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A ROTATIONAL ISOMERIC STATE APPROACH TOWARDS UNDERSTANDING ELASTOMER CHAIN CONFORMATIONS IN TIRES

Suvrajyoti Kar
University of Rhode Island, kar.suvraj@gmail.com

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A ROTATIONAL ISOMERIC STATE APPROACH TOWARDS

UNDERSTANDING ELASTOMER CHAIN CONFORMATIONS IN TIRES

BY

SUVRAJYOTI KAR

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OF

SUVRAJYOTI KAR

APPROVED:

Thesis Committee:

Major Professor   Michael L. Greenfield

Arijit Bose

Sze C. Yang

Nasser H. Zawia
DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND

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ABSTRACT

Rubber tires undergo viscoelastic losses at high and low frequencies. High frequency losses lead to traction while low frequency losses lead to rolling resistance. High rolling resistance tires require greater amount of fuel to travel a particular distance as compared to low rolling resistance tires, and thus they have a negative impact on vehicle fuel economy. Traction is needed for vehicle braking ability and propulsion. Maintaining a balance between reducing rolling resistance and maintaining wear resistance and traction is a technical challenge. Factors that decrease rolling resistance tend to worsen traction, and vice versa, while both types of changes reduce wear resistance. Experiments have found that strengthening interactions between rubber and reinforcement fillers can be used to maintain a balance between reducing tire rolling resistance without compromising on wear resistance and traction, but why this works is not known. Rolling resistance on the macroscale connects directly to energy losses occuring due to changes in elastomer chain conformations on the microscale. Thus, understanding the statistical mechanics of elastomer chain conformations provide us a vital molecular link towards quantifying rolling resistance. This thesis provides a first step towards this link.

Molecular modeling is used to study the size and shape distribution, and

characteristics of cis- and trans-1,4-polybutadiene chains. Computations are conducted using Flory's Rotational Isomeric State approach (RIS), in which energy distribution is considered over discrete rotational isomeric states. The Rotational Isomeric State approach is chosen because it allows generating a large number of polybutadiene chains in a computationally cheap manner using less resources and computation time , and also because the RIS approach allows each chain realization to be treated as an independent sample.

Numerous (100,000) isolated single cis- and trans-1,4-polybutadiene chains of uncorrelated random conformations are considered under unperturbed conditions (balanced attractive and repulsive polymer-solvent interactions, i.e. theta-conditions). Using a single chain in each computation is justified because a flexible polymer surrounded by the same polymer takes on the same average shape as a single random polymer chain in a theta solvent. Chain size and shape properties are computed at different chain lengths and over a range of temperatures.

Characteristic ratios are in good agreement with experimental and prior computed values (cis-1,4-polybutadiene), and slightly higher than prior computed values (trans-1,4-polybutadiene). Characteristic ratios increased with increasing chain length for both cis and trans chains with this effect being more prominent for

trans than for cis chains. Small absolute changes in chain size probability densities with temperature are observed. Larger relative increase in probability density of larger chains and smaller relative decrease in probability density of smaller chains result in increased average chain size with increasing temperature. This effect increases characteristic ratios with increasing temperature. The larger chains show a much higher increase in characteristic ratios with temperature than smaller chains, and this effect is stronger for trans than for cis chains.

Eigenvalues of the radius of gyration matrix quantify chain shapes by providing eigenvalues along the three principal directions (eigenvectors). Average shape measures differ between cis and trans chains. With increasing chain length, trans chains are slightly compressed along the principal direction while cis chains are slightly stretched. Resultantly, trans chains are slightly more spherical with increasing chain length while cis chains are slightly less spherical. At the same chain length, trans chains are slightly less spherical than cis chains. At long chain lengths, trans and cis chains have similar spherical shapes. With increasing temperature, little or no variation in shape is computed for cis chains, whereas trans chains are slightly stretched along the principal direction, and thus are slightly less spherical. Most changes in shapes arise from changes along the longest principal

direction.

Cis and trans chains show similar asphericity (a parameter that quantifies deviation from spherical shape) at longer chain lengths. Little or no change in acylindricity (a parameter that quantifies deviation from cylindrical shape) is computed for either cis or trans polybutadiene chains. Relative shape anisotropy (a shape parameter) follows the same trends like asphericity as functions of both chain length and temperature for cis and trans polybutadiene chains.

Joint correlation studies reveal that size and shape parameters are mutually dependent properties of chains. For asphericity, rod-like small size and spherical medium size cis chains show anti-correlation between chain size and shape. Spherical small size, near rod-like medium and large size chains show correlation between chain size and shape.

For acylindricity, medium size chains of flattened cross section, and small and large size chains of round cross section showed correlation between chain size and shape. Round cross section medium size chains show anti-correlation between chain size and shape. Trans chains show similar behavior as cis chains with correlation and anti-correlation between chain size and shape occuring to a greater extent.

The next use for the detailed conformation results in this work is to relate

probability densities to the work done to alter chain size and shape. Cis and trans chains show different probability density distributions implying different amounts of deformation work to alter chain size and shape. When a tire revolves and deflects while in motion, affine deformation of the elastomer-filler system takes place. The deformation leads to changes in elastomer chain conformations, which results in entropy losses of the elastomer-filler system (since entropy is related logarithmically to chain conformations). These entropy losses lead to computing irreversible work, viscoelastic losses and rolling resistance. The effects of fillers on these conformation distributions thus will quantify interaction effects on loss modulus and rolling resistance.

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DEDICATION

I dedicate this dissertation to my parents.

Ma and Baba, thank you for instilling in me virtues, teaching me that there

is no alternative to hard work and how important it is to be patient in life.

Everything I will ever achieve in life will always be dedicated to you.

PREFACE

The following work is presented in manuscript format in accordance with the guidelines set by the University of Rhode Island Graduate School. The thesis consists of one manuscript which is prepared for submission to the journal Polymer.

Chapter 1 introduces the concept of rolling resistance, brief history of rubber tires, viscoelastic properties of rubber tires, relevant literature and prior work done by other researchers, and the role of chain conformations in affecting viscoelastic properties and rolling resistance of rubber tires.

Chapter 2 is the manuscript "Sizes and shapes of amorphous cis- and trans-1,4 polybutadiene".

Chapter 3 is the supplementary material for chapter 2.

Chapter 4 is conclusions, current work and future work.

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CHAPTER 1

Introduction

Rolling resistance in rubber tires results in reduced fuel economy in vehicles whereas traction (grip) is needed for braking ability and force transmission. Maintaining balance between reducing rolling resistance and optimizing traction can be achieved by using reinforcement fillers. Viscoelastic properties (storage and loss moduli) [1] of rubber tires can help to quantify rolling resistance and traction. The overall aim of this project is to use modeling tools to understand how elastomer-filler interactions affect viscoelastic properties of rubber tires and to obtain lower rolling resistance (improved vehicle fuel economy) systems, without compromising on wear resistance and traction of tires.

1.1 Brief History and Functions of Tires

The most important application of rubber worldwide is in the manufacture of rubber tires. Rubber tire development started in the 1800s. A major step in rubber tire production happened in the year 1845 when a Scottish engineer by the name Robert William Thomson invented and patented the world's first vulcanized pneumatic tire. It was made up of vulcanized rubber tubes and filled

with compressed air which meant the tires could be inflatable. The pneumatic tire worked well and provided vehicle control, wear resistance but the expenses of manufacture of the tires had a detrimental effect towards the commercial viability and success of these tires [2].

A Scottish veterinarian by the name John Boyd Dunlop is credited as the inventor of the first commercially viable or practical pneumatic tire. In 1887, John Boyd Dunlop developed the first practical pneumatic tire and used it on his son's tricycle with success. He later filed for and was awarded a patent for bicycle tires in the year 1888 [2].

Tires perform several crucial vehicular functions such as supporting weight of the vehicle, providing braking capability and propulsion, reducing impact from the road, providing vehicle direction and control. A tire can be classified as a good tire if it i) can generate good traction between the road and tire which enables braking and propulsion, ii) is able to provide good steering control, iii) has a long shelf life i.e. good wear resistance and iv) has low rolling resistance leading to greater fuel economy [3, 4].

