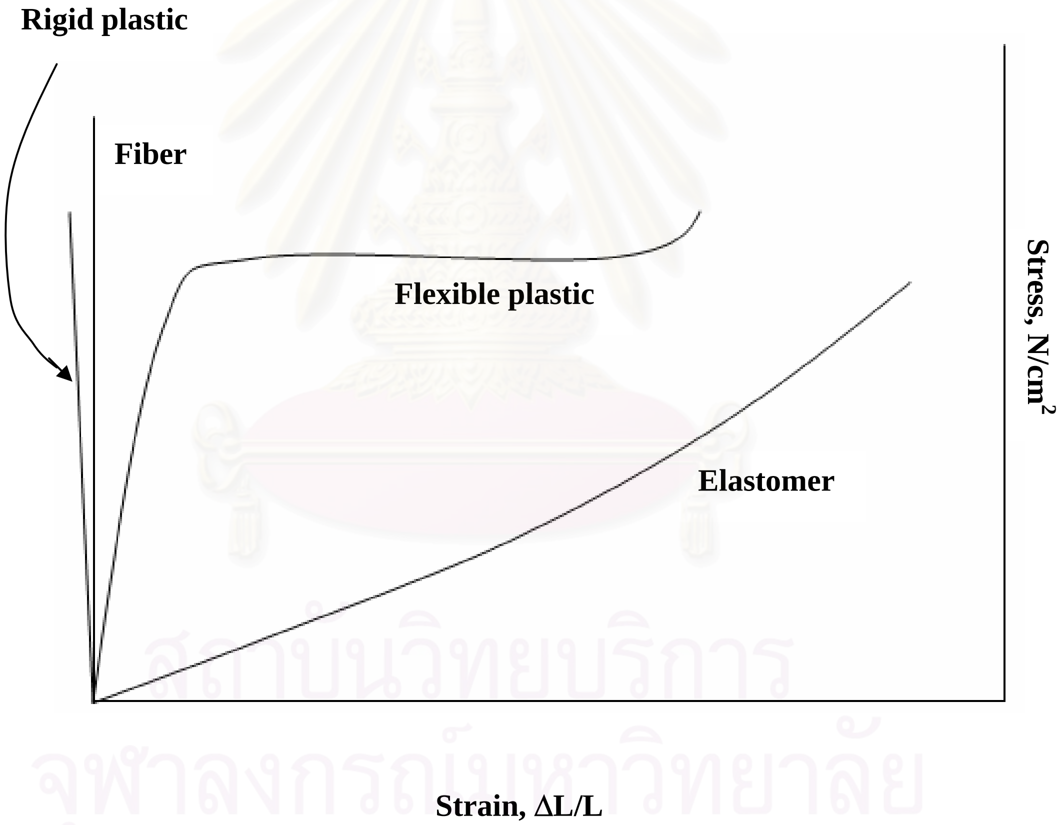


Figure 1.1 Stress-strain plots for a typical elastomer, flexible plastic, rigid plastic, and fiber

Most elastomers obtain the needed strength via crosslinking and the incorporation of reinforcing inorganic fillers e.g., carbon black, silica. The T_m of the crystalline regions must be below or not significantly above the use temperature of the elastomer in order that the crystals melt and deformation be reversible when the stress is removed. Polyisoprene (natural rubber) is a typical elastomer with amorphous structure, is easily crosslinked, has a low T_g (-73 °C), and has a low T_m (28 °C).

Fibers are polymers that have very high resistance to deformation, they undergo only low elongations (< 10-50 %) and have very high moduli (> 35000 N/cm^2) and tensile strengths (> 35000 N/cm^2). A polymer must be very highly crystalline and contain polar chains with strong secondary forces in order to be useful as a fiber. Mechanical stretching is used to impart very high crystallinity to a fiber. The crystalline melting temperature of a fiber must be above 200 °C so that it will maintain its physical integrity during the use temperatures encountered in cleaning and ironing. However, Tm should not be excessively high (not higher than 300 °C) otherwise, fabrication of the fiber by melt spinning may not be possible. The glass transition temperature should have an intermediate value; too high a T_g interferes with the stretching operation as well as with ironing, while too low a T_g would not allow crease retention in fabrics. Poly(hexamethylene adipamide) is a typical fiber. It is stretched to high crystallinity and its amide groups yield very strong secondary forces due to hydrogen bonding; the result is very high tensile strength (70000 N/cm^2), very high modulus (500000 N/cm^2), and low elongation (< 20%).

Plastics include a large group of polymers that have a wide range of mechanical behaviors in between those of the elastomers and fibers. There are two types of plastics, flexible plastics and rigid plastics. The flexible plastics possess moderate to high degrees of crystallinity and a wide range of Tm and T_g values. They have moderate to high moduli (15000-350000 N/cm^2), tensile strengths (1500-7000 N/cm^2), and ultimate elongations (20-800%). Thus polyethylene, polypropylene, and poly(hexamethylene adipamide), for instance, is a typical flexible plastics.

Poly(hexamethylene adipamide) is used as both a fiber and a flexible plastic. It is a plastic when it has moderate crystiallinity, while stretching converts it into a fiber. Many flexible plastics undergo large ultimate elongations, some as large as those of elastomers. However, they differ from elastomers in that only a small portion of the ultimate elongation is reversible. The elongation of a plastic past the reversible region results in its permanent deformation, that is, the plastic will retain its elongated shape when the stress is removed.

The rigid plastics are quite different from the flexible plastics. The rigid plastics are characterized by high rigidity and high resistance to deformation. They have high moduli (70000-350000 N/cm^2) and moderate to high tensile strengths (3000-8500 N/cm^2), but more significantly, they undergo very small elongations (< 0.5-3 %) before rupturing. The polymers in this category are amorphous polymers with very rigid chains. The high chain rigidity is achieved in some cases by extensive crosslinking, for example, phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde polymers. In other polymers the high rigidity is due to bulky side groups on the polymer chains resulting in high T_g values, for example, polystyrene (T_g = 100°C) and poly(methyl methacrylate) (T_g = 105°C).

1.4 Motivation

Polymers are viscoelastic materials that can possess properties of viscous liquid, elastic rubber, or glassy substances, depending on the temperature. For example, a polymer may be glassy at low temperatures, rubber-like at higher temperatures and viscous liquid at still higher temperatures. The unique properties of polymers are attributed to their long chain structure. Linear polymers, such as polyethylene, are thermoplastics, which can be remolded many times and have a degree of solubility. Cross-linked polymers are thermoset materials, which cannot be reprocessed and are insoluble. The interaction between molecular chains, the flexibility of chains, and the spacing of polar groups affect the mechanical properties of polymers. In macromolecules, the flexibility of chains arises from a rotational motion around chain bonds. Crystalline polymers with high molecular weight are hard materials; the linear crystalline region provides strength while the branching provides toughness. The elasticity depends on the ability of the disordered chain segments to stretch under the influence of stress.

Interest in the physics of polymers was pushed by the need of new materials in all fields of everyday life. Polyethylene and polypropylene are well known homopolymer which widely used in the commercial. The properties of polymer materials were investigated by experiments and for some a theory has been established, but polymer is still not easy to understood of its behavior. Nevertheless computer simulations can give a more detailed picture in this context. Polymer can be modeled for computational purposes.

The simulation is very useful to demonstrate special effects as important physical parameters, e.g. potential and kinetic energy, are calculated and plotted during the simulation, it can be used to demonstrate the effect of different forces and the time development of certain observables. All of these structural data lead to an understanding and the explanation of the polymer chain behavior.

1.5 Literature survey

Kavassalis and Sundararajan(8) have studied the molecular dynamics simulations of model polyethylene chains of various lengths. The occurrence of a few gauche states promotes long range attractive interaction between segments and caused the chain to fold into lamellae. The molecular dynamics simulations for models of 170 repeating units of isotactic polypropylene were also examined to understand the possible origin of melt state incompatibility of those polyethylene and polypropylene mixtures.(9) Incompatibility between PE and PP was indicated also by observation of mutual solutions in a common solvent.(10) As quantum, density functional study of the structure of a single chain isotactic polypropylene has been optimized, and calculations have been performed for smaller molecules with closely related structures.(11)

1.6 Goals of study

The aim of this research is to employ molecular modeling techniques to investigate 3D structure of polyethylene, polypropylene, and ethylene-propylene copolymer at 0 K, glass transition temperature (T_g), and melting temperature (T_m). Apart from structural properties, mechanical properties such as shear strength are also interested. Attempt to predict shear strength of polymers from their structural data was also persuade.

CHAPTER II
THEORY

During the development of polymer science, two types of classification of polymers have come into use. One classification divides polymers into condensation and addition polymers and anothers to step and chain polymers. The condensation-addition classification is primarily applicable to the composition or structure of polymers. The step-chain classification is based on the mechanism of the polymerization reactions.

2.1 Condensation and addition polymers

Polymer was originally classified by Carothers into condensation and addition polymers on the basis of the compositional difference between the polymer and the monomer(s) from which it was synthesized. Condensation polymers are polymers that are formed from polyfunctional monomers by various condensation reactions of organic chemistry with the elimination of some small molecules such as water. An example of condensation polymer is the polyamides formed from diamines and diacids with the elimination of water according to

$$n\ H_2N\text{-}R\text{-}NH_2 \quad + \quad n\ HO_2C\text{-}R'\text{-}CO_2H \quad \longrightarrow$$

$$H \left[NH - R - NHCO - R' - CO \right]_n OH \quad + \quad (2n\text{-}1)\ H_2O$$

where R and R′ are aliphatic or aromatic groupings.

The unit in parentheses in the polyamide formula repeats itself many times in the polymer chain and is termed the repeating unit. The composition of the repeating unit differs from that of the two monomers by the elements of water.

Addition polymers are classified as those formed from monomers without a loss of a small molecule. Unlike condensation polymers, the repeating unit of an addition polymer has the same composition as the monomer. The major addition polymers are those formed by polymerization of monomers containing the carbon-carbon double bond. Such monomers will be referred as vinyl monomers. Vinyl monomers can be made to react with themselves to form polymers by conversion of their couple bonds into saturated linkages, for example,

$$n\ CH_2{=}CHY \longrightarrow -\!\left[CH_2-CHY\right]\!-_n$$

where Y can be any substituent group such as hydrogen, alkyl, aryl, nitrile, ester, acid, ketone, ether, and halogen.

In summary, a polymer is classified as the condensation polymer if its synthesis involves the elimination of small molecules, or it contains functional groups as part of the polymer chain, or its repeating unit lacks certain atoms that are present in the monomer to which it can be degraded. If a polymer does not fulfill any of these requirements, it is classified as the addition polymer.

In addition to the structural and compositional differences between polymers, polymerizations are classified into step and chain polymerizations based on the polymerization mechanism. Step polymerizations proceed by the stepwise reaction between the functional groups of reactants as in reactions. The size of the polymer molecules increases at a relatively slow rate in such polymerizations. One proceeds slowly from monomer to dimer, trimer, tetramer, pentamer, and so on until eventually large polymer molecules containing large numbers of monomer molecules have been formed. Any two molecular species can react with each other throughout the course of the polymerization. The situation is quite different in chain polymerizations where full-sized polymer molecules are produced almost immediately after the start of the reaction.

Chain polymerizations require an initiator from which is produced an initiator species R* with a reactive center. The reactive center may be either a free radical, cation, or anion. Polymerization occurs by the propagation of the reactive center by the successive additions of large numbers of monomer molecules in a chain reaction, happening in a matter of a second or so at most, and usually in much shorter times. Monomer can react only with the propagating reactive center, not with monomer.

The chain polymerization will show the presence of high-molecular weight polymer molecules at all percents of conversion. The only change that occurs with conversion (i.e., reaction time) is the continuous increase in the number of polymer molecules. Polymer size is generally independent of percent conversion, although the amount of polymer certainly depends on it. On the other hand, high-molecular weight polymer is obtained in step polymerizations only near the very end of the reaction (> 98 % conversion). Thus both polymer size and the amount of polymer are dependent on conversion in step polymerization.

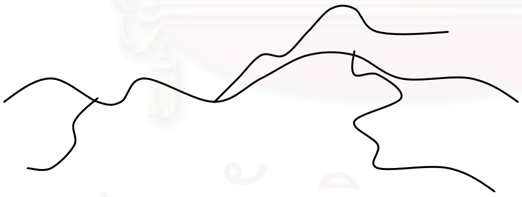
2.2 Linear, Branched, and Crosslinked Polymers

Polymers can be classified as linear, branched, or crosslinked polymers depending on their structure. Branched polymers are often obtained in both step and chain polymerizations. Branched polymer molecules are those in which there are side branches of linked monomer molecules protruding from various central branch points along the main polymer chain. The difference between the shapes of linear and branched polymer molecules can be seen from the structural representations in Figure 2.1, there are several different kinds of branched polymers.

The branched polymer can be comblike in structure with either long or short branches. When there is extensive branching, the polymer can have a dendritic structure in which there are branches protruding from other branches, that is branched branches. the presence of branching in a polymer usually has a large effect on many important polymer properties. The most significant property change brought about by branching is the decrease in crystallinity. Branched polymers do not pack as easily into a crystal lattice as do linear polymers.

Branched polymer does not refer to linear polymers containing side groups that are part of the monomer structure. Only those polymers that contain side branches composed of complete monomer units are termed “branched polymers”. The structures of linear and branched polymer are shown as Figure 2.1 below.

Linear



Long branches

Short branches

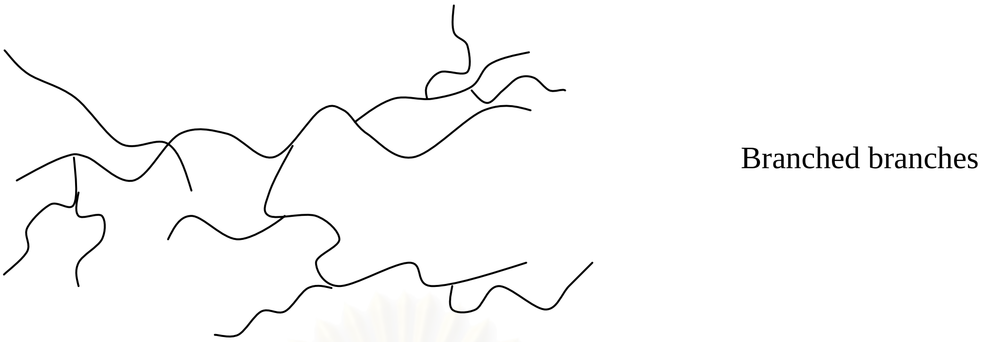


Figure 2.1 Structures of linear and branched polymer(7)

When polymers are produced in which the polymer molecules are linked to each other at points other than their ends, the polymers are said to be crosslinked (Figure 2.2). Crosslinking can be made during the polymerization process by the use of appropriate monomers. It can also be brought about after the polymerization by various chemical reactions.

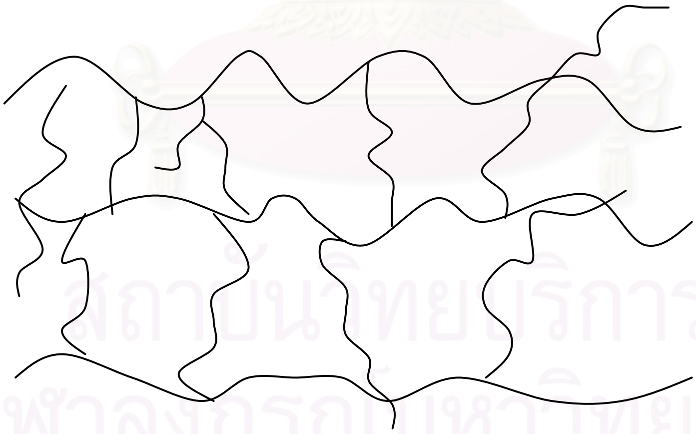


Figure 2.2 Structure of crosslinked polymers(7)

When the number of crosslinks is sufficiently high, a three-dimensional or space network polymer is produced in which all the polymer chains in a sample have been linked together to form one giant molecule. Light crosslinking is used to impart good recovery (elastic) properties to polymers to be used as rubbers. High degrees of crosslinking are used to impart high rigidity and dimensional stability (under conditions of heat and stress) to polymers such as the phenol-formaldehyde and urea-formaldehyde polymers.

2.3 Copolymer

Depending on monomer which composed, polymer can be classified into two types, i.e. homopolymer and copolymer. Homopolymer is made up of a single repeating unit as shown below

● = monomer

Copolymer is made up of chemically different repeating units which is made to alter properties of polymer, the properties which could not be achieved based on either of the homopolymer alone.

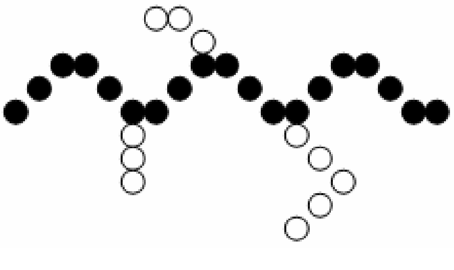
Based on ways of monomer arrangement, copolymer can be classified into four types :

1. Random copolymer. Different monomers are randomly arranged within the polymer chain. If white and black circle represent two different monomers, the arrangement can be schematically illustrated as follows :

2. Alternating copolymer. Different monomers are orderly altered as in

3. Block copolymer. Different monomers blocks are orderly altered as in

4. Graft copolymer. One type of monomer chain is attached to the long chain of the other type



Most natural polymer, as same as most synthetic polymer, is homopolymer except protein and nucleic acid.