Traction depends on the friction properties of the tire tread and is determined by the road conditions and temperatures i.e. wet traction, ice traction and winter

traction. Steering control depends on the stiffness properties of the tread. Wear and tear depends on the abrasion resistance of the tread compound. Rolling resistance depends on the viscoelastic losses or loss modulus of the tread compound [3, 4]. Thus the tire tread, which is the rubber covering the circumference of the tire, plays an important role in determining tire properties.

1.2   Tires and Viscoelastic properties

Rubber tires undergo viscoelastic losses both at high as well as low frequencies. During rolling, the strains on a tire tread exert stresses through both elastic and viscous mechanisms. Viscoelastic losses at low frequencies (around 5 to 20 Hz) result in rolling resistance which dissipate energy during rounding and re-flattening of tires. Rolling resistance occurs during an entire cycle of tire rotation (greater time and thus lower frequencies). Viscoelastic losses at high frequencies result in traction since it occurs during a much shorter time length of contact between the tire tread and the road (lesser time and thus higher frequencies). Low rolling resistance requires compounds which absorb low amounts of energy (low hysteresis compounds) i.e. compounds which have low loss modulus at those frequencies. Traction requires compounds which absorb high amounts of energy (high hysteresis compounds) i.e. compounds which comply with the road conditions, presence of

particles, stones, unevenness of the roads.

Vehicles with tires having higher rolling resistance require greater amount of fuel to travel a certain distance as compared to vehicles with tires having lower rolling resistance. Resultantly, vehicles with higher rolling resistance tires have poor fuel economy which is a detrimental factor for automobile consumers. Methods have to be developed to reduce tire rolling resistance (to improve vehicle fuel economy) but not at the expense of reduced traction and wear resistance of tires.

Rolling resistance, traction and wear resistance comprise the "magic triangle of tires" [5]. It is a technical challenge to reduce one aspect of the magic triangle without compromising on the others. In the 1980s, thick and hard tires were designed in order to reduce tire rolling resistance [3]. While they achieved the purpose of reducing rolling resistance, the traction was greatly compromised.

Balance between reducing rolling resistance and maintaining traction and wear resistance can be achieved by using reinforcement fillers with rubber tires. Reinforcement fillers have been found to lower rolling resistance of tires, increase tensile strength (higher storage modulus), improve wear resistance and durability [4]. Carbon black and silica are the two most prominent and widely used reinforcement fillers with rubber tires. Our collaborators at Ford Motor Company, Dearborn,

MI USA, are looking experimentally at several novel filler systems such as Silanol, BR-Acrylate Terpolymer, Hybrid-CB Silica, Treated Aramid Fiber Granule and Broad Aggregate CB as reinforcement fillers with the rubber elastomer system [6].

Parameters such as the geometry and type of filler, rubber-filler adhesion, and so on need to be considered in rubber-filler systems. Non-linear interactions between the rubber (elastomer) and filler make it difficult for experimentation alone to optimize the system and thus models need to be develped to understand elastomer-filler interactions. Our work involves developing computational models to understand how molecular-level changes in elastomer-filler interactions affect rolling resistance and viscous losses.

1.3 Hypothesis for This Work and Relevant Prior Literature

The hypothesis of our work is quantifying deformation force and estimating tire rolling resistance as a result of changes in elastomer chain conformations. During rolling, the tire tread flattens against the road and as a result, the elastomer chains undergo a change in their conformations and affine deformation of the elastomer-filler system takes place. This deformation changes the number of ways the elastomer chains and filler particles can be arranged and thus affects the entropy of the system, which is logarithmically related to the number of confor-

mations [7]. The original distribution of the chains is restored after an entire cycle

of tire rotation by random fluctuations after the deformation and this change in

entropy requires work which is dissipated as heat, leading to rolling resistance.

One approach to decrease the work dissipated as heat will be to reduce the extent

to which the polybutadiene chains change their shapes under deformation. This

will be accounted for within the simulations by directly bonding the polybutadi-

ene chains to the filler particles. Favorable elastomer-filler interactions will lead

to lower rolling resistance and conversely, poor elastomer-filler interactions will

lead to higher rolling resistance. Thus studying the chain conformations and the

changes in the conformations under deformation and presence of filler particles is

of utmost importance in our work.

Mohsin, Berry and Treloar [8] determined viscoelastic properties (storage and

loss moduli) of polybutadiene samples using an experimental approach known as

the torsional pendulum method. The samples studied were "high cis" containing

98% cis by weight and "cis-trans" containing 52% cis, 48% trans by weight. In

the torsional pendulum method, samples of polybutadiene were held between a

lower and a higher clamp connected to an inertia bar which was suspended by

a steel wire carrying weight. A hand operated lever enabled the lower clamp

to be rotated through a small angle to cause oscillations. The oscillations were recorded by a capacitative oscillatory gauge which were connected to an amplifier and a pen recorder. These oscillations helped measure viscoelastic properties of polybutadiene samples. The samples were housed in a chamber filled with liquid nitrogen and the temperature was varied between -170°C to 20°C at a heating rate of 1°C/minute. Storage modulus for both "high cis" and "cis trans" polybutadiene samples were found to be around 1 GPa at -170°C. It reduced to around 1 MPa when heated to around -80°C and remained at that value for the remaining heating cycle. All the temperature studies were carried out at a frequency of 1 Hz. The drop in storage modulus value of polybutadiene could be attributed to the glass transition (transition from solid, glassy state to soft,rubbery state in amorphous polymers) happening on heating the polybutadiene samples above their glass transition temperature (T_g of polybutadiene is around -90°C to -70°C [1]). The tan δ [1] plot for "cis trans" polybutadiene showed two peaks corresponding to two different glass transitions for cis and trans parts.

Moraglio [9] and Abe and Fujita [10] used experimental viscosity measurements to compute characteristic ratio [11] (an important chain conformation property which is being discussed in detail in chapter 2). Using Mark-Houwink's equa-

tion [12] for theta-solvent, Moraglio and Abe and Fujita predicted the K factor (Mark-Houwink parameter) for cis-1,4-polybutadiene in n-heptane and diethyl ketone respectively. Obtaining the K factor allowed them to compute the characteristic ratio of cis-1,4-polybutadiene under theta-conditions.

Mark [13, 14], Abe and Flory [15] studied random conformations of cis- and trans-1,4-polybutadiene using Flory's Rotational Isomeric State approach (RIS) [11]. Details of the RIS method and a brief summary of the conformational properties obtained by Mark, and Abe and Flory are being discussed in chapter 2. Mattice and Li [16] used molecular dynamics (MD) simulation method to simulate single chain and bulk amorphous cis-1,4-polybutadiene systems. The low energy states computed were in accordance with the ones suggested by Mark [13] and by Abe and Flory [15]. Different population probability distributions about bond angle supplements and torsion angles were observed for single chains and bulk structures. They also computed cohesive energy of the bulk system. Cohesive energy can be defined as the energy needed to remove a molecule from the bulk system and it was found to be around 4100 cal/mol.

1.4 Overview of this Project

I have used cis- and trans-1,4-polybutadiene as the elastomer systems in my research. The polybutadiene can exist as the single elastomer in the rubber tires or could exist as a constituent of the styrene-butadiene rubber (SBR) co-polymer [3]. Numerous (100,000) isolated single chains of uncorrelated random conformations of polybutadiene are generated at different chain lengths and over a range of temperatures. Using a single chain is justified since a flexible polymer surrounded by the same polymer takes on the same average shape as a single random polymer chain. These chains are generated under unperturbed conditions (attractive and repulsive forces balanced between polymer-solvent i.e. theta conditions) using the RIS method. The RIS parameters suggested by Mark [13, 14] and later on used by Abe and Flory [15] are used in our work. Probability density distribution of different chain conformations of cis- and trans-1,4 polybutadiene are obtained. These probability densities are related to the deformation work done in order to alter chain size and shape, leading to mechanical and viscoelastic properties of chains and ultimately to rolling resistance.

My Master's thesis looks at random chain conformations (chain size and shape), probability density distribution of cis- and trans-1,4-polybutadiene chains

under unperturbed conditions, and also at joint correlations between chain size and shape. Amongst several findings, a key finding of this work is explanation of chain swelling on heating occuring due to increase in average chain size, which is attributed to the "*taut conformation effect*" (discussed in detail in chapter 2).

Currently I am working on applying deformation forces on the same ensemble [17] of isolated single chains as generated under unperturbed conditions, studying the changes in chain conformations and quantifying the deformation work to bring about the changes in chain conformations. This can give quantifiable values of deformation force and stress, ultimately leading to estimating loss modulus and rolling resistance. Future work involves incorporating fillers in the elastomer systems and studying the changes in chain conformations and rolling resistance due to the elastomer-filler interaction. Results of chain conformation changes due to deformation and elastomer-filler interaction are to be included in my PhD dissertation.

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CHAPTER 2

"Sizes and shapes of amorphous cis- and trans-1,4-polybutadiene"

by

Suvrajyoti Kar and Michael Greenfield [*]

Department of Chemical Engineering, University of Rhode Island, Kingston, RI -

02881, USA

is prepared for submission to Polymer

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[*]Corresponding author email: greenfield@egr.uri.edu

Abstract

Flory's Rotational Isomeric State approach is used to generate isolated single cis- and trans-1,4-polybutadiene chains of uncorrelated random conformations in unperturbed conditions based on discrete rotational states defined by Mark and by Abe and Flory. Squared end-to-end distance, squared radius of gyration, and shape parameters are studied at 343 K for chain lengths ranging from 50 to 120 repeat units and for the 50-unit chain size for temperatures at 275 K to 400 K. The calculated characteristic ratios are in good agreement with experimental and prior computed values. Small absolute changes in chain size probability densities with temperature were observed. Larger relative increase in probability density of larger chains and smaller relative decrease in probability density of smaller chains result in increased average chain size with increasing temperature. This effect increases characteristic ratios with increasing temperature. The larger chains show a much higher increase in characteristic ratios with temperature than smaller chains, and this effect is stronger for trans than for cis chains. Eigenvalues of the radius of gyration matrix quantify chain shapes along the three principal directions (eigenvectors). Averaged shape measures differ between cis and trans chains, and most changes in shapes arise from changes along the longest principal direction. With

increasing chain length, cis chains are slightly less spherical, whereas trans chains are slightly more spherical. With increasing temperature, little or no variation is computed for cis chains while trans chains are slightly less spherical. Joint correlation studies between chain size and shape show that they are mutually dependent properties of chains.

Keywords: Rotational Isomeric State, cis-1,4-polybutadiene, trans-1,4-polybutadiene, squared radius of gyration, Gaussian distribution, polymer shape.

2.1 Graphical Abstract
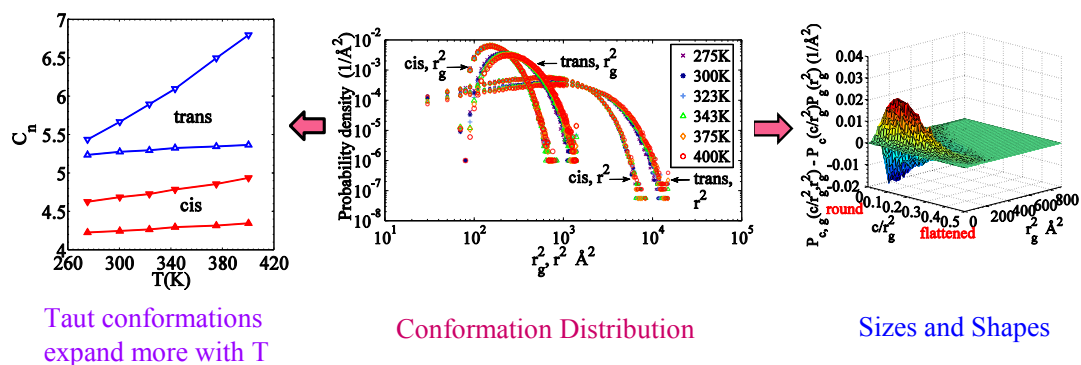
Figure 1. Graphical abstract

2.2 Introduction

Vehicle tires are the most important application of rubber worldwide. Methods have been looked at to develop tires which would give better fuel economy without

compromising on wear resistance and traction [1, 2, 3, 4]. Rolling resistance results from the energy a tire absorbs as it revolves and deflects when in contact with the roads. Tires with higher rolling resistance consume more fuel and thus result in poor vehicle fuel economy. Rolling resistance on the macroscale connects directly to energy losses from changes in chain conformations on the microscale.

This paper takes steps toward understanding how elastomer chains contribute to rolling resistance. It is part of an overall project to quantify how irreversible work resulting from changes in chain conformations in the presence of interactive fillers leads to entropy changes, which lead to energy losses that contribute to rolling resistance. Thus, studying and understanding the statistical mechanics of chain conformations is a vital molecular link toward understanding the role of chain conformations in determining rolling resistance.

A rubber tire comprises one or more different types of elastomers such as styrene-butadiene rubber (SBR), polybutadiene, or polyisoprene. Apart from the elastomers, tires are made up of materials such as reinforcement fillers, curing agents, processing oil, antidegradant, stearic acid, etc.[5]. Our work focuses on polybutadiene as an elastomer system. A single chain in our calculation can represent either an elastomer chain in a tire or a butadiene component within an SBR

block co-polymer.

In this work we have generated numerous (100,000) isolated single chains of uncorrelated random conformations of cis- and trans-1,4-polybutadiene chains under unperturbed conditions (balanced attractive and repulsive polymer-solvent interactions, i.e. theta-conditions). Using a single chain in each computation is justified because a flexible polymer surrounded by the same polymer takes on the same average shape as a single random polymer chain in a theta solvent [6, 7, 8]. The polybutadiene chains were generated using Flory's Rotational Isomeric State approach (RIS) [9]. Each chain realization in RIS provides an independent sample. Thus while the standard Molecular Dynamics and Monte Carlo methods provides sequences of related states, the small changes that occur in each step lead to correlations that must be relaxed to sample an equilibrium distribution. The RIS method offers an advantage of generating a large number of uncorrelated random chain conformations in a computationally cheap manner.

Mark [10, 11] and Abe and Flory [12] previously used the RIS method to generate random conformations of cis- and trans-1,4-polybutadiene chains. Mark's work focused on computing and comparing characteristic ratios of chains with experimentally obtained values, obtaining temperature coefficients of mean squared

end-to-end distance of chains, as well as comparing intramolecular energies between different rotational isomeric states per repeat unit of polybutadiene. In addition to the properties computed by Mark, Abe and Flory computed various other properties of random polybutadiene chain conformations including strain-birefringence coefficients and coefficients of rotational isomerization under stretching.

Mattice and Li [13] used molecular dynamics to simulate single chains and bulk structures of amorphous cis-1,4-polybutadiene under unperturbed conditions. A single chain of cis-1,4-polybutadiene consists of 99 repeat units. The low energy states computed were in accordance with the ones suggested by Mark [10] and by Abe and Flory [12]. Population probability distributions about the bond angle supplements and torsion angles were found to be different for single chain and bulk structures. This difference suggested intermolecular origin conformational differences between single chain and bulk structures. The bulk structure of polybutadiene allowed Mattice and Li to compute cohesive energy of the system. Cohesive energy is defined as the energy needed to remove a molecule from the bulk system and it was around 4100 cal/mol.

Our focus is on studying size and shape properties of random chain conformations of polybutadiene. We computed characteristic ratios of cis- and trans-1,4

polybutadiene chains at different chain lengths and over a range of temperatures. Comparing the probability density distribution of the chains at different temperatures has explained the reason behind average swelling of chains with increasing temperature. We also studied chain shapes at different chain lengths and over a temperature range. Finally, we looked at joint probability correlations between chain size and shape and the extents of correlation and anti-correlation for cis- and trans-1,4-polybutadiene chains.

2.3 Methodology

In the RIS approximation, torsions about bonds are treated as existing in one or more discrete rotational states, with each of these states chosen to coincide with a region of low potential energy. States differ in relative energy and thus in Boltzmann-weighted probability. Discrete states are defined only around bonds that allow torsion. Rotations about the double bond are not allowed.