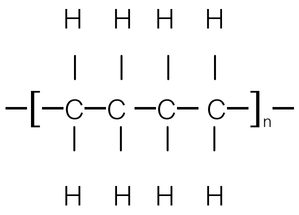
2.4 Polyethylene (PE)

Polyethylene or polyethene is one of the materials we most frequently come across in our daily lives and constitutes 40% of total world plastic production. In other words, roughly half of what we generically call “plastic” objects has been made from polyethylene. From a chemical point of view, it is a basic plastic material, i.e. a semi-finished product used as a raw material by the transformation industry to create a wide range of finished products, from the most simple object to the most sophisticated item. At a structural level, polyethylene is derived from ethylene, which is itself a by-product of oil refinement.

Polyethylene is one of the simplest and most inexpensive polymers. It is waxy, chemically inert plastic. Polyethylene is the most popular plastic in the world. There is a wide variety of grades and formulations available that have an equally wide range of properties. In general, the outstanding characteristics of polyethylene are:

- toughness
- ease of processing
- chemical resistance
- abrasion resistance
- electrical properties
- impact resistance
- low coefficient of friction
- near zero moisture absorption

This is the polymer that makes grocery bags, shampoo bottles, children’s toys, even bullet proof vests, etc. For such a versatile material, it has a very simple structure, the simplest of all commercial polymers. A molecule of polyethylene is nothing more than a long chain of carbon atoms, with two hydrogen atoms attached to each carbon atom as shown in Figure 2.3.



$$-\left[-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\right]_n-$$

Figure 2.3 Chemical structure of polyethylene

In the liquid state, the kinetic energy of a polymer molecule may provide translational motion of the molecule as a whole, rotation of parts of the molecule, or individual bond vibrations, which can produce conformational changes. However, in the solid state, molecular motions will be restricted, although impeded rotational motions may still occur subject to the availability of sufficient kinetic energy.(4) The chain bending is necessary to accommodate long chains within the crystal entity, and it is associated with all lameller single crystals. The occurrence of a few gauche states promotes long range attractive interactions between segments and causes the chain to fold into lamella, via a global collapse mechanism. In which the chain forms local collapsed domains, which then coalesce into a large lamella.(8)

The chain axis of the molecule is approximately normal to the plane of the lamella, although the thickness of the lamella is considerably less than the chain. Such an arrangement also conforms to the concept of the chain folding. It has been suggested that the mechanism of a chain refolding may involve a simultaneous displacement of all the chains in the same direction in a cooperative manner, occurring at a sufficiently high temperature. It should be noted that a polymer chain, subjected to an extentional flow during crystallization, can align in the direction of flow, resulting in a fibrillar structure with extended chain crystals in which the chains will be aligned parallel to one another over long distances. For such a case, the chain folding will be minimal.

Polyethylene has a wide range and combination of desirable properties. Its very low T_g of about -120 °C, and moderately high T_m of about 135 °C give it flexibility and utility over a wide temperature range. It has high crystallinity with a good combination of strength, flexibility, and melt-flow behavior over a range of molecular weights. The alkane structure of polyethylene imparts good solvent, chemical, thermal, oxidation, water, and electrical resistance.

A wide range of fabrication techniques can be used to process polyethylene into products. Polyethylene can be classified as *low-density polyethylene (LDPE)* or *high-pressure polyethylene* and according to their synthetic pathway *low-pressure polyethylene* or *high-density polyethylene (HDPE)*. The structures of LDPE and HDPE are presented in Figures 2.4 and 2.5 below.

Figure 2.4 A Molecule of linear polyethylene, or HDPE

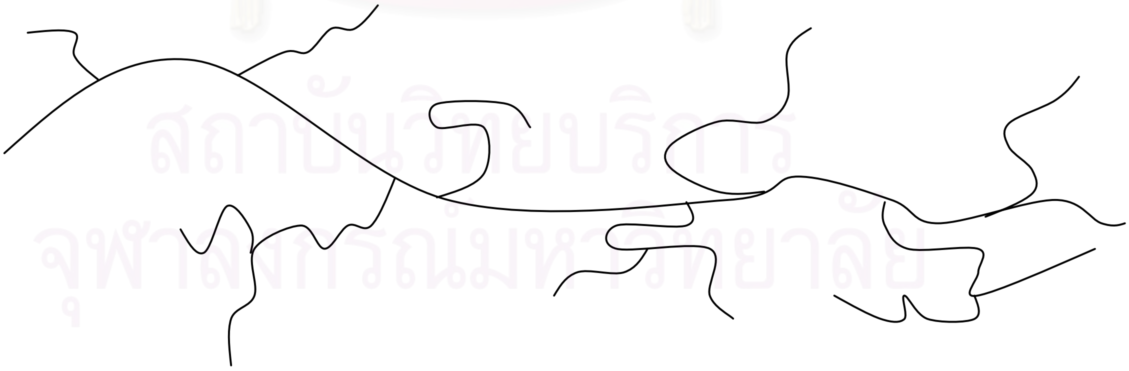


Figure 2.5 A molecule of branched polyethylene, or LDPE

HDPE is more rigid and harder than lower density materials. It also has a higher tensile strength, four times that of low density polyethylene. HDPE has virtually no branching and thus stronger intermolecular forces and tensile strength. The lack of branching is ensured by an appropriate choice of catalyst (e.g. Ziegler catalysts) and reaction conditions. The extremely high molecular weight combined with its very low coefficient of friction provides and excellent abrasion resistant product preventing gouging, scuffing and scraping. HDPE is one of the highest impact resistant thermoplastics available and maintains excellent processibility and self-lubricating characteristics. Properties are maintained even at extremely low temperatures. Moisture and water (including saltwater) have no affect on HDPE. It can be used in fresh and salt water immersion applications. It has very good chemical resistance of corrosives as well as stress cracking resistance (with the exception of strong oxidizing acids at high temperatures). The main applications of HDPE are:

- bottle and containers for food products, detergents and cosmetics
- industrial cases
- toys
- household items
- industrial packaging
- film and sheets
- fuel tanks and liquid containers

Low-density polyethylene was the first of the polyethylenes to be developed. It is a corrosion resistant, low density extruded material that provides low moisture permeability. LDPE has a fairly low wording temperature, soft surface and low tensile strength. It is an excellent material where corrosion resistance is and important factor, but stiffness, high temperature and structural strength are not important considerations.

Low-density polyethylene (LDPE) is more highly branched (both long and short) than high-density polyethylene (HDPE), which means that the chains do not fit well together, and is therefore lower in crystallinity (50-70 % vs 80-90 %). It has also less strong intermolecular forces as the instantaneous-dipole induced-dipole attraction is less. This results in an increased malleability, faster degradation, and a lower tensile strength and density than HDPE (0.91-0.93 g/cm^3 vs 0.94-0.96 g/cm^3). LDPE is created by free radical polymerization.

LDPE with a melt index of approximately 9g/10min has adequate flow characteristics with minimal surface cracking, as compared to material with extremely low (2g/10min) or extremely high (60g/10min) melt indexes. And because it has a lower shrinkage factor, LDPE is more successful than high-density polyethylene for large scale pours.

As a flexible plastic, a wide range of applications can be found for LDPE. About 55 % of all low-density polyethylene is produced as extruded film and sheet, mostly for packaging and household uses (bags, pouches and wrap for food, garments and dry cleaning, trash), but also for agricultural and construction applications (greenhouses, tank liners, moisture, and protective barriers). Injection molding of toys and housewares accounts for another 10-15 %. About 15 % or more of the LDPE produced is used in wire and cable insulation for power and communication transmission and extruded as well as hot melt coatings (on paper, metal foil, other plastic films). Other uses of LDPE include blow-molded bottles and containers, pipe, and tubing for agricultural irrigation.

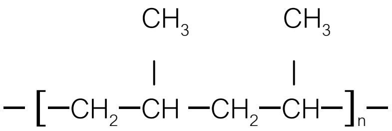
Polyethylene’s resistance to chemical attack is one of the main reasons for its widespread use in many diverse applications. At ambient temperatures, polyethylene is insoluble in virtually all organic solvents and is resistant to many acids and caustic solutions. However, polyethylene can be attacked and degradable with some condition such as radiation induced.

Photodegradation of polyethylene exposed to ultraviolet radiation can cause deterioration of structural integrity. Four chemical reactions are generally responsible for the effects of radiation on polyethylene are cross-linking, chain scission, increased unsaturation, and oxidation. Of these, cross-linking is the predominant effect. Increased unsaturation has little effect on the mechanical properties, but it occurs with nearly the same yield as cross-linking. Each of these two reactions results in the production of hydrogen on a 1:1 basis. Chain scission is a minor reaction, occurring at a rate of about 5 percent of cross-linking and increased unsaturation. Oxidation is generally neglected, but it could play a significant role. The occurrence of each of these reactions is linearly dependent on the absorbed dose of radiation.

2.5 Polypropylene (PP)

Polypropylene is a rather versatile polymers. It serves double duties, i.c. a plastic and a fiber. As a plastic it is used to make things like dishwasher-safe food containers since it does not melt below 160 °C. As a fiber, polypropylene is used to make indoor-outdoor carpeting, such as those find around swimming pools and miniature golf courses. Polypropylene works well as outdoor carpet and thus easy to dye because polypropylene does not absorb water like nylon.

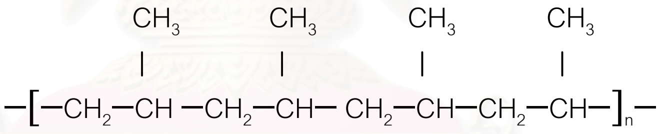
Structurally, PP is a vinyl polymer, and is similar to polyethylene. The difference from PE is that there is methyl group attached only on every other carbon atom in the backbone chain like as shown in Figure 2.6.



$$-[-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-]_n-$$

Figure 2.6 Chemical structure of polypropylene

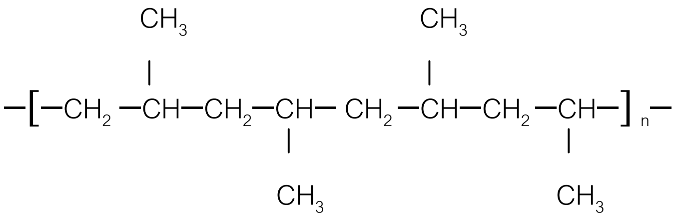
In the melt state, polypropylene shows some helical segments in the collapsed structure which different from a local order of polyethylene melt structure.(9) Polypropylene can be made with different tacticities. Most polypropylene we use is isotactic. This means that all the methyl groups are on the same side of the chain, such as these display in Figure 2.7.



$$-[-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-]_n-$$

Figure 2.7 Chemical structure of isotactic polypropylene

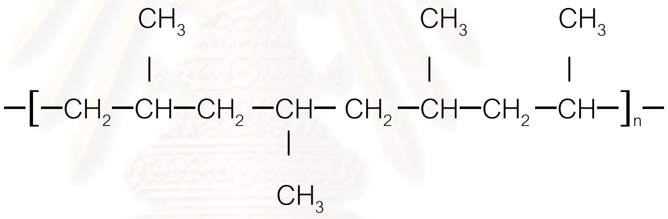
But sometimes we use syndiotactic and atactic polypropylene. Syndiotactic polypropylene means that the methyl groups are placed alternately on both sides of the chain, as illustrated in Figure 2.8.



$$-[-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-]_n-$$

Figure 2.8 Chemical structure of syndiotactic polypropylene

Atactic polypropylene means that the methyl groups are placed randomly on both sides of the chain, its configuration can be shown in Figure 2.9.



$$-[-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-]_n-$$

Figure 2.9 Chemical structure of atactic polypropylene

Polymers vary widely in their mechanical behavior depending on the degree of crystallinity, degree of crossslinking, and the values of T_g and T_m. High strength and low extensibility are obtained in polymers by having various combinations of high degrees of crystallinity or crosslinking or rigid chains (characterized by high T_g). High extensibility and low strength in polymers are synonymous with low degrees of crystallinity and crosslinking and low T_g values. The temperature limits of utility of a polymer are governed by its T_g and/ or T_m. Strength is lost at or near T_g for an amorphous polymer and at or near T_m for a crystalline polymer.

Some polymers are used in more than one category because certain mechanical properties can be manipulated by appropriate chemical or physical means, such as by altering the crystallinity or adding plasticizers or copolymerization.

2.6 Computer Modeling

Today, computer is used to generate the model of a molecular system prior to synthesizing that molecule in the laboratory. Although computational models may not be perfect, they are often good enough to rule out of possible compounds as being unsuitable for their intended use. This is very useful information because synthesizing a single compound could require months of labor and raw materials, and generate toxic waste.

Computer modeling is also used to make an understanding a problem more completely. There are some properties of a molecule that can be obtained computationally more easily than by experimental means. There are also insights into molecular bonding, which can be obtained from the results of computations, that cannot be obtained from any experimental method. Thus, many experimental chemists are now using computer modeling to gain additional understanding of the compounds being examined in the laboratory.

Molecules are traditionally considered as being “ composed ” of atoms or, in a more general sense, as a collection of charged particles, positive nuclei and negative electrons. The only important physical force for chemical phenomena is the Coulombic interaction between these charged particles. Molecules differ because they contain different nuclei and number of electrons, or the nuclear centres may be in different geometrical positions.

When starting a molecular modeling study the first thing to do is to generate a model of the molecule in the computer by defining the relative positions of the atoms in space by a set of Cartesian coordinates. A reasonable and reliable starting geometry essentially determines the quality of the following investigations. It can be obtained from several sources. The four basic methods for generating 3 D molecular structures are

1. use of X-ray crystallographic databases,
2. compilation from fragment libraries with standard geometries, and
3. simple drawing of 2D-structures using an approach called ‘ sketch ‘,
4. 2D to 3D conversion using automated approaches.

2.7 Force Field Method

The molecules tend to be composed of units which are structurally similar in different molecules. The picture of molecules being composed of structural units, “functional groups”, which behave similarly in different molecules forms the very basis of organic chemistry. The drawing of molecular structures where alphabetic letters represent atoms and lines represent bonds is used universally. Organic chemists often build ball and stick models of their molecules to examine their shapes. Force field methods are in a sense a generalization of these models, with the added feature that the atoms and bonds are not fixed at one size and length. Furthermore, force field calculations enable predictions of relative energies and barriers for interconversion of different conformations.

Molecular structures generated should always be geometry optimized to find the individual energy minimum state. This is normally done by applying a molecular mechanics method. The “molecular mechanics” is used to define a widely accepted computational method employed to calculate molecular geometries and energies.

Molecular mechanics enables the calculation of the total steric energy of a molecule in terms of deviations from reference “unstrained” bond lengths, angles and torsions plus non-bonded interactions. A collection of these unstrained values, together with what may be termed force-constants (but in reality are empirically derived fit parameters), is know as the force field. Given such an energy function of the nuclear coordinates, geometries and relative energies can then be calculated. Stable molecules correspond to minima on the potential energy surface, and they can be located by minimizing E_{tot} as a function of the nuclear coordinates.

In the framework of the molecular mechanics method the atoms in molecules are treated as rubber balls of different sizes (atom types) joined together by springs of varying length (bonds). For calculating the potential energy of the atomic ensemble use is made of Hooke’s law. In the course of a calculation the total energy is minimized with respect to atomic coordinates. The force field energy is written as a sum of terms, each describing the energy required for distorting a molecule in a specific fashion.

$$E_{tot} = E_{str} + E_{bend} + E_{tors} + E_{vdw} + E_{elec} + \ldots \qquad \mathbf{1)}$$

Where E_{tot} is the total energy of the molecule, E_{str} is the bond-stretching energy term, E_{bend} is the angle-bending energy term, E_{tors} is the torsional energy term, E_{vdw} is the van der Waals energy term, and E_{elec} is the electrostatic energy term.(12)

The first tem in Eq. 1), E_{str}, is the energy function for stretching a bond between two atom types A and B. It describes the energy change as a bond stretches and contracts from its ideal unstrained length. It is assumed that the interatomic forces are harmonic so the bond-stretching energy term can be described in simplest form by a simple quadratic function given in Eq. 2):

$$E_{str} \quad = \quad \frac{1}{2}\ k_l\,(\,l - l_0\,)^2 \qquad\qquad 2)$$

Where **k$_l$** is the bond-stretching force constant, **l$_0$** is the unstrained bond length, and **l** is the actual bond length.

Also for angle bending mostly a simple harmonic, spring-like representation is employed. Vibrational spectroscopy reveals that, for small displacements from equilibrium, energy variations associated with bond angle deformation are as well modeled by polynomial expansions as are variations associated with bond stretching. Thus, the typical force field function for angle strain energy is

$$E_{bend} \quad = \quad \frac{1}{2}\ k_\theta\,(\theta - \theta_0\,)^2 \qquad\qquad 3)$$

Where **k$_\theta$** is the angle-bending force constant, **θ** is the bond angle, and **θ$_0$** is the equilibrium value for **θ.**

If consider four atoms connected in sequence, ABCD, the torsion angle (or dihedral angle) associated with the ABCD linkage. The torsional angle is defined as the angle between bonds AB and CD when they are projected into the plane bisecting the BC bond. The convention is to define the angle as positive if one must rotate the bond in front of the bisecting plane in a clockwise fashion to eclipse the bond behind the bisecting plane. By construction, the torsion angle is periodic. An obvious convention would be to use only the positive angle, in which case the torsion period would run from 0 to 2π radians (0 to 360°). A common expression for the dihedral potential energy term is a cosine series, as equation 6):

$$E_{tors} \quad = \quad \frac{1}{2}\,k_\omega\,[\,1 + \cos\,(\,n\omega - \omega_0\,)] \qquad\qquad 4)$$

Where $\mathbf{k_{\omega}}$ is the torsional barrier, $\boldsymbol{\omega}$ is the actual torsional angle, n is the periodicity (number of energy minima within one full cycle), and $\boldsymbol{\omega_0}$ is the reference torsional angle.