2.3.1 Chain Generation

Each polybutadiene chain was built in an atom-by-atom manner considering three torsional angles per repeat unit (ϕ_i, ϕ_{i+1}, ϕ_{i+3}) around the three single C–C bonds, as shown in figure 2. Atom positions in a single repeat unit depend on these three torsion angles. Torsion angles ϕ_i and ϕ_{i+3} affect positions of the pendant H

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atoms (H_i, $H_{i'}$, H_{i+3}, and $H_{i+3'}$) attached to the backbone C atoms (C_i and C_{i+3}) joined by i and $i+3$ bonds. They also directly affect positions of the C atoms (C_{i+1} and C_{i+4}). Torsion angle ϕ_{i+1} affects positions of the pendant H atoms (H_{i+1} and H_{i+2}) attached to the C atoms (C_{i+1} and C_{i+2}). It also directly affects positions of the C atoms (C_{i+2} and C_{i+3}). Bond angle supplements and bond lengths used in our computations were obtained from Mark [10, 11] and are shown in Table 1. Abe and Flory [12] used the same values in their calculations.
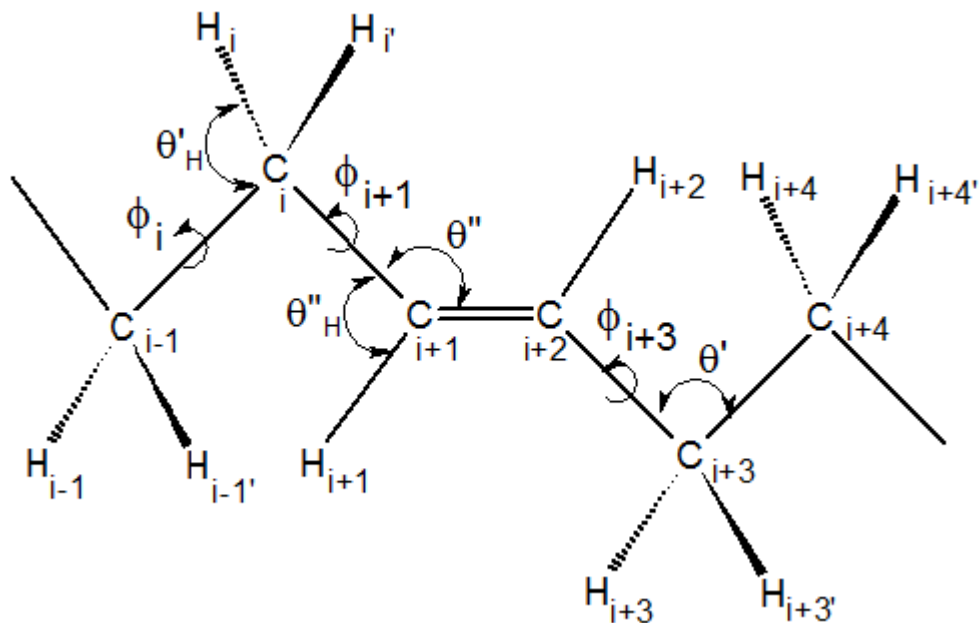

Figure 2. Trans-1,4-polybutadiene structure showing bonds, bond angles and torsion angles. Atoms from C_i to C_{i+3} and their pendant hydrogens comprise a single repeat unit. Numbering employs Flory's convention [9].

Table 1. Bond and angle geometries [10]

Bond lengths	Å
C–C	1.53
C=C	1.34
C–H	1.10

Bond Angles	Supplement
∠ CH_2–CH=CH (θ'')	55°
∠ CH–CH_2–CH_2 (θ')	68°
∠ CH_2–CH–H (θ''_H)	62.5°
∠ CH_2–CH_2–H (θ'_H)	70°

Transformation matrices are orthogonal matrices which are used to transform bond vectors from one reference system to another [9]. These transformation matrices were used in determining atom positions for each single chain of polybutadiene. A total of four transformation matrices were used per repeat unit of polybutadiene i.e. three for the C–C single bonds and one for the C=C double bond. For the C=C double bond, the torsional angle (ϕ) is zero. For the C–C single bond, the torsional angles were chosen based on regions of low potential energy.

Mark [10, 11] chose to use six discrete rotational isomeric states for each torsional bond of polybutadiene. These isomeric states were chosen based on their low potential energy. These isomeric states correspond to ϕ = -120°,-60°, 0°,60°,120°,180°, with $\phi = 0°$ defined as the trans state (Flory convention [9]). Statistical weight matrices [9] were suggested by Mark [10] for 1,4-polybutadiene

systems. The same set of matrices and statistical weights were used in our work.

The partition function [9] shows each possible combination of rotational isomeric states of a chain. The pair wise probability of a single conformation equals its contribution to the partition function, divided by the partition function. Please refer to the appendix for a discussion on statistical weights, statistical weight matrices, partition function, and transformation matrices.

Total energy of the system is a summation of the torsional energy [9] and the energy resulting from the dispersion interactions between non-bonded atoms calculated using the Lennard-Jones (6-12) potential [15]. Non-bonded atoms separated by three or more bonds contribute to the non-bonded interaction energy computed using the Lennard-Jones (6-12) potential. Every conformation of polybutadiene generated in our work have fixed bond lengths and bond angles, and thus the bond energies do not affect the overall energy of the system.

100,000 isolated single chains of cis- and of trans-1,4-polybutadiene were simulated at each state of various conformations and lengths ranging over degrees of polymerization $n = 15$, 25, 50, 75, 100, and 120 repeat units, all at 343 K. Additional simulations were carried out for a single chain length ($n = 50$) at different temperatures T = 275, 300, 323, 343, 375, and 400 K. Ensemble averages

of the various chain size and shape parameters were calculated in order to under-

stand behavior of cis and trans chains over different ranges of chain length and

temperature. Further calculations obtained correlations among chain size, length

and shape. The chains were generated based on pair probabilities and thus the

ensemble averages are Boltzmann-weighted probability averages.

2.3.2 Chain size and shape parameters

An important chain size parameter is the squared end-to-end distance r^2,

which is calculated as

$$r^2 = (r_x^2 + r_y^2 + r_z^2) \tag{1}$$

where r_x, r_y, r_z are the x, y and z coordinates of the end-to-end distance vector $\mathbf{r}$.

The squared radius of gyration (r_g^2) is computed using the distance of each atom

in the polymer chain to the center of mass,

$$r_g^2 = \frac{1}{N}\sum_{j=1}^{N}(\mathbf{r}_j - \mathbf{r}_{com})^2 \tag{2}$$

$\mathbf{r}_j$ is the position vector of atom j of a polymer chain, $\mathbf{r}_{com}$ is the position vector

of the center of mass of a polymer chain, and N is the total number of atoms in

the chain.

Theodorou and Suter [16] used the eigenvalues (λ_1, λ_2, λ_3) of a radius of gyration matrix (S) to quantify contributions directed along the three principal directions (eigenvectors) of a chain conformation.

$$S = \begin{pmatrix} \overline{x^2} & \overline{xy} & \overline{xz} \\ \overline{xy} & \overline{y^2} & \overline{yz} \\ \overline{xz} & \overline{yz} & \overline{z^2} \end{pmatrix} \tag{3}$$

where

$$\overline{x^2} = \frac{1}{N}\sum_{j=1}^{N}(x_j - x_{com})^2 \tag{4}$$

$$\overline{y^2} = \frac{1}{N}\sum_{j=1}^{N}(y_j - y_{com})^2 \tag{5}$$

$$\overline{z^2} = \frac{1}{N}\sum_{j=1}^{N}(z_j - z_{com})^2 \tag{6}$$

x_j, y_j, z_j are the x, y, and z coordinates of atom j of a polymer chain, and x_{com}, y_{com}, z_{com} are the x, y, and z coordinates of the center of mass of the polymer chain. The overbar indicates average over all chain atoms. We transformed the radius of gyration matrix to a principal axis system, which diagonalised the radius of gyration matrix in such a manner that the eigenvalues of the matrix were in

descending order ($\lambda_1 \geq \lambda_2 \geq \lambda_3$). Eigenvalue λ_1 corresponds to the longest principal direction while λ_2 and λ_3 correspond to secondary directions. This effectively represents the size of a polymer chain in each direction, rather than with the radius r_g of a hollow sphere having the same mass and moment of inertia as the polymer chain. The squared radius of gyration equals the sum of the three eigenvalues,

$$r_g^2 = \lambda_1 + \lambda_2 + \lambda_3 \tag{7}$$

Computing the radius of gyration matrix (equation 3) enabled quantifying chain shape. The chain shape parameters studied were b (asphericity or deviation from spherical shape), c (acylindricity or deviation from cylindrical shape) and κ^2 (relative shape anisotropy) [16]:

$$b = \lambda_1 - \left(\frac{\lambda_2 + \lambda_3}{2} \right) \tag{8}$$

$$c = \lambda_2 - \lambda_3 \tag{9}$$

$$\kappa^2 = \left(\frac{b^2 + \frac{3}{4}c^2}{r_g^4} \right) \tag{10}$$

Averages of r^2, r_g^2, b/r_g^2, c/r_g^2, and κ^2 used an equal weighting for each chain at each condition. This is appropriate because relative Boltzmann-weighted probabilities are taken into account while generating the chain conformations.