The van der Waals interactions between not directly connected atoms are usually represented by the simplest functional form that tends to be used in force fields to represent the combination of the dispersion and repulsion energies is defined as " Lennard-Jones" potential :

$$E_{vdw} = \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \qquad \text{5)}$$

Where $\mathbf{A_{ij}}$ is the repulsive term coefficient, $\mathbf{B_{ij}}$ is the attractive term coefficient, and $\mathbf{r_{ij}}$ is the distance between the atom i and j.

An additional function is used to describe the electrostatic forces. The simplest approach is to assign to exact van der Waals atom a partial charge, in which case the interaction energy between atoms A and B is simply. In general it is made use of the Coulomb interaction term as

$$E_{elec} = \frac{1}{\varepsilon} \frac{Q_1 Q_2}{r_{12}} \qquad \text{6)}$$

Where $\boldsymbol{\varepsilon}$ is the dielectric constant, $\mathbf{Q_1}$, $\mathbf{Q_2}$ are atomic charges of interacting atom, and $\mathbf{r}$ is the interatomic distance.

For simplicity, the charges are permanent, in the sense that all atoms of a given type are defined to carry that charge in all situations. Thus, the atomic charge is a fixed parameter. Alternatively, the charge can be determined from a scheme that depends on the electronegativity of the atom in question, and also on the electronegativities of those atoms to which it is defined to be connected. Thus, the atomic electronegativity becomes a parameter and some functional form is adopted in which it plays a role as a variable.

Some force fields also include cross terms, out of plane terms, hydrogen bonding terms etc. and use more differentiated potential energy functions to describe the system.

The basic idea of molecular mechanics is that the bonds have “natural” lengths and angles. The equilibration values of these bond lengths and bond angles and the corresponding force constants used in the potential energy function are defined in the force field and will be denoted as force field parameters. Each deviation from these standard values will result in increasing total energy of the molecule. So, the total energy is a measure of intramolecular strain relative to a hypothetical molecule with ideal geometry. By itself the total energy has no physical meaning.

The objective of a good and generally employable force field is to describe as many as possible different classes of molecules with reasonable accuracy. The reliability of the molecular mechanics calculation is dependent on the potential energy functions and the quality of the parameters incorporated in these functions. So, it is easy to understand that a calculation of high quality can not be performed if parameters for important geometrical elements are missing. To avoid this situation it is necessary to choose a suitable force field for a particular investigation.

As already mentioned almost certainly the generated 3D model of a given molecule does not have ideal geometry; therefore, a geometry optimization must be performed subsequently. One of the key motivations in early force field design was the development of an energy functional that would permit facile optimization of molecular geometries. While the energy of an arbitrary structure can be interesting, real molecules vibrate thermally about their equilibrium structures, so finding minimum energy structures is key to describing equilibrium constants, comparing to experiment, etc. Thus, as emphasized above, one priority in force field development is to adopt reasonably simple functional forms so as to facilitate geometry optimization.

In the course of the minimization procedure the molecular structure will be relaxed. Optimization is a general term for finding stationary points of a function, i.e. points where the first derivative is zero. In the majority of cases the desired stationary point is a minimum, i.e. all the second derivatives should be positive.

The main advantage of force field methods is the speed at which calculations can be performed. This enables large systems to be treated. Even with modest size computers, molecules with several thousand atoms can be optimized. This makes applications viable for modeling biomolecular macromolecules, such as proteins and DNA.

2.8 Molecular Dynamics Simulations

Molecular dynamics is a simulation of the time-dependent behavior of a molecular system, such as vibrational motion or Brownian motion. It requires a way to compute the energy of the system, most often using a molecular mechanics calculation. This energy expression is used to compute the forces on the atoms for any given geometry.

Molecular dynamics simulations is the one of an effective means used for exploring conformational space, especially for molecules containing hundreds of rotatable bonds. The aim of this approach is to reproduce the time-dependent motional behavior of a molecule. Molecular dynamics are based on molecular mechanics. It is assumed that the atoms in the molecule interact with each other according to the rules of the employed force field. At regular time intervals the classical equation of motion represented by Newton’s second law is solved:

$$F_i(t) = \frac{m_i\, dv_i(t)}{dt} \qquad 7)$$

$$= -\nabla V \qquad 8)$$

Where F_i is the force on atom *i* at time *t*, m_i is the mass of atom *i*, v_i is the velocity of atom i and *V* is potential energy. The gradient of the potential energy function is used to calculate the forces on the atoms while the initial velocities on the atoms are generated randomly at the beginning of the dynamics run. Based on the initial atom coordinates of the system, new positions and velocities on the atoms can be calculated at time *t* and the atoms will be moved to these new positions.

As a result of this, a new conformation is created. The cycle will then be repeated for a predefined number of time steps. The collection of energetically accessible conformations produced by this procedure is called an *ensemble*. The steps in a molecular dynamics simulation of an equilibrium system are as follows:(13)

1. Choose initial positions for the atoms. For a molecule this is whatever geometry is available, not necessarily an optimized geometry.

2. Choose an initial set of atom velocities. These are usually chosen to obey a Boltzmann distribution for some temperature, then normalized so that the net momentum for the entire system is zero.

3. Compute the momentum of each atom from its velocity and mass.

4. Compute the forces on each atom from the energy expression. This is usually a molecular mechanics force field designed to be used in dynamical simulations.

5. Compute new positions for the atoms a short time later, called the time step. This is a numerical integration of Newton’s equations of motion using the information obtained in the previous steps.

6. Compute new velocities and accelerations for the atoms.

7. Repeat steps 3 through 6.

8. Repeat this iteration long enough for the system to reach equilibrium. In this case, equilibrium is not the lowest energy configuration; it is a configuration that is reasonable for the system with the given amount of energy.

9. Once the system has reached equilibrium, begin saving the atomic coordinates every few iterations. This information is typically saved every 5 to 25 iterations. This list of coordinates over time is called a trajectory.

10. Continue iterating and saving data until enough data have been collected to give results with the desired accuracy.

11. Analyze the trajectories to obtain information about the system. This might be determined by computing radial distribution functions, diffusion coefficients, vibrational motions, or any other property computable from this information.

The application of Newton’s equations of motion is uniform in all different available molecular dynamics approaches, but they differ in the employed integration algorithms.

In the application of molecular dynamics to search conformational space it is a common strategy to select conformations at regular time intervals and minimize them to the associated local minimum. This procedure has been used in several conformational analysis studies on small molecules, including ring systems.

Unlike quantum mechanical approaches the electrons and nuclei of the atoms are not explicitly included in the calculations. Molecular mechanics considers the atomic composition of a molecule to be a collection of masses interacting with each other via harmonic forces. As a result of this simplification molecular mechanics is a relatively fast computational method practicable for small molecules as well as for larger molecules and even oligomolecular systems.

2.9 Quantum Mechanical Methods

Quantum mechanical methods are very valuable additional tools in computational chemistry. In general, properties like molecular geometry and relative conformational energies can be calculated with high accuracy for a broad variety of structures by a well-parameterized general force field. However, if force field parameters for a certain structure are not available quantum chemical methods can be used for geometry optimization. In addition, the calculation of transition states or reaction paths as well as the determination of geometries influenced by polarization or unusual electron distribution in a molecule is the domain of quantum mechanical calculations. Their disadvantages relative to other methods are the computational costs and the limitation to rather small molecules. So, the use of quantum mechanical methods should be reserved for the treatment of special problems.

Electrons are very light particles, and they cannot be described even qualitatively correctly by classical mechanics. The time-independent Schrödinger equation, which in short-hand operator form is given as(14)

$$H\Psi \quad = \quad E\Psi \qquad \textbf{9)}$$

Where **H** is the classical-mechanical Hamiltonian operator, **Ψ** is a wave function, and **E** is the energy. In the language of mathematics, the equation of this form is called an eigenvalue equation. **Ψ** is then called the eigenfunction and **E** an eigenvalue.

The wave function **Ψ** is a function of the electron and nuclear positions. To describe the state of a system in quantum mechanics, we postulate the existence of a function of the particles’ coordinates called the wave function or state function **Ψ**. As the name implies, this is the description of an electron as a wave. This a probabilistic description of electron behavior. As such, it can describe the probability of electrons being in certain locations, but it can not predict exactly where electrons are located. The wave function is also called a probability amplitude because it is the square of the wave function that yields probabilities. This the only rigorously correct meaning of a wave function.

The Hamiltonian function is equal to the energy, which is composed of kinetic **(T)** and potential **(V)** energies. For a one particle, three-dimentional system, the classical-mechanical Hamiltonian is

$$H \quad = \quad T + V \qquad \textbf{10)}$$

Hamiltonian is a function of coordinates and momenta :

$$H = \frac{1}{2m}(p_X{}^2 + p_Y{}^2 + p_Z{}^2) + V(x,y,z) \qquad 11)$$

From 11), introducing the quantum-mechanical operators, the Hamiltonian operator is(15)

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z) \qquad 12)$$

The operator in parentheses in equation 12) is call **Laplacian operator** ∇^2

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad 13)$$

The equation is then :

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z) \qquad 14)$$

The Hamiltonian operator for an n-particle, three dimensional system is then

$$H = -\sum_{i=1}^{n} -\frac{\hbar^2}{2m}\nabla^2 + V(x_1,\ldots,z_n) \qquad 15)$$

Where ***h*** is Planck's constant and has the value 6.62618 * 10 $^{-34}$ J.s.

The typical form of the Hamiltonian operator takes into account five contributions to the total energy of a system: the kinetic energies of the electrons and nuclei, the attraction of the electrons to the nuclei, and the interelectronic and internuclear repulsions. In more complicated situations, e.g., in the presence of an external electric field, in the presence of an external magnetic field, in the event of significant spin-orbit coupling in heavy elements, taking account of relativistic effects, etc., other terms are required in the Hamiltonian. Casting the Hamiltonian into mathematical notation as:(14)

$$H = -\sum_{i}\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{k}\frac{\hbar^2}{2m_k}\nabla_k^2 - \sum_{i}\sum_{k}\frac{e^2 Z_k}{r_{ik}} + \sum_{i<j}\frac{e^2}{r_{ij}} + \sum_{k<l}\frac{e^2 Z_k Z_l}{r_{kl}} \qquad 16)$$

Where **i** and **j** run over electrons, **k** and **l** run over nuclei, $\bar{\mathbf{h}}$ is Planck's constant divided by 2π, $\mathbf{m_e}$ is the mass of the electron, $\mathbf{m_k}$ is the mass of nucleus **k**, ∇^2 is the Laplacian operator, **e** is the charge on the electron, **Z** in an atomic number, and $\mathbf{r_{ab}}$ is the distance between particles *a* and *b*. Note that **Ψ** is thus a function of *3n* coordinates where *n* is the total number of particles (nuclei and electrons), e.g., the *x*, *y*, and *z* Cartesian coordinates specific to each particle.

2.10 Born-Oppenheimer approximation

In fact, accurate wave functions for such systems are extremely difficult to express because of the correlated motions of particles. That is, the Hamiltonian in Eq. 16) contains pairwise attraction and repulsion terms, implying that no particle is moving independently of all of the others. In order to simplify the problem somewhat, we may invoke the so-called *Born-Oppenheimer* approximation.(16)

Under typical physical conditions, the nuclei of molecular systems are moving much more slowly than the electrons (recall that protons and neutrons are about 1800 times more massive than electrons and note the appearance of mass in the denominator of the kinetic energy terms of Hamiltonian in Eq. 16)). For practical purposes, electronic relaxation with respect to nuclear motion is instantaneous. As such, it is convenient to decouple these two motions, and compute electronic energies for fixed nuclear positions. That is, the nuclear kinetic energy term is taken to be independent of the electrons, correlation in the attractive electron-nuclear potential energy term is eliminated, and the repulsive nuclear-nuclear potential energy term becomes a simply evaluated constant for a given geometry. Thus, the electronic Schrodinger equation is taken to be

$$H_{elec}\Psi_{elec} = E\Psi_{elec} \qquad \textbf{17)}$$

Born-Oppenheimer approximation is based on the fact that the masses of the nuclei are much greater than the electrons, hence the electrons can respond almost instantaneously to any change in the nuclear positions. Consequently, the motions of the electrons can be reasonably assumed to depend only on the coordinates and not the momentum of the nuclei. In this case, the electronic motions can be solved separately as if they are in the potential of fixed nuclei. Written in atomic units, the electronic Hamiltonian becomes

$$H_{elec} = -\sum_{i} \frac{\hbar^2}{2} \nabla_i^2 - \sum_{i}\sum_{k} \frac{Z_k}{r_{ik}} + \sum_{i<j} \frac{1}{r_{ij}} \qquad \textbf{18)}$$

Note that both $\mathbf{H}_{\mathbf{elec}}$ and $\mathbf{E}_{\mathbf{elec}}$ depend parametrically on the positions of the nuclei. Normally solution of the electronic Schrodinger equation is represented in term of the total potential energy which is the sum of the total electronic energy of the molecular system $\mathbf{E}_{\mathbf{elec}}$ and nuclear repulsion term $\mathbf{E}_{\mathbf{nuc.}}$

$$E_{tot} = E_{elec} + E_{nuc} \qquad \textbf{19)}$$

2.11 Slater Determinant

Mathematically, the eigenfunction associated with a sum of independent operators is the product of the eigenfunctions of these operators. Therefore, the eigenfunction of the N-electron is a product of spin orbitals called a Hartree product, Ψ^{HP}, with electron-one being described by the spin orbital χ_i, electron-two being described by the spin orbital χ_j, etc.

$$\Psi^{HP} = \chi_i(x_1)\,\chi_j(x_2)\ldots\,\chi_n(x_N) \qquad \textbf{20)}$$

Hartree products, however, do not satisfy the Pauli exclusion principle via the antisymmetry principle, which states that the sign of any many-electron wave function must be antisymmetric with respect to the interchange of the coordinates, both space and spin, of any two electrons. The antisymmetry principle prevents two electrons with the same spin from occupying the same spatial orbital. Since the Hartree product wave function is constructed on the assumption that the electrons are non-interacting, there exists a non-zero probability of finding two electrons occupying the exact same point in space.

Since the Hartree products have the correct asymptotic limit at infinite separation, one can use them as primitive functions to construct a new trial wave function, which can satisfy the Pauli exclusion Principle. One of such a function is the *Slater determinant* of N spin-orbitals.

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \ldots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \ldots & \chi_N(x_2) \\ \chi_1(x_N) & \chi_2(x_N) & \ldots & \chi_N(x_N) \end{vmatrix} \qquad 21)$$

2.12 Hartree-Fock Approximation

One further approximation, taking the trial wave function to consist of a single *Slater determinant*. This implies that electron correlation is neglected, or equivalently, the electron-electron repulsion is only included as an average effect. Having selected a single determinant trial wave function the variational principle can be used to derive the Hartree-Fock (HF) equations.(14)

The Hartree-Fock (HF) theory first assumes that the N-electron wave function can be represented by a single Slater determinant constucted from a set of N orthonormal spin orbitals (χ_a).

$$|\Psi> \quad = \quad |\chi_1\,\chi_2\,\ldots\,\chi_a\,\chi_b\,\ldots\,\chi_N> \qquad 22)$$

Within this formulation, it is easy to show that the total energy of the system can be written as

$$E_0 \quad = \quad < \Psi_0 \mid \hat{H} \mid \Psi_0 > \qquad 23)$$

$$= \quad \sum_{a=1}^{N} h_{aa} \; + \; \tfrac{1}{2} \sum_{a=1}^{N} \sum_{b=1}^{N} J_{ab} \; - \; K_{ab}$$

Where $\hat{H}$ is the full Hamiltonian. The variational flexibility in the wave function is in the choice of spin orbitals. The $\mathbf{h_{aa}}$ is core Hamiltonian which expanded to the average kinetic and nuclear attraction energy of an electron described by the wave function Ψ_a. The integral called coulomb integral is denoted by $\mathbf{J_{ab}}$ and exchange integral is denoted by $\mathbf{K_{ab}}$.

By minimizing $\mathbf{E_0}$ with respect to the choice of spin orbitals, one can derive and equation, called the Hartree-Fock equation, which determines the optimal spin orbitals. Hartree-Fock equation is an eigenvalue equation of the form

$$f(i) \; \chi(x_i) \quad = \quad \varepsilon \chi(x_i) \qquad 24)$$

Where f **(i)** is an effective one-electron operator, called the Fock operator, of the form

$$f(i) \quad = \quad -\tfrac{1}{2} \nabla_i^2 \; - \; \sum_{k=1}^{M} \frac{Z_k}{r_{ik}} \; + \; v^{HF}(i) \qquad 25)$$

Where $\nu^{\mathbf{HF}}\mathbf{(i)}$ is the average potential experienced by the **i**th electron due to the presence of the other electrons. The essence of the Hartree-Fock approximation is to replace the complicated many-electron problem by a one-electron problem in which electron-electron repulsion is treated in an average way.

The Hartree-Fock potential $\nu^{\mathbf{HF}}\mathbf{(i)}$**,** or equivalently the field seen by the **i**th electron, depends on the spin orbitals of the other electrons (i.e., the Fock operator depends on its eigenfunctions). Thus the Hartree-Fock equation is nonlinear and must be solved iteratively. The procedure for solving the Hartree-fock equation is called the self-consistent-field (SCF) method.

The basic idea of the SCF method is making an initial guess at the spin orbitals, then calculate the average field (i.e., $\nu^{\mathbf{HF}}$) seen by each electron and then solve the eigenvalue equation for a new set of spin orbitals. Using these new spin orbitals, new fields and repeat the procedure until self-consistency is reached (i.e., until the fields no longer change and the spin orbitals used to construct the Fock operator are the same as its eigenfunctions).

A restricted orbitals at ground state is

$$|\Psi_0 > \; = \; |\chi_1\, \chi_2\, \dots\, \chi_{N-1}\, \chi_N > \; = \; |\, \psi_1\, \overline{\psi}_1 \,\dots\, \psi_a\, \overline{\psi}_a \,\dots\, \psi_{\frac{N}{2}}\, \overline{\psi}_{\frac{N}{2}} > \qquad \mathbf{26)}$$

To convert the general spin orbital Hartree-Fock equation 24) to a spatial eigenvalue equation where each of the occupied spatial molecular orbitals $\psi_{\mathbf{a}}$ is doubly occupied. The Hartree-Fock equation is then

$$f(\mathbf{r}_1)\;\; \psi_i(\mathbf{r}_1) \;=\; \varepsilon_i\;\; \psi_i(\mathbf{r}_1) \qquad \mathbf{27)}$$

As this equation, numerical solutions are common in atomic calculations. No practical procedures are presently available, however, for obtaining numerical solutions for molecules. The contribution of Roothaan introducing a set of known spatial basis functions, the differential equation could be converted the set of Hartree-Fock differential equations to a set of algebraic equations and solved by standard matrix techniques.

Therefore, introduce a set of **K** known linearly independent basis functions **{ ϕ_μ (r)| μ=1, 2, …, K }** which are normalized and the unknown molecular orbitals (or spatial orbitals, ψ_i) can be expanded in terms of these linear basis functions as

$$\psi_i = \sum_{\mu=1}^{K} C_{\mu i}\ \phi_\mu \qquad i = 1, 2, \ldots, K \qquad \textbf{28)}$$

If the basis set $\{\phi_\mu\}$ was complete, this would be an exact expansion, and any complete set $\{\phi_\mu\}$ could be used. Finite the set of K basis functions is restricted for practical computational reasons. As such, it is important to choose a basis that will provide, as far as is possible, a reasonably accurate expansion for the exact molecular orbitals $\{\psi_i\}$, particularly, for those molecular orbitals $\{\psi_a\}$ which are occupied in $|\Psi_0>$ and determine the ground state energy $\mathbf{E_0}$.

From Eq.28), the problem of calculating the Hartree-Fock molecular orbitals reduces to the problem of calculating the set of expansion coefficients $\mathbf{C_{\mu i}}$. A matrix equation for the $\mathbf{C_{\mu i}}$ by substituting the linear expansion Eq.28) into the Hartree-Fock equation 27). Using the index ν, gives

$$f(1)\sum_{\nu} C_{\nu i}\,\phi_{\nu}(1) = \varepsilon_i \sum_{\nu} C_{\nu i}\,\phi_{\nu}(1) \qquad 29)$$

Thus, the integrated Hartree-Fock equation can be written as

$$\sum_{\nu} F_{\mu\nu}\,C_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu}\,C_{\nu i} \qquad i = 1, 2, \ldots, K \quad 30)$$

These are the *Roothaan* equations, which can be written as the single matrix equation(17)

$$FC = SC\varepsilon \qquad 31)$$

Where ε is a diagonal matrix of the orbital energies ε_i, **C** is an M*M square matrix of the expansion coefficient $C_{\nu i}$. **S** and **F** are defined as the overlap matrix and the Fock matrix, respectively.

If the basis function expansion Eq.28) is substitute to the molecular orbitals for obtain the energy, which is readily evaluated from quantities available at any stage of the SCF iteration procedure, i.e.,

$$E_0 = \tfrac{1}{2} \sum_{\mu}\sum_{\nu} P_{\nu\mu}\,(H_{\mu\nu}^{core} + F_{\mu\nu}) \qquad 32)$$

Where $\mathbf{F}_{\mu\nu}$ is Fock matrix, $\mathbf{P}_{\nu\mu}$ is density matrix, and $\mathbf{H}_{\mu\nu}^{\mathrm{core}}$ is a core Hamiltonian matrix.

If $\mathbf{E}_0$ is calculated using the same matrix P as was used to form F, then $\mathbf{E}_0$ will be an upper bound to the true energy at any stage of the iteration and will usually converge monotonically from above to the converged result. If one adds the nuclear-nuclear repulsion to the electronic energy $\mathbf{E}_0$ one obtains the total energy $\mathbf{E}_{\mathrm{tot}}$

$$E_{tot} = E_0 + \sum_{k}\sum_{l>k} \frac{Z_k Z_l}{R_{kl}} \qquad 33)$$

This is commonly the quantity of most interest, particularly in structure determinations, because the predicted equilibrium geometry of a molecule occurs when $\mathbf{E}_{\mathrm{tot}}$ is minimum.

The two electron molecules H_2 and HeH^+ are prototypes for homonuclear and heteronuclear diatomic molecules. Both molecules will be considered in the approximation of a minimal basis set, $\{\phi_\mu\}$, consisting of only two function, one on each nucleus. The limitation of these models is only I the basis set. Larger bases sets would lead to correspondingly more accurate results. Since both molecules are simple two electron systems, essentially exact calculations, corresponding to an infinite basis set, will be available for comparison with the very approximate calculations.

2.13 Basis Sets

One of the approximations inherent in essentially all ab initio methods is the introduction of a basis set. Expanding an unknown function, such as a molecular orbital, in a set of known functions is not an approximation, if the basis is complete. However, a complete basis means that an infinite number of functions must be used, which is impossible in actual calculations. An unknown MO can be thought of as a function in the infinite coordinate system spanned by the complete basis set. When a finite basis is used, only the components of the MO along those coordinate axes corresponding to the selected basis can be represented. The smaller the basis, the poorer the representation. The type of basis functions used also influence the accuracy. The better a single basis function is able to reproduce the unknown function, the fewer are basis functions necessary for achieving a given level of accuracy. Knowing that the computational effort of ab initio methods scales formally as at least M4, it is of course of prime importance to make the basis set as small as possible without compromising the accuracy.

The basis set is the set of mathematical functions from which the wave function is constructed. Each MO in HF theory is expressed as a linear combination of basis functions, the coefficients for which are determined from the iterative solution of the HF SCF equations. The full HF wave function is expressed as a Slater determinant formed from the individual occupied MOs. In the abstract, the HF limit is achieved by use of an infinite basis set, which necessarily permits an optimal description of the electron probability density. In practice, however, one cannot make use of an infinite basis set. Thus, much work has gone into identifying mathematical functions that allow wave functions to approach the HF limit arbitrarily closely in as efficient a manner as possible.

There are two types of basis functions (also called Atomic Orbitals, AO) commonly used on electronic structure calculations: Slater Type Orbitals (STO) and Gaussian Type Orbitals (GTO). Slater type orbitals is based on the hydrogen atom. They are described by the function depending on spherical coordinates. The radial part of orbitals (**exp** $(-\zeta \bar{r})$) is an exponentially decaying function:

$$\phi(\vec{r}) \qquad = \qquad N\exp(-\zeta\vec{r}) \qquad 34)$$

N is a normalization constant, ζ is called "exponent". The exponential dependence on the distancer between the nucleus and the electron mirrors the exact or bitals for the hydrogen atom. However, STOs do not have any radial nodes, modes in the radial part are introduced by making linear combinations of STOs. The exponential dependence ensures a fairly rapid convergence with increasing number of functions, however, the calculation two-electron integrals cannot be performed analytically and time consuming to evaluate using STOs.

An alternative to the use of STOs is to use the Gaussian Type Orbitals (GTOs). All that is required for there to be an analytical solution of the general integral formed from such functions is that the radial decay of the STOs be changed from **exp** $(-\vec{r})$ to **exp** $(-\vec{r})^2$. That is, the AO-like functions are chosen to have the form of a Gaussian function. The general functional form of a normalized Gaussian-type orbital (GTO) is expressed as:

$$\phi(\vec{r}) \qquad = \qquad N\exp(-\alpha|\vec{r}|^2)\,x^l y^m z^n \qquad 35)$$

Where α is called "exponent". The x, y, and z are Cartesian coordinates. The l, m, and n are not quantum numbers but simply integral exponents at Cartesian coordinates ($\vec{r}^{\,2} = x^2 + y^2 + z^2$).

The major differences between the two functions **exp** $(-\vec{r})$ and **exp** $(-\vec{r})^2$ occur at $\vec{r}=0$ and at larger $\vec{r}$.(17) At $\vec{r}=0$, the Slater function has a finite slope and the Gaussian function has a zero slope, i.e., GTOs are more smooth and differentiable at the nucleus $\vec{r}=0$. At large values of $\vec{r}$, the Gaussian function **exp** $(-\vec{r})^2$ decays much more rapidly than the Slater function radial decay **exp** $(-\vec{r})$, this results in too rapid a reduction in amplitude with distance for the GTOs.

The GTOs do not have the correct behaviors as $\vec{r}$ approaching zero and infinity. However, we can use them as primitive functions to represent STOs orbitals. The advantage of such an approach is that two-electron integrals can be evaluated analytically. Accuracy can be achieved if a larger number of primitive Gaussian functions are use.

Thus, use of basis functions that are approximate atomic Hartree-Fock functions, Slater-type functions, etc., while still evaluating integrals only with primitive Gaussian functions. A procedure that has come into wide use is to fit a Slater-type orbital to a linear combination of L = 1, 2, 3, … primitive Gaussian functions. This is the STO-LG procedure.(17) In particular, STO-3G basis sets are often used in polyatomic calculations, in preference to evaluating integrals with Slater functions. The Figure 2.10 express the comparison of quality of the least squares fit of a 1s Slater function obtained by increasing the number of Gaussian in the contraction.

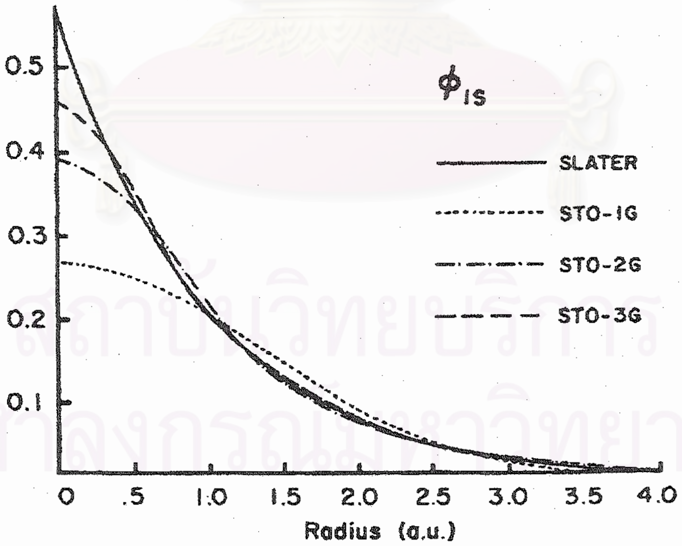


Figure 2.10 Comparison of the quality of the least-squares fit of a 1s Slater function (ζ= 1.0) obtained at STO-1G, STO-2G, and STO-3G levels.

The **STO-LG** basis sets are minimal basis sets, where each STO is approximated by L Gaussian primitive functions. The smallest basis set commonly used is the **STO-3G.**

Since most chemical properties only electrons in the valence shell are important, thus the more cost effective way to improve the basis set is to have more flexibility for the valence electrons only. This is the basis of the split-valence basis sets where the inner-shell orbitals are represented by minimal basis set while valence shell orbitals are represented by more than one basis function. For example, the 3-21G basis set has one contracted Gaussian function that is a linear combination of three primitive Gaussian functions for each inner-shell atomic orbital and two basis function, one contracted Gaussian function that is a linear combination of two primitive Gaussians and one primitive Gaussian function, for each valence orbital.

6-31G is also a split valence basis, where the core orbitals are a contraction of six primitive Gaussian function, the inner part of the valence orbitals is a contraction of three primitive Gaussian function and the outer part of the valence represented by one primitive Gaussian function. The designation of the carbon/hydrogen 6-31G basis is (10s4p/4s) → [3s2p/2s]. In terms of contracted basis functions it contains the same number as 3-21g, but the representation of each functions is better since more primitive Gaussian function are used.

To allow for the polarization of charge density due to nearby nuclei, orbitals for which the 1 quantum number is greater than maximum value of the valence orbitals in the ground state atom are added to the basis set. For example, 6-31G* (or 6-31G(d)) six-type Gaussian functions for each non-hydrogen atom in the second or third row atoms are included in the 6-31G basis set.

6-31G** (or 6-31G(d,p)) basis differs from the 6-31G*, i.e., indicates additional set of p-functions is also included for each hydrogen atom. The 6-31G** contraction is thus (11s4p1d/4s1p) → [4s2p1d/2s1p] and each hydrogen now includes five basis functions. There is no limit on the number of polarization functions included in the basis set, however, it does increase the computational demand significantly.

2.14 Density Function Theory

The electronic wave function of an n-electron molecule depends on $3n$ spatial and n spin coordinates. Since the Hamiltonian operator contains only one and two electron spatial terms, the molecular energy can be written in terms of integrals involving only six spatial coordinates. In a sense, the wave function of a many electron molecule contains more information than is needed and is lacking in direct physical significance. This has prompted the search for functions that involve fewer variables than the wave function and that can be used to calculate the energy and other properties.

This method can be considered a practical, reliable and economical tool for predicting the electronic and spectroscopic properties of a large class of chemical system especially in the inorganic field and particularly for transition metals containing systems. The difficulties of *ab initio* methods in these cases derive from the presence of many valence electrons, and the occupancy of d and f orbitrals. These systems require extensive treatment of electron correlation. Molecular orbital based (or HF- based) correlated other methods which are too expensive even for simple molecules.

The main idea of DFT is that the electronic ground state of any interacting system can be represented by its electron density. This provides a way to calculate physical observables of a variety of system without having to construct the whole electronic many body wavefunction, which is computationally a very expensive task.

The premise behind DFT is that the energy of a molecule can be determined from the electron density instead of a wave function. This theory originated with a theorem by Hohenburg and Kohn that stated this was possible. The original theorem applied only to finding the ground state electronic energy of a molecule. A practical application of this theory was developed by Kohn and Sham who formulated a method similar in structure to the Hartree-Fock method.

2.15 Hohenburg-Kohn theorem

The first Hohenburg-Kohn theorem states that "for a given external potential $V_{ext}(r)$, the electron density $\rho(r)$ of the ground state of a system uniquely determines the ground state wave function and hence all properties of the ground state". To prove this theorem, the assumption that there were two external potentials $V_{ext}(r)$ and $V'_{ext}(r)$ differing by more than a constant, each giving the same $\rho(r)$ for its ground state, we would have two Hamiltonians $\hat{H}$ and $\hat{H}'$ whose ground state densities were the same although the normalized wave functions ψ and $\psi^{\wedge}$ would be different. Taking $\psi^{\wedge}$ as a trial wave function for the $\hat{H}$ problem.

$$E_0 < \langle \psi' | \hat{H} | \psi' \rangle = \langle \psi' | \hat{H}' | \psi' \rangle + \langle \psi' | \hat{H} - \hat{H}' | \psi' \rangle$$

$$= E'_0 + \int \rho(r) \left[V_{ext}(r) - V'_{ext}(r) \right] dr \qquad 36)$$

Where $\mathbf{E_0}$ and $\mathbf{E'_0}$ are the ground state energies for the $\hat{H}$ and $\hat{H}'$, respectively. Similarly, taking ψ as a trial function for the $\hat{H}'$ problem,

$$E'_0 < \langle \psi | \hat{H}' | \psi \rangle = \langle \psi | \hat{H}' | \psi \rangle + \langle \psi | \hat{H}' - \hat{H} | \psi' \rangle$$

$$= E_0 + \int \rho(r) [V_{ext}(r) - V'_{ext}(r)] \, dr \qquad 37)$$

Adding Eq.36) and 37), obtaining $E_0 + E'_0 < E'_0 + E_0$, a contradiction, and so there cannot be two different $V_{ext}(r)$ that give the same $\rho(r)$ for their ground state.

Therefore $\rho(r)$ determines N and $V_{ext}(r)$ and hence all the properties of the ground state, for example the kinetic energy $T(\rho)$, the potential energy $V(\rho)$, and the total energy $E(\rho)$. Now we can write the total energy as

$$E[\rho] = E_{NE}[\rho] + T[\rho] + E_{ee}[\rho] = \int \rho(r) V_{NE}(r) \, dr + F_{HK}[\rho] \qquad 38)$$

Where $F_{HK}[\rho] = T[\rho] + E_{ee}[\rho]$

Where $E_{NE}[\rho]$ is potential energy due to electron-nuclei attraction, $E_{ee}[\rho]$ represents electron-electron repulsion energy and $T[\rho]$ is kinetic energy of electron. The functional F_{HK} is and universal functional. If it is known we would solved the Schrödinger equation exactly. F_{HK} contains the functional for the kinetic energy $T[\rho]$ and the electron-electron interaction, $E_{ee}[\rho]$. However, the classical part $J[\rho]$ from the $E_{ee}[\rho]$ is

$$E_{ee}[\rho] = \tfrac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{r_{12}} \, dr_1 \, dr_2 + E_{ncl} \qquad 39)$$

$$= J[\rho] + E_{ncl} \qquad 40)$$

E$_{ncl}$ is the non-classical contribution to the electron-electron interaction, self-interaction correction, exchange and Colomb correlation.

The second Hohenburg-Kohn theorem states that **F$_{HK}$[ρ]**, the functional that delivers the ground state energy of the system, delivers the lowest energy if the input density is the true ground state density.

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{NE}[\tilde{\rho}] + E_{ee}[\tilde{\rho}] \qquad 41)$$

2.16 Kohn-Sham equation

The Kohn-Sham formulation provides a way to map the system of interacting particles to an ensemble of electrons which only interact through their total density. As we have known the ground state energy of the system can be rewritten as

$$E_0 = \min_{\rho \rightarrow N} \left(F[\rho] + \int \rho(r)\, V_{Ne}\, dr \right) \qquad 42)$$

Where the universal functional **F[ρ]** contains the contribution of the kinetic energy, the classical Coulomb interaction and the non-classical portion:

$$F[\rho] = T[\rho] + J[\rho] + E_{ncl}[\rho] \qquad 43)$$

Only **J[ρ]** ks known. The main problem is to find the expression for **T[ρ]** and **E_{ncl}[ρ]**. To solve the problem Kohn and Sham proposed the approach described following.