2.4 Results and Discussion
2.4.1 Chain size

Characteristic ratio (C_n) of unperturbed chains [9, 17] is defined as the ratio of mean squared end-to-end distance of a real chain under the theta condition to that of a freely jointed chain with the same number of bonds and bond length,

$$C_n = \frac{\langle r^2 \rangle_0}{nl^2} \tag{11}$$

n is the number of backbone bonds along a polymer chain and l is the bond length. C_n quantifies chain expansion due to bond angle and torsion angle correlations. The subscript 0 of the mean squared end-to-end distance represents unperturbed conditions.

We computed characteristic ratios of cis- and of trans-1,4-polybutadiene chains of different chain lengths at one temperature ($T = 343$ K) and of a single chain length ($n = 50$) at multiple temperatures. Figures 3 and 4 illustrate C_n results for different chain lengths and over different temperatures, respectively. Experimental

values are taken from Moraglio [7] and Abe and Fujita [8]; computed values are from Mark [10, 11].

Figure 3 shows that calculated characteristic ratios are in good agreement with the experimental and prior computed characteristic ratios in the limit of infinite chain length for cis-1,4-polybutadiene chains. For trans-1,4-polybutadiene chains, the calculated characteristic ratios are slightly higher than prior computed values in the limit of infinite chain length. The characteristic ratios increased with increasing chain length for both cis and trans chains. The higher characteristic ratio for trans chains indicates a greater chain extension, which is potentially a consequence of the greater distance spanned between the carbon atoms bonded to the double bonded carbons. In figure 3, the prior computed characteristic ratio values for cis chains are almost indistinguishable from the experimental values. The characteristic ratio increased with temperature for both cis and trans chains, as shown in figure 4, and the increase was larger for trans than for cis polybutadiene chains. This indicates swelling of the average chain size upon heating.

In the limit of long chains, the mean squared radius of gyration $\langle r_g^2 \rangle_0$ should equal 1/6 of the mean squared end-to-end distance $\langle r^2 \rangle_0$ [9]. Figure 3 shows the ratio $\langle r^2 \rangle_0 / \langle r_g^2 \rangle_0$ was higher than 6 for shorter trans chains and decreased to 6 for

longer chains. The ratio was slightly higher than 6 for cis chains at all chain lengths.

Figure 4 shows that the ratio $\langle r^2 \rangle_0 / \langle r_g^2 \rangle_0$ was almost independent of temperature

for cis chains, whereas for trans chains it increased with increase in temperature.
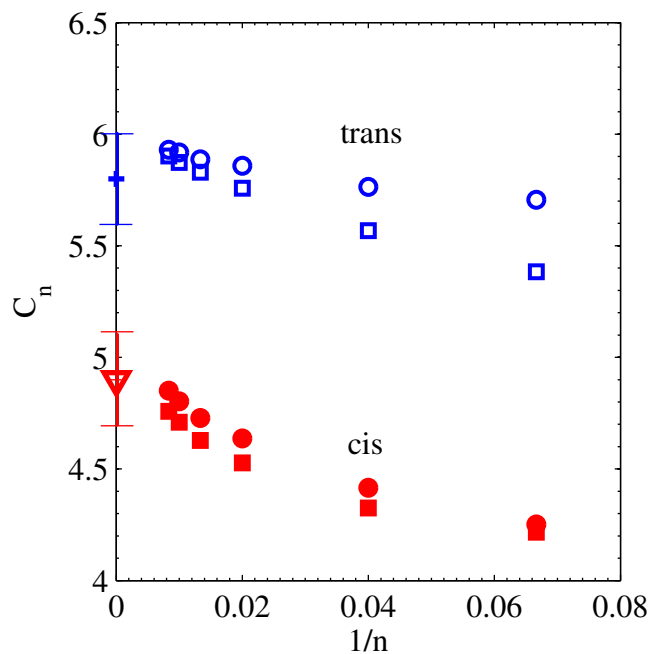

Figure 3. Characteristic ratio vs. inverse of chain length n for cis-(filled) and trans-(unfilled) 1,4-polybutadiene using $\langle r^2 \rangle_0$ (circle) and $6\langle r_g^2 \rangle_0$ (square). Literature results at $1/n = 0$ indicate models [10, 11] ($+$) and experimental values [7, 8] ($\triangledown$). These symbols are used throughout unless otherwise specified.
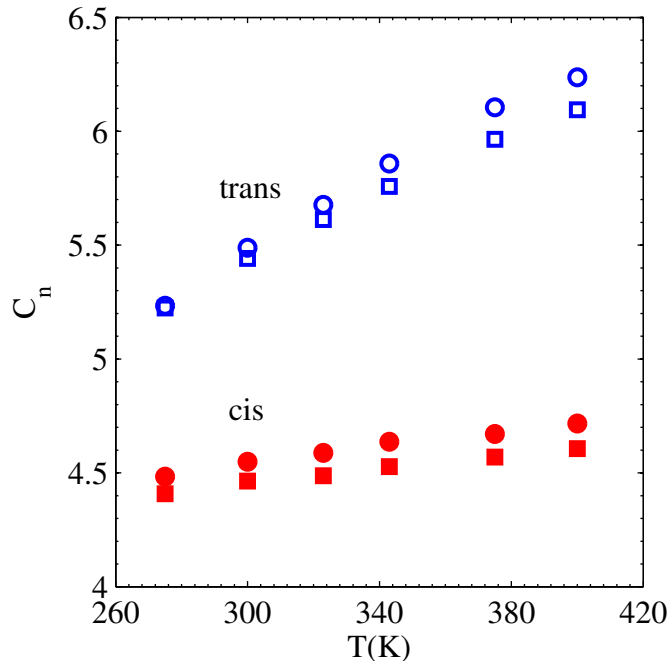
Figure 4. Characteristic ratio vs. temperature for cis- and trans-1,4-polybutadiene chains of 50 repeat units. Symbols match figure 2.

The probability density distribution of the squared end-to-end distance was calculated and compared with a Gaussian probability density distribution [9, 17],

$$P(r^2)dr = \left(\frac{3}{2\pi C_n n l^2}\right)^{\frac{3}{2}} \exp\left(\frac{-3r^2}{2C_n n l^2}\right) 2\pi r dr \tag{12}$$

A Gaussian model assumes each chain behaves like a freely jointed chain. The segments of each chain in such an ensemble can be considered as performing a random walk in three dimensions with the only constraint being that each segment must be joined to its neighbors with a fixed bond length [9, 17].