Calculate the largest component of the kinetic energy by using the non-interacting reference system.

$$T_s = -\tfrac{1}{2}\sum_{i}^{N} \langle \psi_i | \nabla^2 | \psi_i \rangle$$

$$\rho_s(r) = \sum_{i}^{N} \sum_{s} | \psi_i(r,s) |^2 = \rho(r) \qquad 44)$$

where ψ_i are the orbitals of the non-interacting system. $\mathbf{T_s}$ is not equal to the true kinetic energy of the system.

Introduce the separation of the **F[ρ]**

$$F[\rho] = T_s[\rho] + J[\rho] + E_{XC}[\rho] \qquad 45)$$

where $\mathbf{E_{XC}}$ [ρ], the so-called exchange-correlation energy.

The solution of determine the wavefunction of orbital for non-interaction system, ψ_i, is write down the expression for the energy of the interacting system in the term of

$$E[\rho] = T_s[\rho] + J[\rho] + E_{XC}[\rho] + E_{Ne}[\rho] \qquad 46)$$

The resulting of minimized energy equation are the Kohn-Sham equation.

$$\left(-\tfrac{1}{2}\,\nabla^2 + \left(\int\frac{\rho(r_2)}{r_{12}} + V_{XC}(r_1) - \sum_{A}^{M}\frac{Z_A}{r_{1A}}\right)\right)\psi_i = \left(\tfrac{1}{2}\,\nabla^2 + V_{KS}(r_1)\right)\psi_i$$

$$= \varepsilon_i\,\psi_i \qquad 47)$$

Where the exchange correlation potential is given by the functional derivative

$$V_{XC} = \partial E_{XC}/\partial\rho \qquad 48)$$

$$V_{KS}(r) = V_{el} + V_{XC} + V_{nuc} \qquad 49)$$

The exact ground state density $\rho(\mathbf{r})$ of an N electron system is

$$\rho(r) = \sum_{i=1}^{N}\psi_i(r)^*\,\psi_i(r) \qquad 50)$$

where the single particle wave function $\psi_i(\mathbf{r})$ are the N lowest energy of the Kohn-sham equation.

The advantage of using electron density is that the integrals for Coulomb repulsion need be done only over the electron density, which is a three dimensional function, thus scaling as N^3. Furthermore, at least some electron correlation can be included in the calculation. This results in faster calculations than HF calculations which scale as N^4 and computations that are a bit more accurate as well. The better DFT functionals give results with high accuracy.

CHAPTER III
CALCULATION DETAILS

Three types of polymers i.e. polyethylene (PE), polypropylene (PP), and ethylene-propylene (EPM) block copolymer were studied. Three models, i.e. single chain, double chain, and bundle polymer with the chain length of 5, 10, 100 and 500 repeating units were used in this study. For PE and PP, their initial geometries with specified chain length (N) were taken from the library of crystalline polymers within Cerius2 package. For the EPM block copolymer, its starting geometries with various N chain length were obtained using Polymer Builder program in Cerius2 package. Using molecular dynamics (MD) simulation, structures of the 3 polymers at 3 different temperatures, 0 K, glass transition temperature (T_g), and melting temperature (T_m) were obtained.

3.1 Models of polymer

Polymer models were built from x-ray structure obtained from the library of Cerius2 package. The procedure for generating the polymer model is described as following.

1. Single chain PE and PP polymer. Using Crystal Builder in Cerius2 package, crystal structures of single chain polymer of up to 500 repeating units were created.

Figure 3.1 Single chain of initial structure of PE and PP, respectively.

2. Double chain PE and PP polymer. Using Crystal Builder in Cerius2 package, crystal structure of double chain polymer of up to 500 repeating units was created.

Figure 3.2 Double chain of initial structure of PE and PP, respectively.

3. Single chain EPM block copolymer. Using Polymer Builder in Cerius2 package, the structure of polymer of 500 repeating units was created. The model of EPM block copolymer is composed of the block of ethylene monomers orderly connected to the block of propylene monomers in the proportional of 80:20.

Figure 3.3 Single chain initial structure of EPM block copolymer.

4. Building bundle PE and PP polymer. Using Crystal Builder in Cerius2 package polymer crystal structure of 10 polymer chains with up to 50 numbers of unit cells approximately 50 repeating units per chain was created.

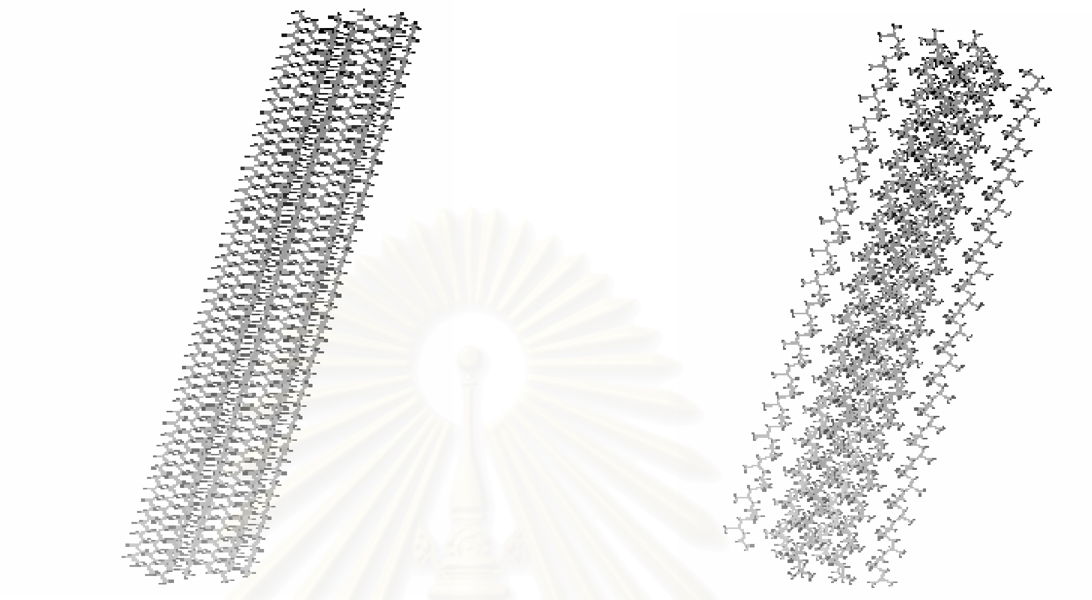


Figure 3.4 Bundle of initial structure of PE and PP, respectively.

3.2 Energy minimization

The energy minimizations were performed to obtain structures at 0 K of the 3 polymers. These were done using Discover program with PCFF force field which is well parameterized for polymer in Cerius2 package.

3.3 Molecular Dynamics Simulations

Structures at T_g and T_m were obtained using classical MD simulations. The NVT simulations were performed and the following set up was used.

3.3.1 Single chain PE, PP, and EPM & double chain PE and PP

1. Equilibration time. For T_g and T_m, the equilibration time of each sample is 12 ps up to 30 ps. All of equilibration time used are shown in Table 3.1 and 3.2.

Table 3.1 The equilibration time for single chain PE, PP, and EPM.

Repeating units		**Equalibration time at**	
		T_g (ps)	**T_m (ps)**
5	**PE**	**12**	**20**
	PP	**20**	**20**
	EPM	**20**	**25**
10	**PE**	**15**	**20**
	PP	**20**	**20**
	EPM	**20**	**30**
100	**PE**	**20**	**20**
	PP	**20**	**20**
	EPM	**20**	**30**
500	**PE**	**25**	**25**
	PP	**20**	**25**
	EPM	**30**	**30**

Table 3.2 The equilibration time of double chain PE and PP, respectively.

Repeating units		**Equalibration time at**	
		T_g (ps)	**T_m (ps)**
5	**PE**	**20**	**20**
	PP	**25**	**25**
10	**PE**	**20**	**20**
	PP	**25**	**25**
100	**PE**	**25**	**20**
	PP	**20**	**30**
500	**PE**	**20**	**30**
	PP	**30**	**30**

2. Time step. The molecular dynamics simulations were applied with 1 fs time step of all single and double chain polymer models and used 1000 output frequency rate.

3. Run time. For T_g and $T_{m,}$ the run time is various and up to 3600 ps. All of run times used are shown as in Table 3.3 and 3.4.

Table 3.3 The run time for single chain PE, PP, and EPM.

Repeating units		Production time at	
		T_g (ps)	T_m (ps)
5	PE	600	2500
	PP	1700	2200
	EPM	1500	1500
10	PE	800	3000
	PP	2500	2500
	EPM	1800	2000
100	PE	1900	3400
	PP	3200	3500
	EPM	2000	2800
500	PE	2700	3600
	PP	3500	3500
	EPM	3200	2500

Table 3.4 The run time for double chain PE and PP.

Repeating units		**Production time at**	
		T_g (ps)	**T_m (ps)**
5	**PE**	**1200**	**1500**
	PP	**1500**	**2000**
10	**PE**	**1800**	**2000**
	PP	**3000**	**3000**
100	**PE**	**1700**	**1700**
	PP	**3400**	**2800**
500	**PE**	**2000**	**3600**
	PP	**3200**	**3500**

3.3.2 Bundle PE and PP

1. The equilibration time and run time of bundle PE and PP at T_g and T_m can be shown in Table 3.5.

2. Time step. The molecular dynamics simulations were applied with 1 fs time step of bundle polymer models and used 1000 output frequency rate.

Table 3.5 The equilibration time and run time for PE and PP bundle.

Bundle models of	Equalibration time at		Production time at	
	T_g (ps)	T_m (ps)	T_g (ps)	T_m (ps)
PE	**30**	**30**	**2500**	**2500**
PP	**30**	**30**	**2000**	**2200**

3.4 **Quantum Calculation**

To approximate shear strength and chain – chain interaction of polymer, quantum calculations were carried out. The density functional theoretical B3LYP/6-31G (d,p) was performed on PE and PP of chain length 5 repeating units.

The shear strength was estimated by computing energy of double chain polymer as one chain moving from the other as shown in Figure 3.5.

Figure 3.5 Profile of double chain polymer as one chain moving pass the other

$\Delta E_{shear} = E_{double\ chain\ move} - E_{single\ chain}$

$E_{double\ chain\ move}$ = Energy of double chain polymer as one chain moving from the other.

$E_{single\ chain}$ = energy of single chain polymer

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Model of Polymers

Molecular Dynamics simulations were performed on single chain, double chain, and bundle of polyethylene (PE), polypropylene (PP), and ethylene-propylene copolymer (EPM) with N of 5, 10, 100, and 500 repeating units at two critical temperatures, i.e., glass transition temperature (T_g) and melting temperature (T_m).

From MD simulations, large numbers of configurations of structures as well as energy associated to them were obtained. To assess the most suitable length of polymer that can be used as representative for single chain and double chain polymer, the energy per unit length of repeating unit (E/N) at various length were compared. Since there are large members of configurations and energies, the most probable energy which is the energy with the highest probability was chosen.

For structure at 0 K, no MD simulation was performed but energy minimizations were carried out to obtain structures and energies of polymers. The E/N of single chain polymers with various unit lengths at three different temperatures are listed in Tables 4.1 – 4.3.

Table 4.1 The E/N (kcal/mol) of single chain PE at 0 K, T_g, and T_m, respectively.

Units	No. of atoms	0 K	T_g(153 K)	T_m(413 K)
5	32	-3.83	-0.93	3.68
10	62	-4.20	-1.33	3.33
100	602	-4.53	-1.90	0.62
500	3002	-4.55	-3.56	-0.22

Table 4.2 The E/N (kcal/mol) of single chain PP at 0 K, T_g, and T_m, respectively.

Units	No. of atoms	0 K	T_g(253 K)	T_m(443 K)
5	47	-5.41	-0.71	4.15
10	92	-5.43	-1.41	3.86
100	902	-5.75	-2.96	1.77
500	4502	-5.72	-3.85	0.83

Table 4.3 The E/N (kcal/mol) of single chain EPM at 0 K, T_g, and T_m, respectively.

Units	No. of atoms	0 K	T_g(173)	T_m(343)
5	**35**	**-4.14**	**0.13**	**3.15**
10	**68**	**-4.44**	**-0.58**	**2.67**
100	**662**	**-4.74**	**-2.50**	**-0.12**
500	**3302**	**-4.78**	**-3.33**	**-0.95**

The E/N of these polymers were plotted against unit length, N, and the plots are displayed in Figures 4.1 – 4.3. It could be seen that for all single chain polymers the E/N is converged to single value as N approaching 500 units. The 0 K structures are the fastest to converge around N=100 units. Thus, the appropriate unit length to be used for model of single chain polymer is 500 units.

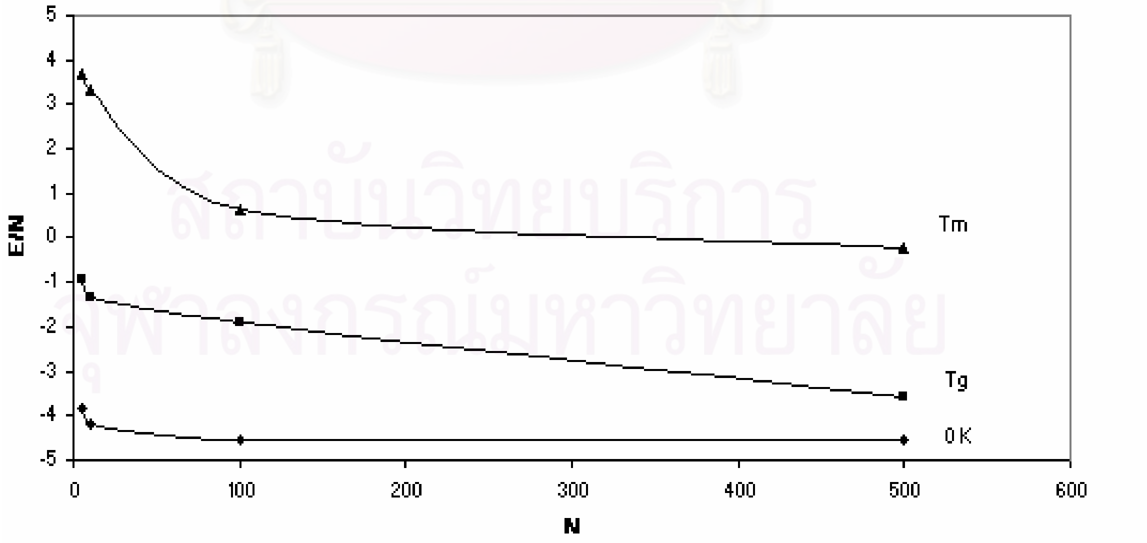


Figure 4.1 Plots of E/N vs N of single chain PE at 3 temperatures

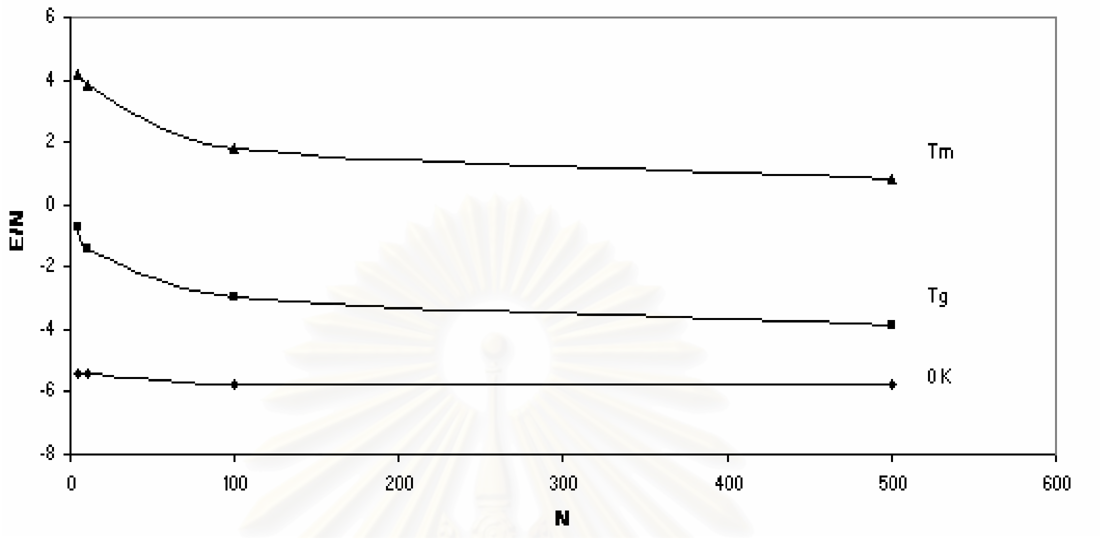


Figure 4.2 Show plots of E/N vs N of single chain PP at 3 temperatures

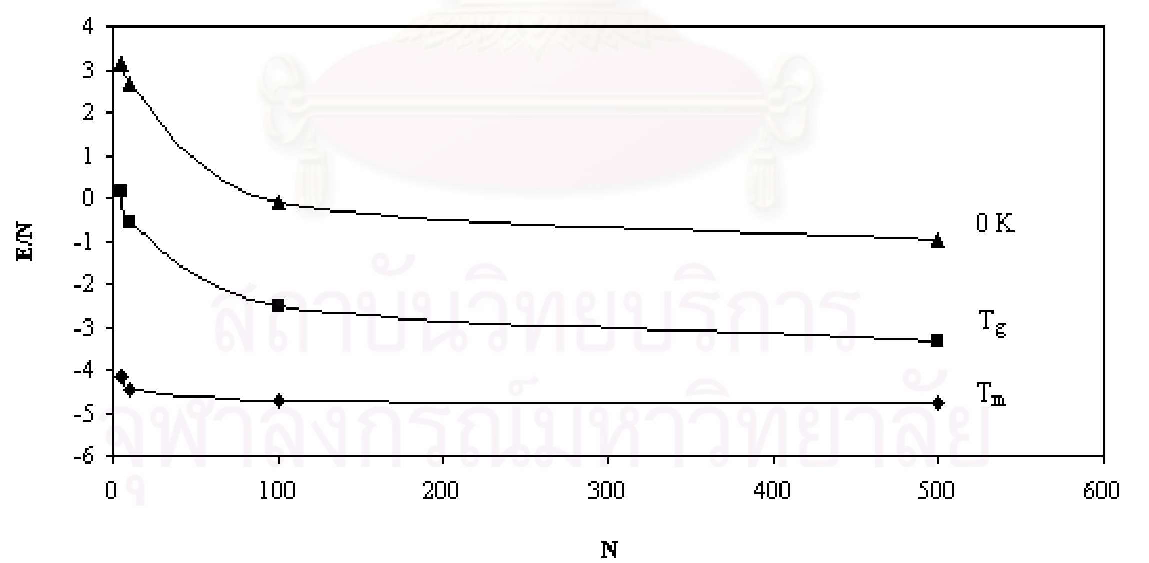


Figure 4.3 Plots of E/N vs N of single chain EPM at 3 temperatures

For double chain polymer, the E/N of PE and PP are given in Tables 4.4 – 4.5 and the plot between E/N vs N of PE and PP are given in Figure 4.4 and 4.5. Similar to single chain polymer, we found that model with repeating unit of 500 is the suitable representative of polymer since E/N is converged at this length. This length is larger than that used in previous studies of PE and i-PP models consisted of single chain with 250 and 170 monomer.(9) The polymer would not be well represented if inappropriated model is used.