Figure 5 compares the probability density distribution of squared end-to-end

distance for cis and trans chains with the Gaussian model. Squared end-to-end distance of the cis chains ranged from around 10 to 7,000 Å^2, and for the trans chains around 10 to 14,000 Å^2. Trans chains have a wider distribution than cis chains and consequently have higher characteristic ratios. For cis chains, agreement between our simulation results and the Gaussian model was observed for chain sizes in the range of around 250 to 500 Å^2 as well as in the range of around 1050 to 3000 Å^2. Our trans chain simulation results showed agreement with the Gaussian model for chain size range of around 250 to 1050 Å^2 as well as in the range of around 3500 to 6500 Å^2. We classify these chain size ranges as medium size considering the entire range of the chain size distribution. These medium size chains have the highest probability of occurence. While smaller chains have a comparable probability density, they span a much smaller range in squared end-to-end distance. The Gaussian model predicted higher probability than the simulation results for shorter (chain size range of around 10 to 250 Å^2 for both cis and trans) chains as well as longer (chain size range of around 3000 to 7000 Å^2 for cis and around 6500 to 14000 Å^2 for trans) chains. Simulation results showed higher probability than those predicted by the Gaussian model for cis chains in the size range of around 500 to 1050 Å^2 and for trans chains in the size range of around 1050 to 3500 Å^2.
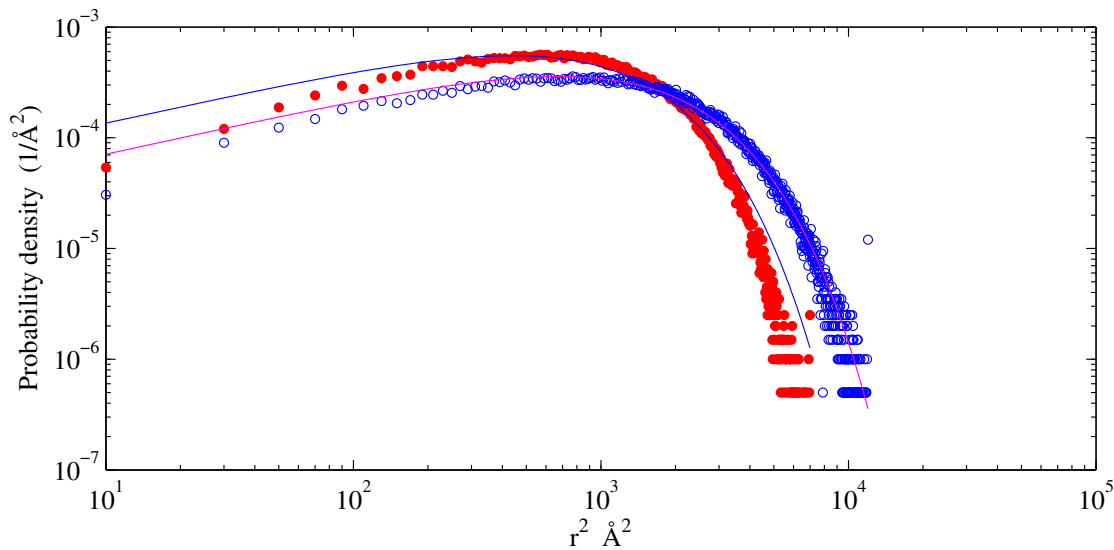
Figure 5. Probability density distribution of squared end-to-end distance for cis-
and trans-1,4-polybutadiene chains of 50 repeat units at 343 K. Lines indicate a
Gaussian distribution.

The temperature dependences of the probability density distributions of chain

sizes for cis- and trans-1,4-polybutadiene are shown in figure 6. Squared end-to-

end distance has a much wider distribution than the squared radius of gyration.

Smaller size trans chains were slightly more probable at lower temperatures than

at higher ones. Cis chains showed probabilities more independent of temperature.
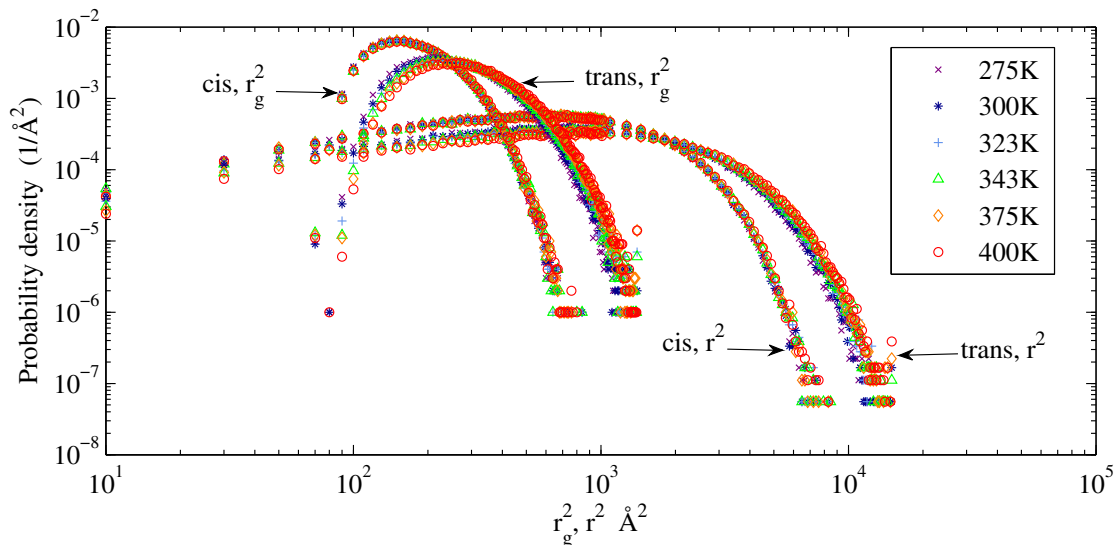
Figure 6. Probability density distribution of r^2 and r_g^2 for cis- and trans-1,4-polybutadiene chains of 50 repeat units at different temperatures.

The temperature dependencies of characteristic ratio and of chain size distribution appear to conflict with each other. The characteristic ratios increased with temperature, as shown in figure 4, though figure 6 suggests similar probabilities for the most probable chains (i.e. medium size chains) at different temperatures. Only small absolute changes in probability densities with temperature were observed for all chain sizes. The contributing factor to the increase in average chain size with temperature was the extended conformations, i.e larger chain sizes. There was a larger relative increase, though smaller absolute change, in probability density for larger chain sizes with temperature, as compared to a smaller relative decrease in probability density for smaller chain sizes. Despite this small change in low prob-

ability conformations, it resulted in an increase in average chain size. This effect was more pronounced for trans chains than for cis polybutadiene chains.

To examine this effect further, the characteristic ratio was calculated using only a subset of the chain size distribution, shown in figure 7. Chains with squared end-to-end distance ranging from 10 to 300 $Å^2$ were considered as smaller chains and chains with squared end-to-end distance greater than 4000 $Å^2$ were considered as larger chains. The characteristic ratios increased more with temperature for larger chain sizes of both cis and trans chains, whereas very little increase in characteristic ratio was observed for smaller chain sizes of cis and trans chains. The increase in charactersitic ratio of larger chain sizes was much more prominent in trans than in cis chains. Increases in characteristic ratio with temperature (figure 4) can thus be attributed to the size increases of extended and taut chain conformations. Polymer chain swelling with heating can be attributed to a size increase of the relatively few extended and taut conformations, rather than expansion uniformly across conformations of all sizes. The greater increase of characteristic ratio with temperature for larger chains, as shown in figures 4 and 7, indicates that this *"taut conformation effect"* was more prominent for trans than for cis polybutadiene chains.
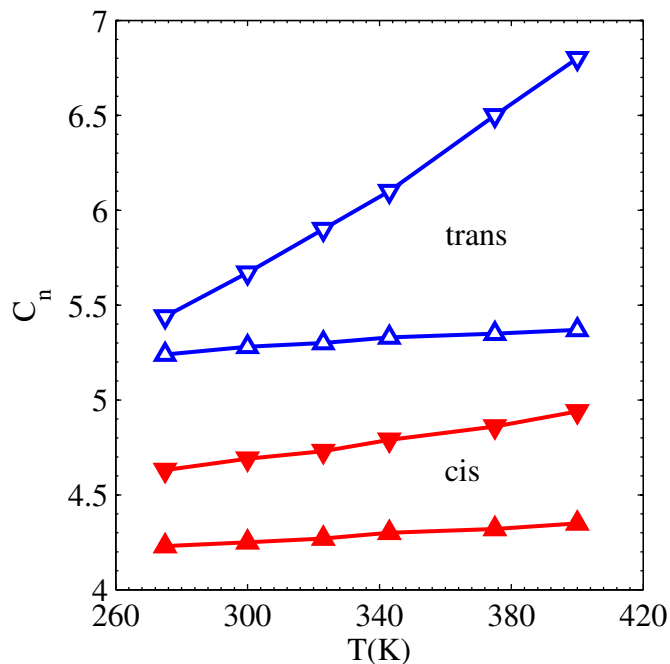
Figure 7. Characteristic ratio for larger (downward triangle) and smaller (upward triangle) subsets of the chain size distribution for cis- and trans-1,4-polybutadiene chains of 50 repeat units.

2.4.2   Chain shape

Ensemble averages of chain shape parameters were obtained in order to quantify shape variations among polybutadiene chains. Since each chain establishes its own principal axes, the analysis uses a different coordinate system for each chain. The results thus emphasize the deviations of each chain from a symmetric shape. Rotation differences between the principal axes and the original (x,y,z) coordinates are not important and were not taken into account when combining the results into averages and distributions.

The eigenvalues λ_1, λ_2, and λ_3 of the radius of gyration matrix indicate the

extents of orthogonal principal axes that span the region occupied by a chain in primary and secondary directions. Ratios of eigenvalues thus indicate if chains are being stretched or compressed. Figures 8 and 9 show the eigenvalue ratios as functions of inverse of chain length and temperature, respectively. These calculations were carried out at 343 K and for 50 repeat units respectively.

Figure 8 shows that trans chains were more stretched than cis chains along the principal direction. For trans chains, the extent of stretching decreased slightly with increasing chain length. For cis chains, the extent of stretching was larger with increasing chain length. The change in ratio between the two secondary directions followed the same trend as the principal direction but more subtly. These behaviors indicate that trans chains were slightly more spherical while cis chains were slightly less spherical with increasing chain length. At the same chain length, trans chains were slightly less spherical than cis chains. At long chain lengths, trans and cis chains have similar spherical shapes. The changes in the ratio between the two secondary directions were small compared to the changes in average chain size $\langle r_g^2 \rangle_0$.

Figure 9 shows there was little or no variation in relative chain extent with temperature for cis chains. The principal direction ratio increased slightly with

temperature for trans chains, while minor variations arose in ratio between the two secondary directions. This shows that as the temperature increased, trans chains were slightly more stretched along the principal direction. Little or no variation in relative chain extent for cis chains meant little or no change in their shape with temperature. Trans chains stretched slightly and thus were slightly less spherical with increasing temperature. Chain shape trends shown in figures 8 and 9 confirm that variations in the eigenvalue (λ_1) corresponding to the longest principal direction have the most significant effects on chain shapes.
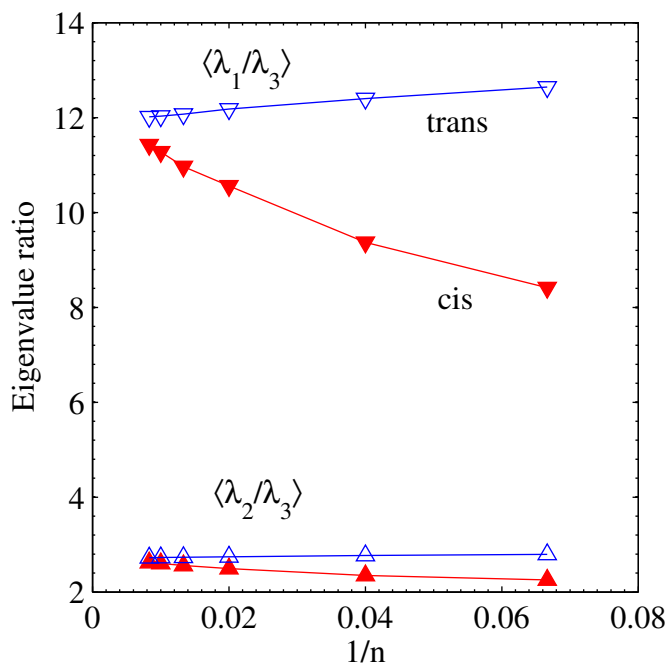

Figure 8. Averaged ratios of the largest and intermediate eigenvalues to the smallest eigenvalue at 343 K.
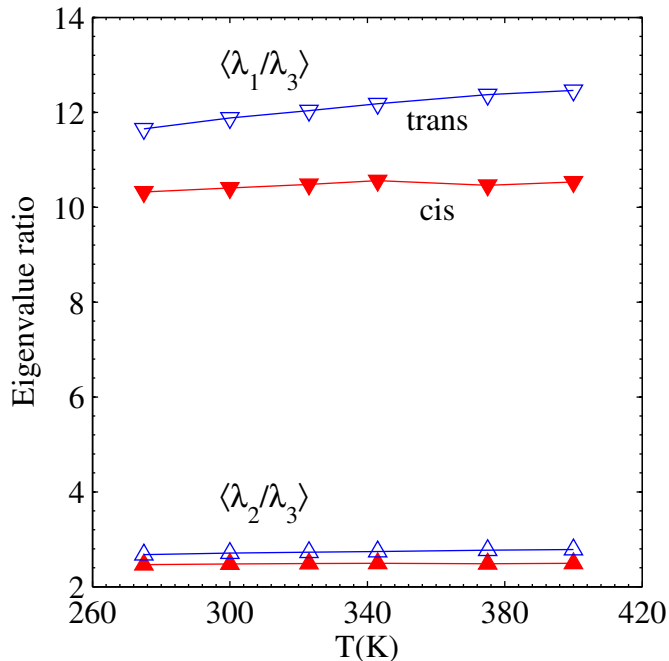
Figure 9. Averaged ratios of the largest and intermediate eigenvalues to the smallest eigenvalue for chains of 50 repeat units.

Figures 10 and 11 show variations in average shape parameters with inverse of chain length and temperature respectively. An asphericity factor (b/r_g^2) of 0 suggests a spherical shape and 1 suggests a rod-like shape, while an acylindricity factor (c/r_g^2) of 0 suggests a round cross section and 0.5 suggests a more flat cross section normal to the longest axis. κ^2 of 0 suggests a rod-like shape whereas 1 suggests structures of tetrahedral or of higher symmetry [16].

Figure 10 shows that both cis and trans chains show similar asphericity of 0.6 at longer chain lengths. An asphericity of 0.6 corresponds to a chain with contribution to the squared radius of gyration that is around 5.5 times larger in

the longest direction; it is also consistent with the 12:2.5:1 ratios shown in figures 8 and 9. Cis chains were more spherical at shorter chain lengths and gradually were slightly less spherical with increasing chain length, whereas trans chains were less spherical at smaller chain lengths and were very slightly more spherical with increasing chain length. This change in shape was more subtle for trans chains than cis. This behavior followed the same trend shown in figure 8.

Figure 11 shows that cis chains exhibited little or no change in shape with temperature. Trans chains were slightly less spherical with increasing temperature. This behavior followed the same trend shown in figure 9.

The relative shape anisotropy followed the same trend as asphericity as functions of both chain length and temperature. The acylindricity did not show much observable deviation with chain length or temperature for either cis or trans polybutadiene chains. Its value of 0.1 indicates chain fluctuations moderately larger in one minor direction compared to the other and thus corroborates the effect of small changes in ratio between the two secondary directions as compared to average chain size, as shown in figures 8 and 9.
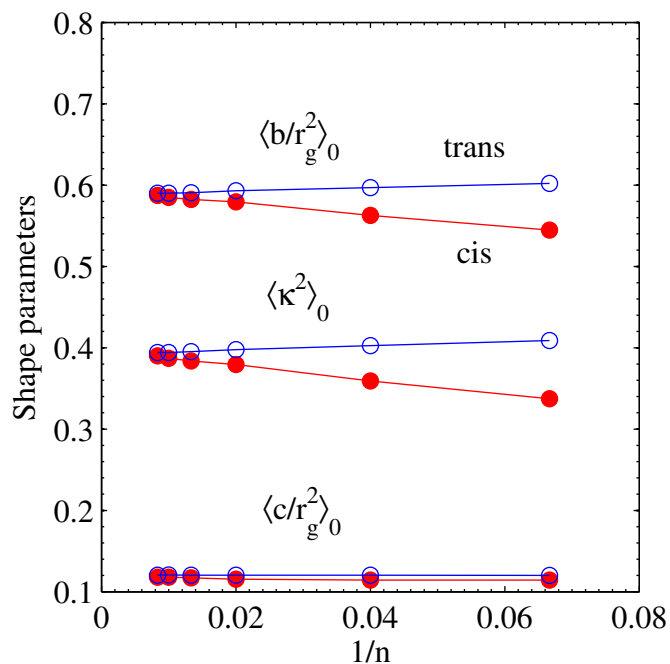
Figure 10. Average shape factors with inverse of chain length at 343 K. Subscript 0 indicates unperturbed conditions.
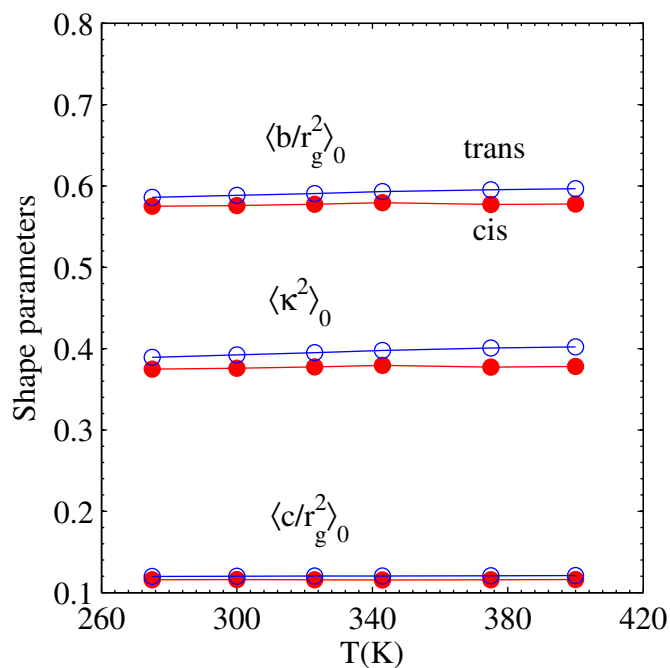