Table 4.4 The E/N (kcal/mol) of double chain PE at 0 K, T_g, and T_m, respectively.

Units	No. of atoms	0 K	T_g(153 K)	T_m(413 K)
5	64	-8.85	-4.05	9.15
10	124	-9.74	-3.56	7.82
100	1204	-10.56	-5.46	0.61
500	6004	-10.63	-7.95	-1.10

Table 4.5 The E/N (kcal/mol) of double chain PP at 0 K, T_g, and T_m, respectively.

Units	No. of atoms	0 K	T_g(253 K)	T_m(443 K)
5	94	-16.50	-1.20	11.58
10	184	-17.80	-3.12	9.24
100	1804	-18.62	-4.37	2.31
500	9004	-18.66	-5.44	1.79

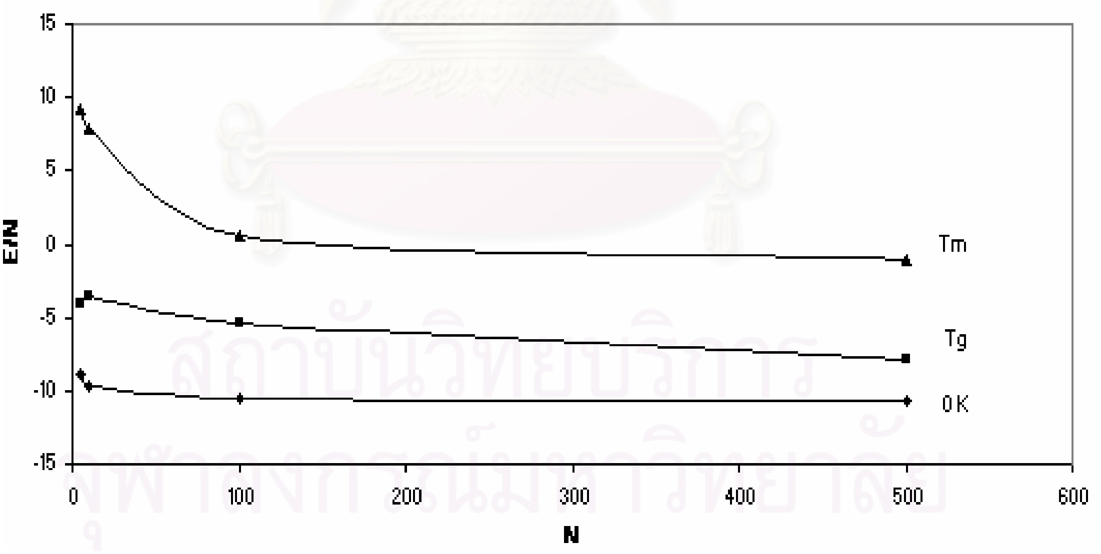


Figure 4.4 Plots of E/N vs N of double chain PE at 3 temperatures

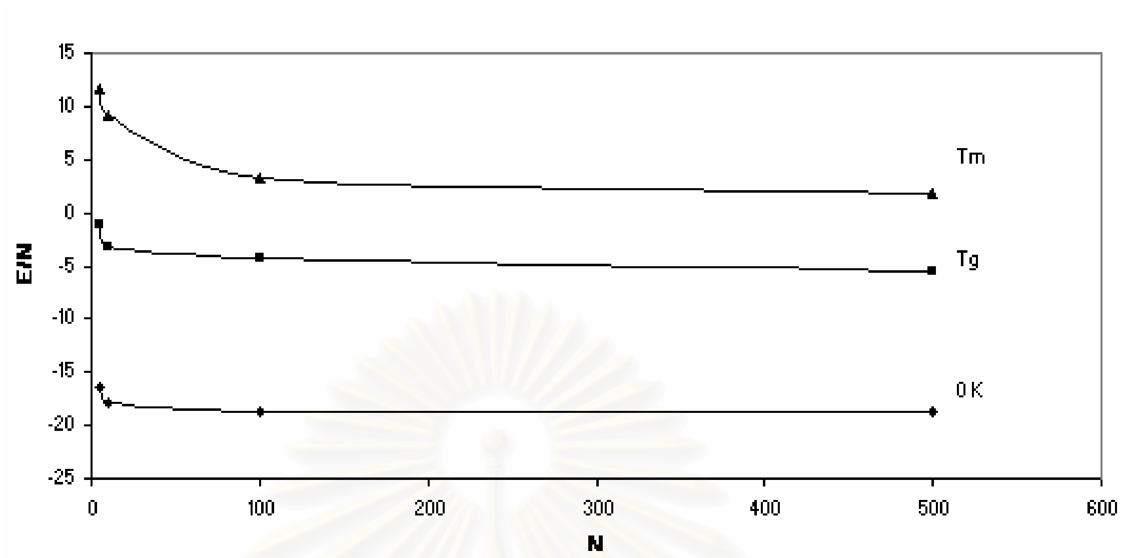


Figure 4.5 Plots of E/N vs N of double chain PP at 3 temperatures

Due to the size of bundle polymer, we limit ourselves to the unit length of 50 for each chain of polymer for MD simulations. This refers to the simulations of 3020 and 4520 atoms for PE and PP, respectively. The E/N of these simulations are shown in Table 4.6.

Table 4.6 The E/N (kcal/mol) of bundle PE and PP at 0 K, T_g, and T_m, respectively.

Sample	Energy(kcal/mol)/ repeating units at		
	0 K	T_g	T_m
PE	-84.17	-64.61	-12.60
PP	-113.45	-56.05	-4.20

To compare between single chain, double chain, and bundle polymer, the E/N from Tables 4.1 – 4.6 were divided by number of chain and listed in Table 4.7. For single and double chain polymer, the E/N at N = 500 were chosen because the models of single and double chain polymers of length 500 repeating units have concluded to be the best representative models.

Table 4.7 The E/N per chain (kcal/mol) of single chain, double chain, and bundle PE and PP at 0 K, T_g, and T_m, respectively.

Polymer	Types	0 K	T_g	T_m
PE	single	-4.55	-3.56	-0.22
	double	-5.31	-3.98	-0.55
	bundle	-8.42	-6.46	-1.26
PP	single	-5.72	-3.85	0.83
	double	-9.33	-2.72	0.89
	bundle	-11.34	-5.60	-0.42

From Table 4.7, it is observed that the E/N per chain is reduced as number of chains increase. This is true for both of PE and PP at all temperatures. This is in exception of double chain PP at T_g and T_m which the E/N per chain values are higher than of single chain PP. These PP may has the steric effect which causes side group and this effect influence the energy of double chain PP increase. In the same reason, the E/N per chain of PE is also lower than of PP at T_g and T_m. As for bundle PP, has many chain interaction compare to double chain PP the E/N per chain of bundle PP is then less than of double chain PP. The E/N per chain in Table 4.7 implies that the polymer becomes more stable as the number of chains increases. Thus, there is a chain-chain interaction. This interaction is largest at 0 K and is smaller when the temperature was raised.

When we subtract E/N of single chain from E/N of double chain and bundle, we arrive at Table 4.8 where this differences at 3 temperatures were listed. Moreover, for the difference with bindle the values were divided by number of pair of polymer chain, which is 5 in this case. For PE, we can see that the differences in Table 4.8 become less negative when going from 0 K to T_g and from T_g to T_m. This trend is true for double chain as well as bundle. For PP, the differences in Table 4.8 are negative at 0 K for both of double and bundle polymer, is positive for double, small negative for bundle at T_g, and small positive at T_m.

The differences in Table 4.8 could suggest orientation of polymer in double chain and bundle. For PE, the difference suggests that there is more chain - chain interaction at 0 K than at T_g and more at T_g than at T_m. This means that at 0 K, PE are more order than at T_g and more at T_g than at T_m.

Table 4.8 Differences between E/N per chain of multiple chain and E/N of single chain at 0 K, T_g, and T_m, respectively. (in parentheses is the difference per pair of chain)

Polymer	Compare	0 K	T_g	T_m
PE	**double-single**	**-0.76**	**-0.41**	**-0.33**
	bundle-single	**-3.87** **(-0.774)**	**-2.9** **(-0.58)**	**-1.04** **(-0.208)**
PP	**double-single**	**-3.61**	**1.11**	**0.04**
	bundle-single	**-5.62** **(-1.124)**	**-1.77** **(-0.354)**	**-1.25** **(-0.25)**

If we look at the difference of bundle per pair of chain which could be compared directly with the difference of double chain, we can see that for PE the values are slightly more negative than those of double chain at 0 K and T_g and less negative than that double chain at Tm. This suggests that the order between chain in bundle and double chain is very similar at 0 K and T_g but at T_m polymer chain are less order in bundle. For PP, the values in the parenthesis is much less negative for bundle at 0 K and more negative for bundle at T_g. Thus, at T_g, structure of bundle PP is tiny deviation from initial geometry and more deviate when compared to double chain at 0 K.

4.2 3D Structure of polymer

From Molecular Dynamics Simulations we obtained not only energy details, but also the molecular conformations. Optimized geometries can be obtained after the simulation terminated and can be shown as Figures 4.6 – 4.26.

4.3.1 Single chain PE

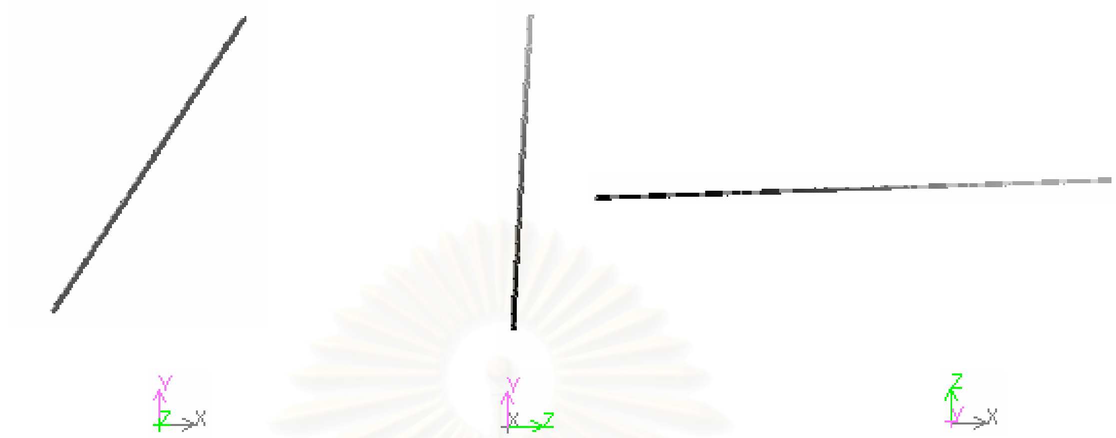


Figure 4.6 The conformation of single chain PE, 500 repeating units at 0 K.

Figure 4.7 The conformation of single chain PE, 500 repeating units at T_g.

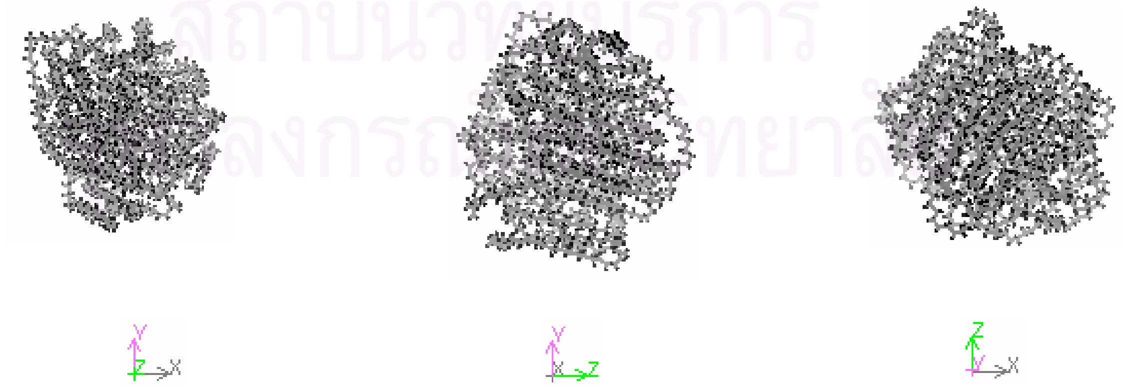


Figure 4.8 The conformation of single chain PE, 500 repeating units at T_m.

4.3.2 Double chain PE

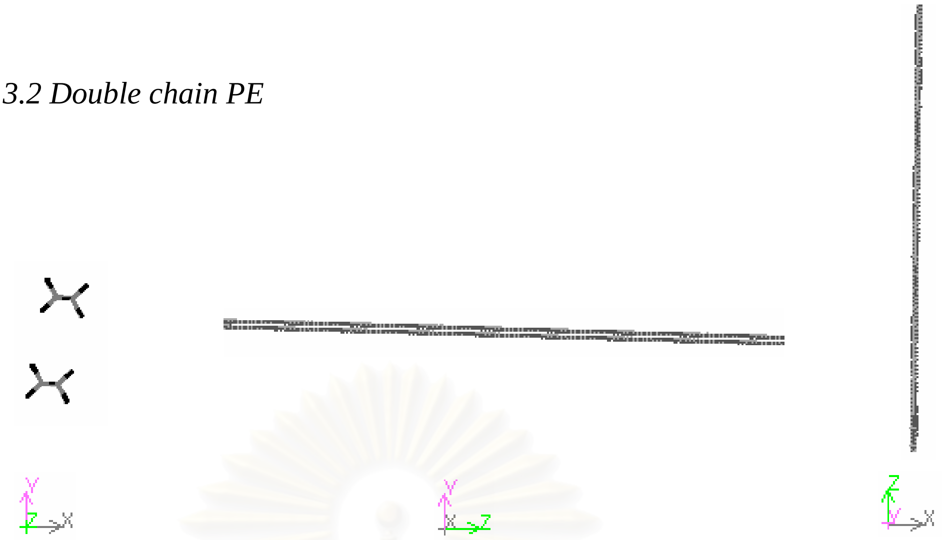


Figure 4.9 The conformation of double chain PE, 500 repeating units at 0K.

Figure 4.10 The conformation of double chain PE, 500 repeating units at T_g.

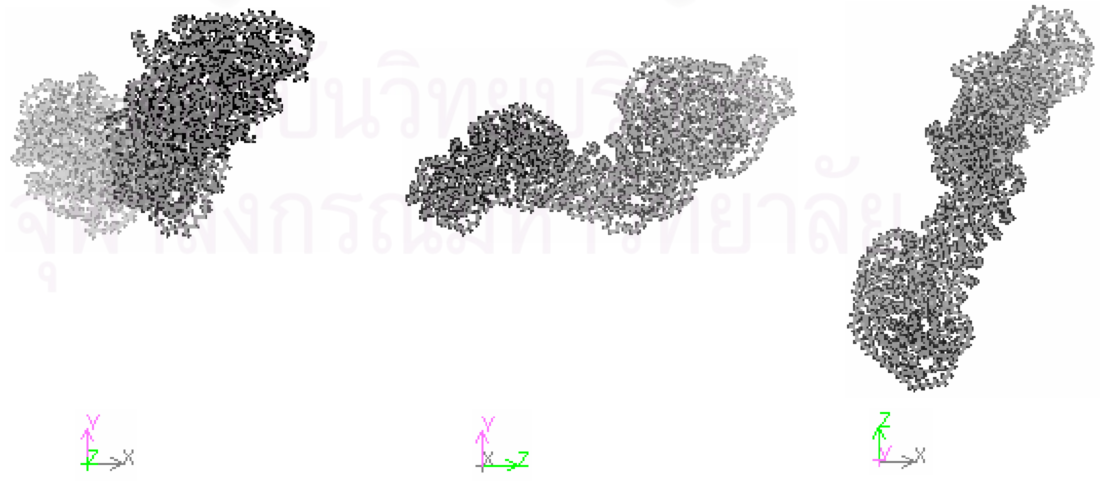


Figure 4.11 The conformation of double chain PE, 500 repeating units at T_m.

4.3.3 Bundle PE

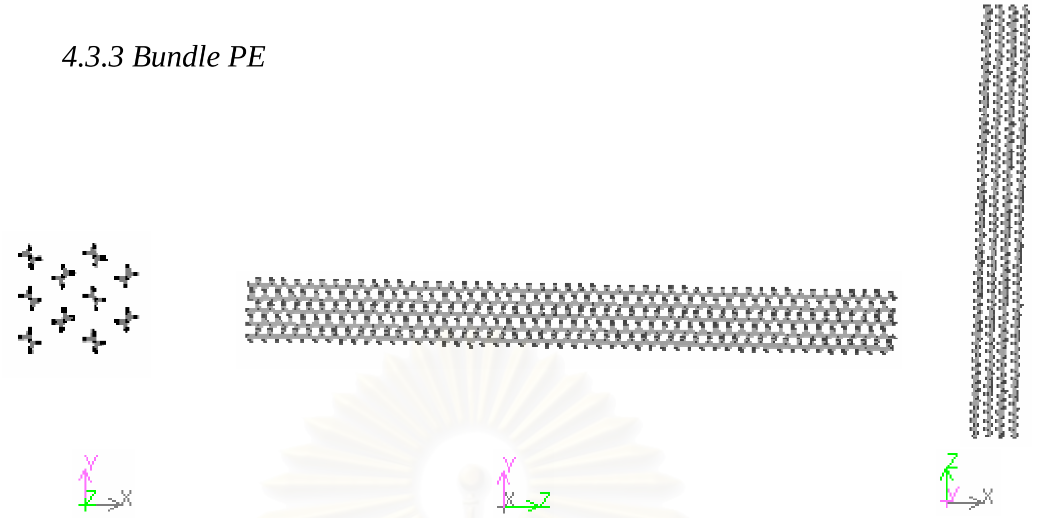


Figure 4.12 The conformation of bundle PE, 10x50 repeating units at 0K.

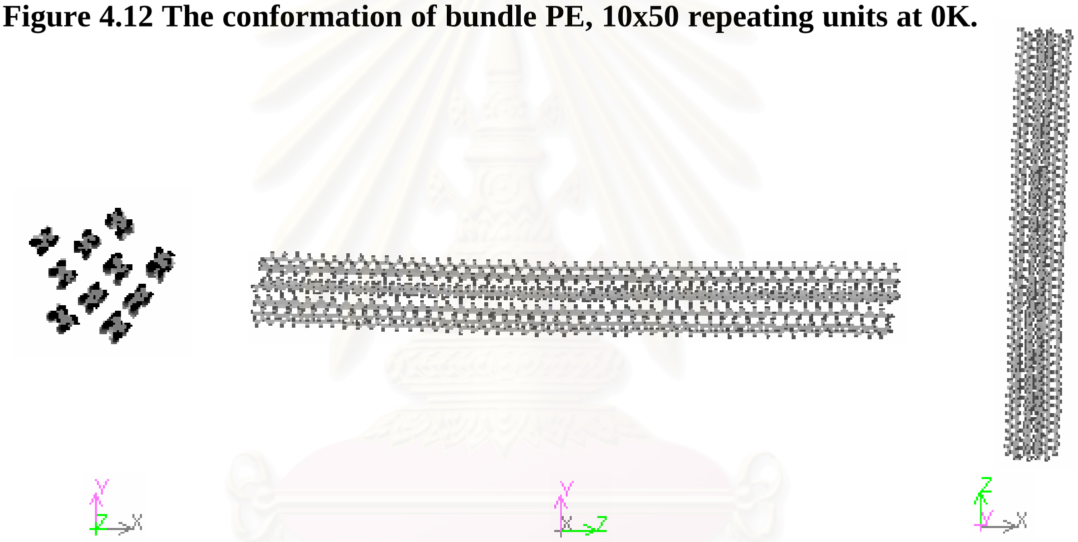


Figure 4.13 The conformation of bundle PE, 10x50 repeating units at T_g.

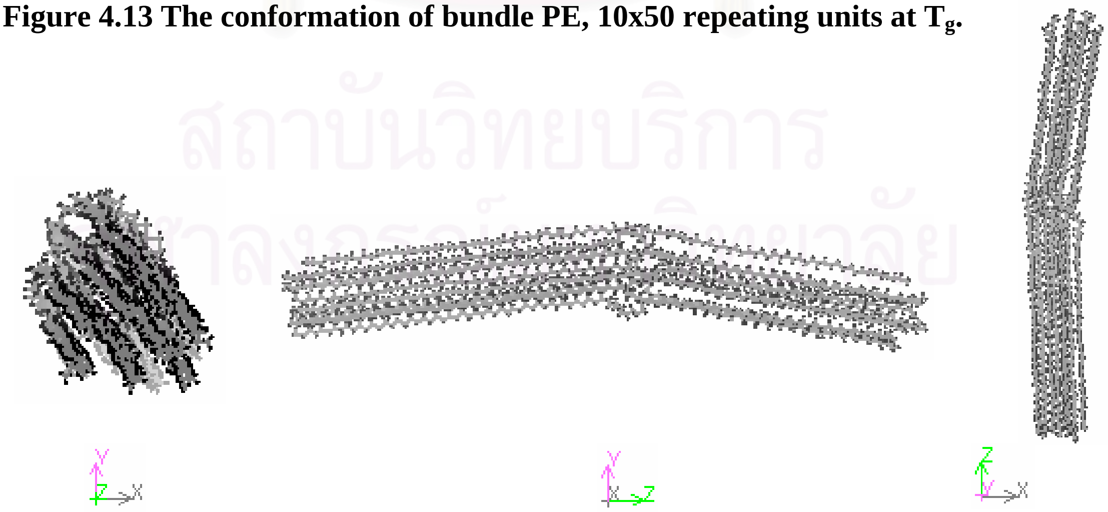


Figure 4.14 The conformation of bundle PE, 10x50 repeating units at T_m.

4.3.4 Single chain PP

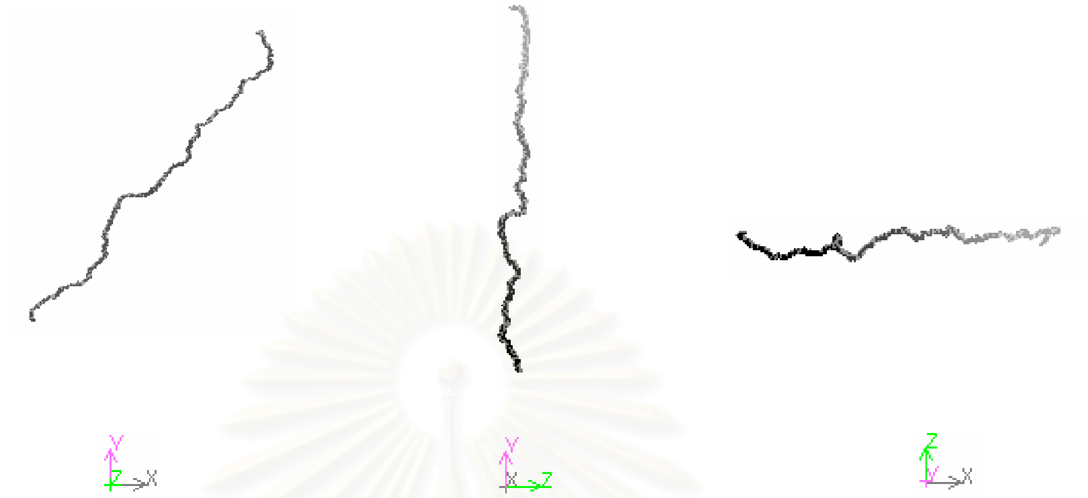


Figure 4.15 The conformation of single chain PP, 500 repeating units at 0K.

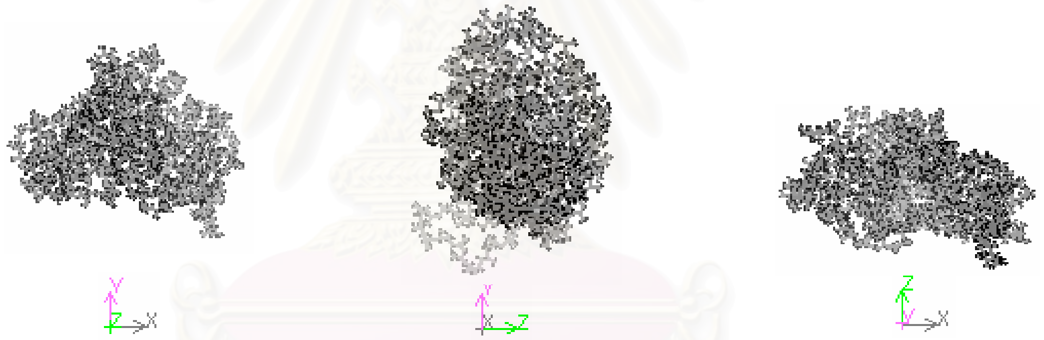


Figure 4.16 The conformation of single chain PP, 500 repeating units at T_g.

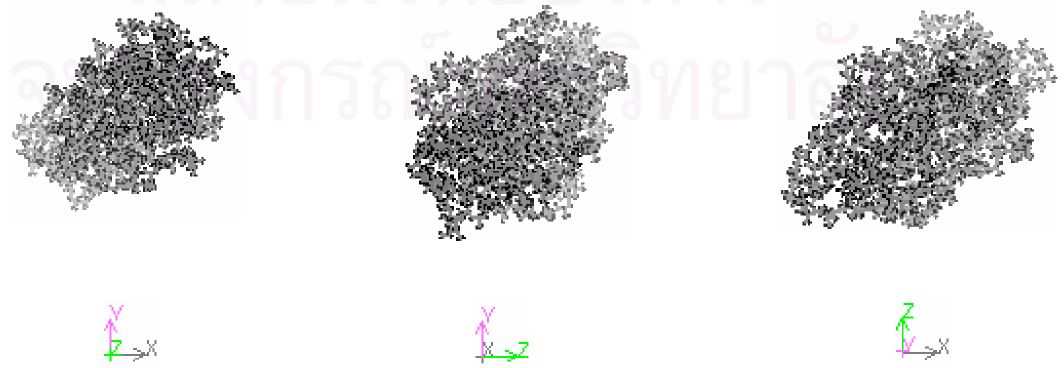


Figure 4.17 The conformation of single chain PP, 500 repeating units at T_m.

4.3.5 Double chain PP

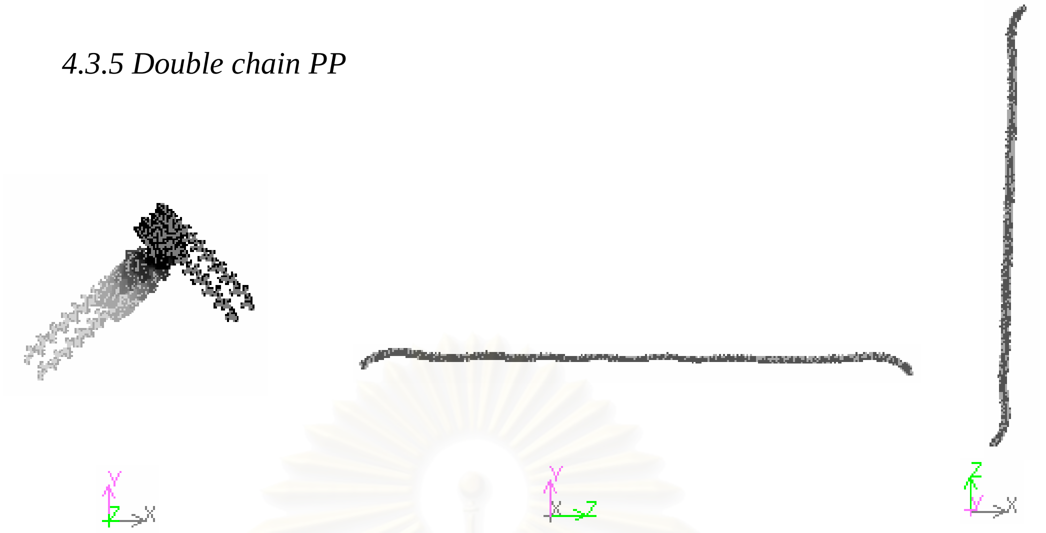


Figure 4.18 The conformation of double chain PP, 500 repeating units at 0K.

Figure 4.19 The conformation of double chain PP, 500 repeating units at T_g.

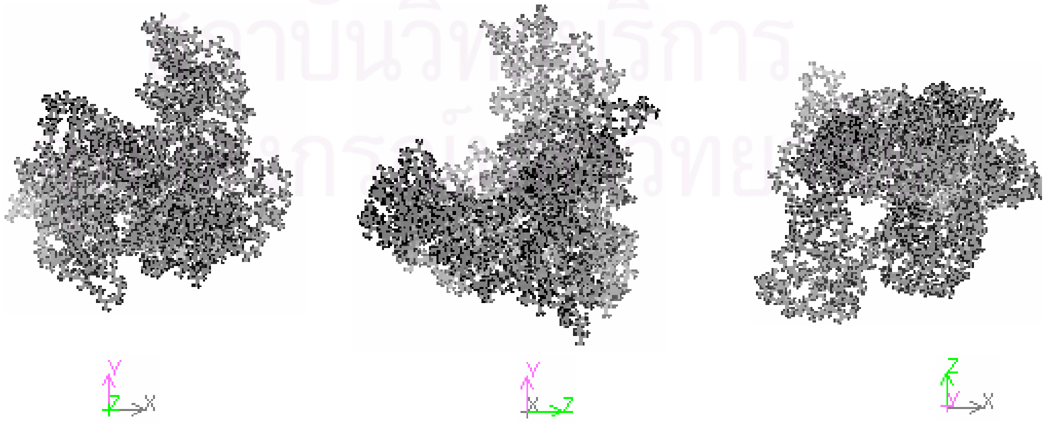


Figure 4.20 The conformation of double chain PP, 500 repeating units at T_m.

4.3.6 Bundle PP

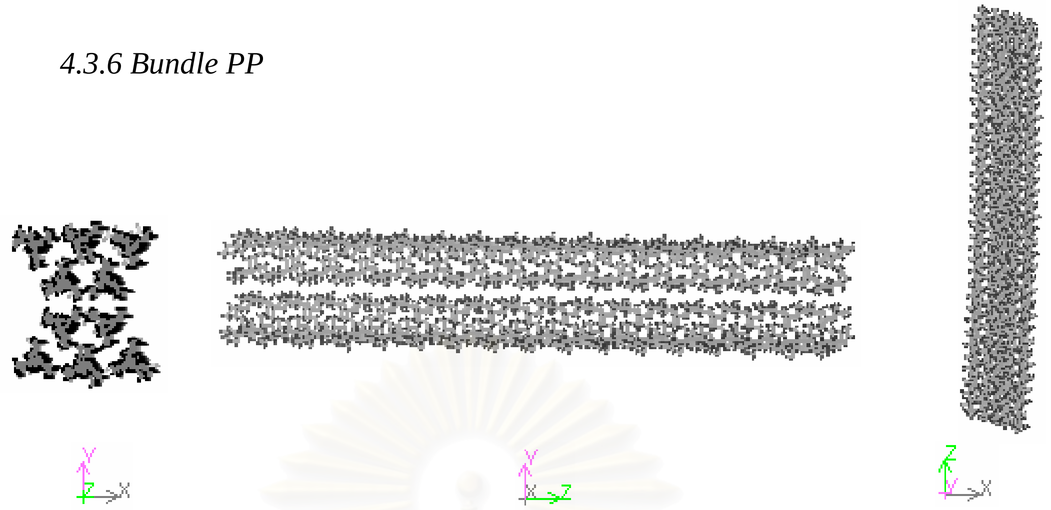


Figure 4.21 The conformation of bundle PP, 10x50 repeating units at 0K.

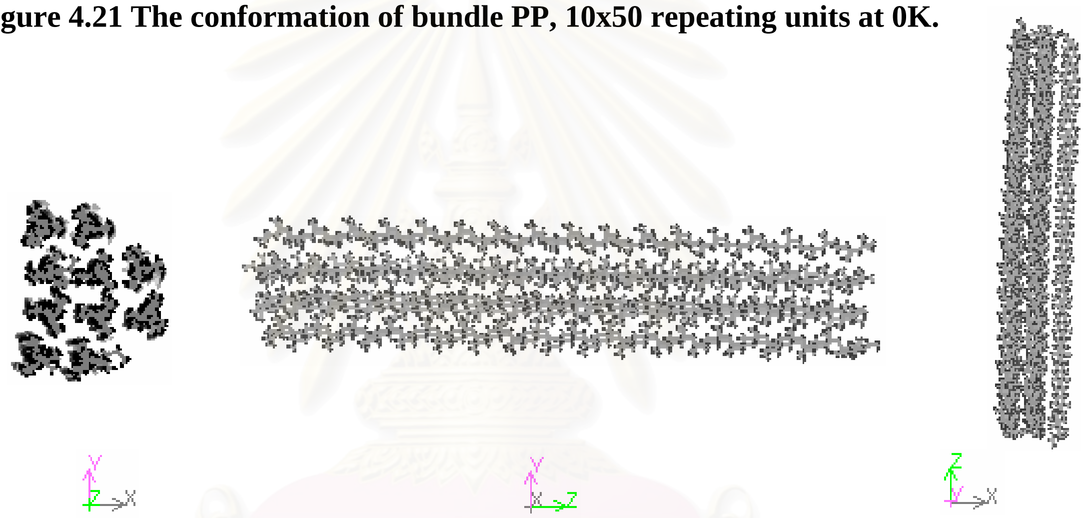


Figure 4.22 The conformation of bundle PP, 10x50 repeating units at T_g.

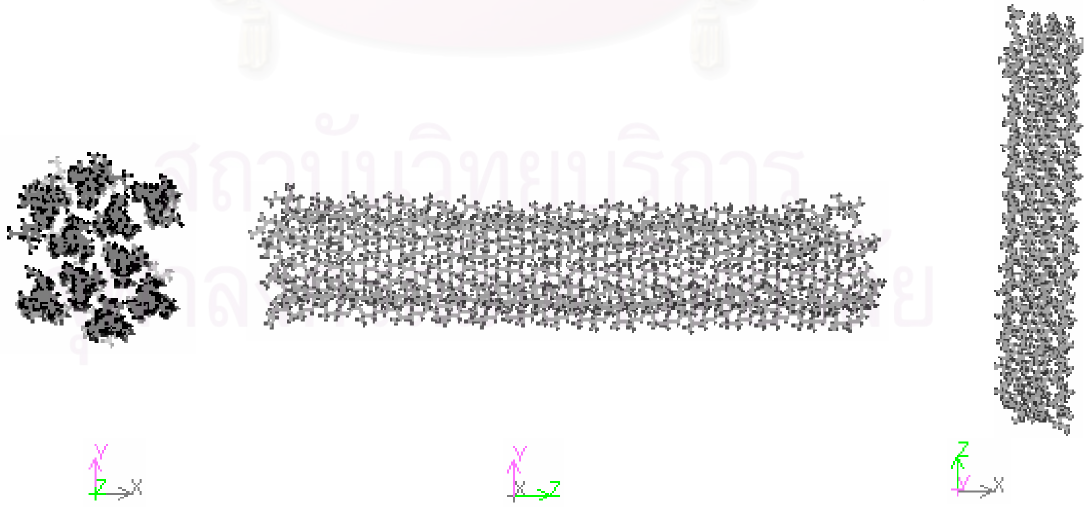


Figure 4.23 The conformation of bundle PP, 10x50 repeating units at T_m.

4.3.7 Single chain EPM

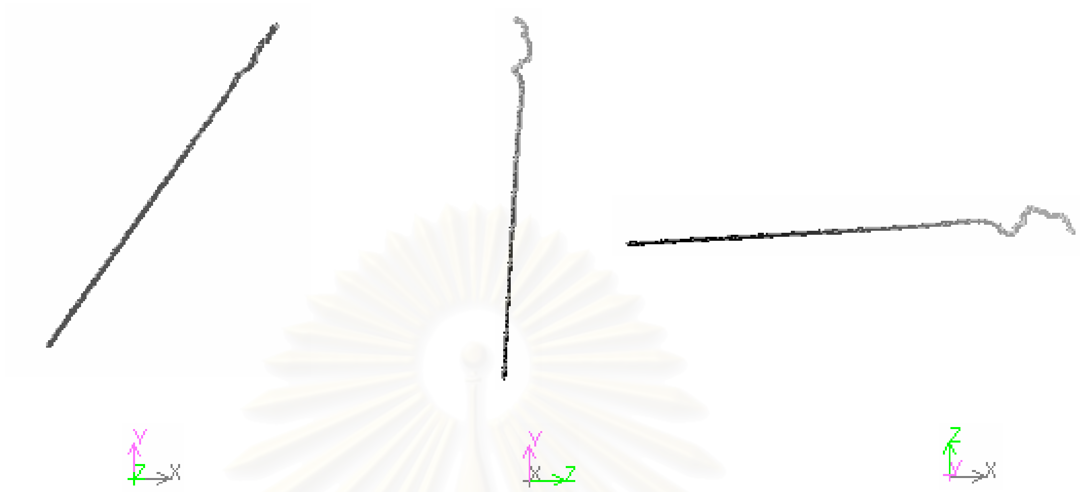


Figure 4.24 The conformation of single chain EPM, 500 repeating units at 0K.

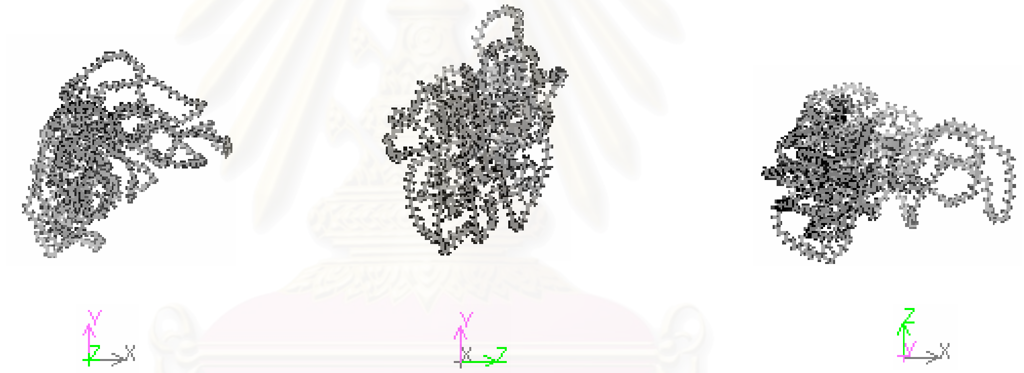


Figure 4.25 The conformation of single chain EPM, 500 repeating units at T_g.

Figure 4.26 The conformation of single chain EPM, 500 repeating units at T_m.

From the structures of 3 polymer models as shown in Figures 4.6 – 4.26, it was found that all polymer models, at 500 repeating units, have linear-like structure at 0 K. The model of propylene polymer seems to possess a twisted form as can be seen from structures of PP and EPM.

For single chain model at higher temperature, T_g, all polymer chains tend to become more entangle and turns into globule. The single chain PE forms less dense globule than PP as observed from the surface area/volume ratios in Table 4.9. The well-entangled chain of PE at T_m demonstrated the locally ordered structure. This feature is not observed in melt state of PP. EPM was found to have a similar tendency as PE, but EPM structure at T_m illustrates some domain of ordered range shorter than long ordered chain PE. Perhaps because the EPM is formed by 20 % PP and 80 % PE.

For double chain, at T_m the double chain structures of PE and PP looks similar to those of single chain PE and PP, but at T_g, PE polymers seems to be more order than the single chain PE as evident from Figure 4.7 and 4.10. The existence of second chain makes polymer chain less flexible.

For bundle polymer PE and PP, structures at T_g and T_m are slightly deviated from the linear structure at 0 K. Thus, the polymer bundle tries to maintain a crystal structure, folding and entanglement are not observed. Probably, the chain length of 50 is too short and, therefore, polymers can not fold, bend, and entangle like in case of double chain. Considered time and cost of simulation, the double chain model with the chain length of 500 repeating units is the most suitable model of polymers.

4.3 Volume of Polymer

Volume and surface area of polymers can be obtained from MD structures. The overall surface area and volume of polymers were provided in Table 4.9. In addition, the surface area/volume of PE, PP, and EPM at three temperatures were also gained. It was demonstrated that at elevated temperature the surface area/volume of all models were decreased. For the reason, when polymers underwent more energy at higher temperature the extent of chain mobility will be enhanced with possible mode of molecular motion results in easily occur of chain orientation. Ordered chain segment was then established that made surface area/volume of polymers were decreased as temperature raise. In general, the formation of locally ordered domains is pronounced for longer chains and for larger structures with overall lower surface/volume ratios.(9) Long chain PE seems to be more order than other models as can be concluded from its lower surface area/volume ratio. These estimations are in agreement with the conformation of PE shown in the 3D structures of polymers, where we observed the long range order of single chain PE conformer. This feature is not obvious in double chain PE, which we can see only short range order. These were supported by the higher surface area/volume value than single chain PE. However, the formation of ordered chain also depends on other factors.

As for PP, although the value of surface area/volume decreased with higher temperature, T_m, the occurrence of chain orientation was not still observed. It is probably caused by the methyl side group of PP hindrance each chain segments to be associated together and becomes to form regular domain. The surface area/volume value of EPM has the same trend as PE, because EPM composed of ethylene monomer amount much more than propylene monomer. From calculations, it can be noted that propylene affects surface area/volume of EPM to be increased as compared to PE, this makes ordered domain decreased as seen in 3D structures of polymers.

Table 4.9 The surface area/polymer volume of PE, PP, and EPM at three different temperatures.

Polymer	Volume of single chain ($\mathring{A}^3$/u.c.)			Volume of double chain ($\mathring{A}^3$/u.c.)			Temp.
	Total volume	Surface area	Surface/volume	Total volume	Surface area	Surface/volume	
PE	**16899.67**	**29436.49**	**1.7418**	**33157.74**	**43292.06**	**1.3056**	**0 K**
PP	**26404.53**	**35430.86**	**1.3418**	**51592.22**	**54422.62**	**1.0548**	
EPM	**19500.48**	**31329.99**	**1.6066**	**-**	**-**	**-**	
PE	**17572.57**	**27652.86**	**1.5736**	**35440.1**	**41320.11**	**1.1659**	**Tg**
PP	**26080.77**	**13249.08**	**0.5080**	**52580.39**	**46005.63**	**0.8749**	
EPM	**18783.2**	**17187.06**	**0.9150**	**-**	**-**	**-**	
PE	**17339.45**	**7271.01**	**0.4193**	**35210.97**	**15049.94**	**0.4274**	**Tm**
PP	**25561.69**	**10821.45**	**0.4233**	**41103.53**	**21207.8**	**0.5159**	
EPM	**19108.86**	**8349.8**	**0.4369**	**-**	**-**	**-**	

Moreover, we observed that the surface area of single chain and double chain PE at 0 K do not very much differ from the surface area which obtained at T_g. But when the T_m was reached, surface area of those polymers were decreased sharply. It can be suggested that single chain and double chain PE have tendancy to form dense globule structure at T_m. In case of PP, change in surface area at 3 temperatures were similar to those of single chain and double chain PE. It can be noted from surface area that single chain PP and single chain EPM had started and turned into globule at T_g already.

4.4 Shear energy and chain-chain interaction

To approximate shear strength and chain-chain interaction, polymer model was examined by quantum calculation. Density functional B3LYP/6-31g(d, p) was applied to PE and PP model by cutting 5 repeating unit from total N of 500 model and applied quantum calculation to these models. The chain-chain interactions were estimated by computing energy of double chain polymer (see Table 4.10) subtracted by the energy of single chain polymer in Table 4.11. The differences of chain – chain interactions were given in Table 4.12.

Table 4.10 The energy of double chain PE and PP moving at step of 1 to 5 in Hartree at different temperatures.

Sample	**Energy of moving double chain (Hartree) at step**					**Temp.**
	1	**2**	**3**	**4**	**5**	
PE	**-788.738**	**-788.739**	**-788.739**	**-788.740**	**-788.740**	$\mathbf{T_g}$
	-788.735	**-788.735**	**-788.736**	**-788.735**	**-788.735**	$\mathbf{T_m}$
PP	**-1181.884**	**-1181.890**	**-1181.780**	**-1181.774**	**-1181.768**	$\mathbf{T_g}$
	-1181.876	**-1181.875**	**-1181.876**	**-1181.874**	**-1181.874**	$\mathbf{T_m}$

Table 4.11 Single chain energy of PE and PP at different temperatures in Hartree unit

Polymer	1 Chain energy at temperatures	
	T_g	T_m
PE	**-394.350**	**-394.314**
PP	**-590.889**	**-590.812**

Table 4.12 Chain – chain interactions at different moving step.

Sample	Different energy of moving double chain ((E_2-$2E_1$, kcal/mol) at step					Temp.
	1	2	3	4	5	
PE	**-23.38**	**-24.22**	**-24.19**	**-25.08**	**-25.05**	T_g
	-66.27	**-66.20**	**-67.13**	**-66.30**	**-66.65**	T_m
PP	**-70.74**	**-74.55**	**-5.81**	**-1.99**	**1.455**	T_g
	-157.35	**-156.67**	**-157.42**	**-156.41**	**-156.25**	T_m

From Table 4.12, PP has the largest chain – chain interactions and these chain – chain interactions are higher at elevated temperature. These chain – chain interaction could then be used to estimate the shear strength. The value in Table 4.12 could tell how much energy is needed to move two chains of polymer away from each other. As moving step by step, the shear energies are almost constant. There are alternation of shear energy. This is of course due to different conformations of polymer chain. Thus, for PE and PP larger shear strength would be expected at T_m. Besides, PP has larger shear strength, which related to rheologistic behavior, than PE and this calculation result is agreed with the experimental data.(18) In addition, the large deviation of the chain – chain interaction energy of moving double chain PP step 3, 4, and 5 at T_g may probably caused moving double chain model which we cut from N=500 repeating units of double chain model is not the best representative model.

CHAPTER V
CONCLUSIONS

1. From energy data, the model of polymer is almost converged at repeating units of 500. At this energy region, polymer has constant physical properties. The model of 500 is then the best representative model of polymer at all temperatures for further computational study of polymeric properties.

2. The temperature affects the behavior of polymer. At low temperature, T_g, polymer is in glassy or solid phase, its structure is not much different from structure at 0 K. At higher temperature, T_m, the polymer chains obtained the energy and start to fold and form globule, their solid state structures are then lost.

3. In PE we can observe domain of long range ordered chain obviously and short range ordered chain in EPM can be also observed, too. But this feature can not observed in PP.

4. The structure of double chain polymers are hardly to seen ordered chain segments than single chain polymers because the influence of second chain in molecule.

5. In addition, the values of surface area/polymer volume are supported the conformation result. PE has the lowest value surface area/volume, it can be then concluded that the chain orientation is hardly occur in PP.

6. The shear energy of polymer models are almost constant and are higher at elevated temperature. The quantum calculations also show that PP has larger shear strength than PE. This makes PE chains to be pull apart from each other in melt state easier than PP that implied PP also has the larger melt flow viscosity than PE, too. The energy of chain folding that makes chain entanglement probably causes the polymer to become more flexible and more strength.

For further studying, the calculation of energy and 3D structures data of other versatile polymers such as polystyrene (PS) is persuaded. The approximation of shear energy as well as tensile energy from its structural data are also suggested.

REFERENCES

1. Michael, M., Gary, S. G., Kurt, K. (1999). “Statics and Dynamic of Symmetric Diblock Copolymers: A Molecular Dynamics Study.” *Macromolecules.* 32, 3, 595-609.

2. John, L. W., Gregory, C. R. (1996). “Simulation of the Structure and Properties of the Polyethylene Crystal Surface.” *J. Phys. Chem.* 100, 25, 10689-10695.

3. Emmanuel, D. (2000). “Molecular dynamic simulation of the interaction, at high energy, between the N_2 molecule and polyethylene.” *Journal of Chemical Physics*. 113, 18, 8187-8193.

4. Dilip, K. D. (1994). “Polyethylene: Structure, Morphology, Molecular Motion and Dielectric Behavior.” *IEEE Electrical Insulation Magazine*. 10, 3, 5-15.

5. Taining, L., Xiaozhen, Y., Xiangyu, Z. (2001). “Prediction of Polyimide Materials with High Glass Transition Temperatures.” *Journal of Polymer Science: Part B: Polymer Physics*. 39, 2243-2251.

6. Ricardo, D. C., Abel, G., Enrique, S., Andrea, H., Ligia, G., Fernando, G., Deodato, R. (2001). “Dynamic Mechanical and Dielectric Relaxational Behavior of Poly(cyclohexylalkyl methacrylate)s.” *Macromolecules*. 34, 18, 6312-6317.

7. George, Odian., Principles of Polymerization, McGraw Hill, New York, 1970, pp1-36.

8. Kavassalis, T.A., Sundararajan, P.R. (1993). “A Molecular Dynamics Study of Polyethylene Crystallization.” *Macromolecules*. 26, 16, 4144-4150.

9. Phillip, C., Henk, P. B., Tom, A. K., Alfred, R. (1995). “Immiscibility of Poly(ethylene) and Poly(propylene): A Molecular Dynamics Study.” *Macromolecules.* 28, 24, 8247-8250.

10. Varennes, S., Charlet, G., Delmas, G. (1984). “Incompatibility between Polyethylene and Polypropylene of Mutual Solutions in A Common Solvent.” *Polym. Eng. Sci*. 24, 98-105.

11. Borrmann, A., Montanare, B., Jones, R. O. (1997). “Density Functional Study of Polypropylene and its Submolecules” *J. Chem. Phys.* 106, 20, 8545-8551.

12. Höltje, H. D., Sippl, W., Rognan, D., Folkers, G., Molecular Modeling, WILEY-VCH Verlag GmbH& Co. KGaA, Weinheim, 2003, pp 9-21.

13. David, Y., Computational Chemistry, John Wiley & Sons, Inc., Canada, 2001, pp 49-61.

14. Frank, J., Introduction to Computational Chemistry, John Wiley & Sons Ltd., England, 1999, pp 8-65.

15. Levine, I. N., Quantum Chemistry, Prentice-Hall, Inc., U.S.A., 2000, pp 12-47.

16.Cramer, J., C., Essential of Computational Chemistry, John Wiley & Sons Ltd., England, 2002, pp 96-120.

17. Szabo, A., Ostlund, S. N., Modern Quantum Chemistry, McGraw-Hill, Inc., New York, 1989, pp 111-158.

18. Liang, J., Z. (2001). “Characteristics of Melt Shear Viscosity during Extrusion of Polymers.” *Polymer Testing*. 21, 307-311.

VITA

Surakiat Kumta

Born December 25th, 1978 in Ubonratchatanee, Thailand

Education

1984-1990 Primary School

Primary School of Ubonratchatanee, Ubonratchatanee, Thailand

1990-1996 Secondary School

Benjamamaharaj School, Ubonratchatanee, Thailand

1996-2000 Bachelor of Science in Industrial Chemistry

Department of Chemistry, Faculty of Science,

King Mongkut's Institute Technology of Ladkrabang, Bangkok, Thailand

2001-2004 Master degree of Science in Petrochemistry and Polymer Science program

Faculty of Science, Chulalongkorn University, Thailand