Figure 11. Average shape factors with temperature for chains of 50 repeat units. Subscript 0 indicates unperturbed conditions.

2.4.3 Joint correlations in size and shape

Joint correlations between chain size and shape were studied to determine if their variations with chain length and temperature were independent or dependent properties. Cis and trans chains showed similar joint correlation behavior, with correlation and anti-correlation between chain size and shape occuring to a greater extent for trans chains as compared to cis chains.

Figures 12 and 13 show joint correlations for cis chains of 50 repeat units. Multiple visualizations of these three-dimensional plots are available as supplementary material (chapter 3). Differences $\left[P(b/r_g^2, r_g^2) - P(b/r_g^2)P(r_g^2)\right]$ and $\left[P(c/r_g^2, r_g^2) - P(c/r_g^2)P(r_g^2)\right]$ of 0 indicate size and shape are completely independent of each other, i.e. they act as mutually exclusive events. A positive difference indicates correlated events, while negative indicates anti-correlation.

For small rod-like chains, which arise less typically than average, figure 12 indicates some anti-correlation between size and shape. Small chains were nearer to spherical in shape, and high correlation between chain size and shape was observed for them. For medium size chains, some correlation was found for chains that are near rod-like, while notable anti-correlation was found for more spherical chains. Rod-like large chains showed correlation between chain size and shape.

Figure 13 shows size-shape correlations for acylindricity in cis chains. Small chains showed good correlation with being nearly round in cross section. Medium size chains showed correlation for chains that were more flattened in cross section. For medium size chains with round cross sections, the relationship between size and shape became anti-correlated. Large chains showed minor correlation between chain size and shape with being nearly round in cross section.
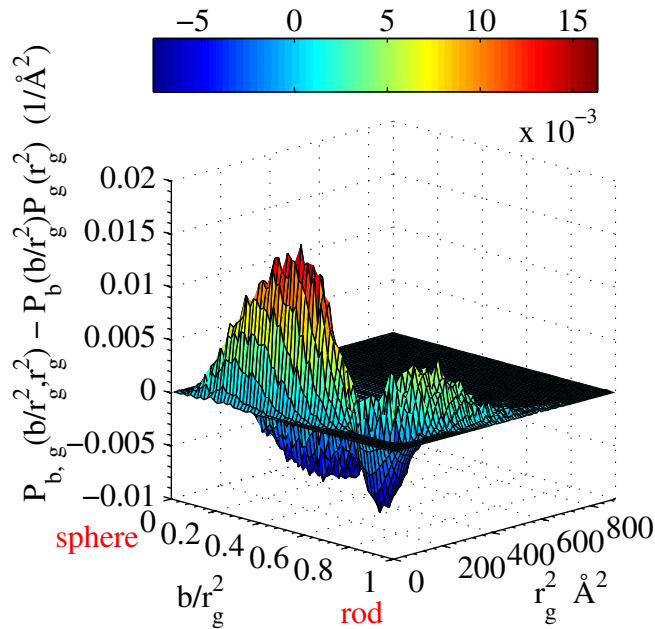
Figure 12. Joint correlations of probability density of chain size (P_g) and asphericity (P_b) for cis chains of 50 repeat units at 343 K.
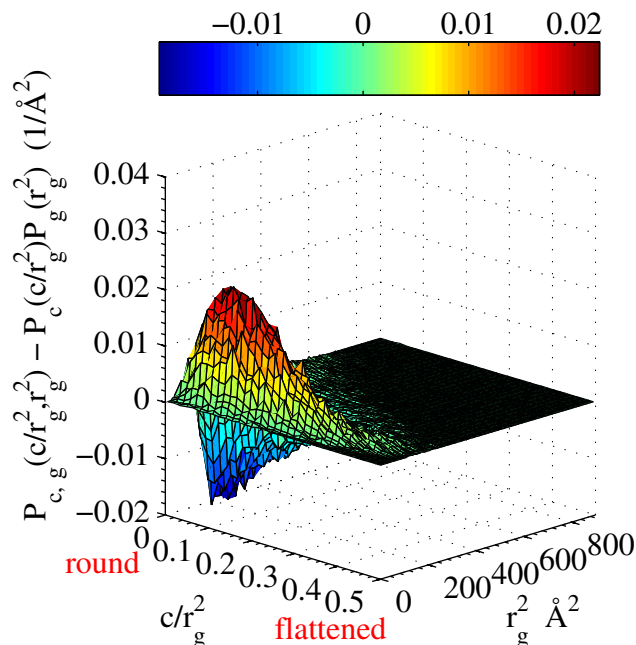
Figure 13. Joint correlations of probability density of chain size (P_g) and acylindricity (P_c) for cis chains of 50 repeat units at 343 K.

In total, different size and shape probability density distributions were found for cis and trans chains over different chain lengths and across a range of temperatures. Probability densities are related to the work required to alter chain size and shape, and thus different probability densities for cis- and trans-1,4-polybutadiene indicate different extents of work that must be done in order to alter chain size and shape. Quantifying this deformation work is the subject of ongoing research.

2.5 Conclusions

Ensemble averages and probability density distributions of sizes and shapes of cis- and trans-1,4-polybutadiene chains have been quantified for isolated single

chains under undeformed theta conditions. Such conformations are considered to be representative for a chain in its own melt.

Characteristic ratios were larger with increasing chain length for both cis and trans chains, and these were in good agreement with experimental and prior computed values (cis-1,4-polybutadiene), and slightly higher than prior computed values (trans-1,4-polybutadiene). Characteristic ratios were higher for trans chains than for cis chains and indicate greater chain extension, which could be due to a greater distance spanned between the carbon atoms bonded to the double bonded carbons.

A Gaussian model predicted higher probability than simulation results at shorter and longer chain sizes for both cis and trans chains. Simulation results predicted a higher probability than the Gaussian model at certain regions of medium size chains for cis and trans chains while at other regions of medium size chains, simulation and Gaussian results were in agreement.

Characteristic ratios increased with increasing temperature for both cis and trans chains, with trans chains showing greater temperature dependence. Small absolute changes in chain size probability densities with increasing temperature was observed. Smaller chain conformations showed a smaller relative decrease in

probability density as compared to a larger relative increase in probability density for larger chain conformations with increasing temperature, thus resulting in an increase in average chain size. For constant chain length, larger chain sizes showed a much higher increase in characteristic ratios with temperature than smaller chain sizes. This accounted for an increase in average characteristic ratio of polybutadiene chains with increasing temperature, which results in chain swelling on heating. This *"taut conformation effect"* was more pronounced for trans- than for cis-1,4-polybutadiene chains.

With increasing chain length, trans chains were slightly compressed while cis chains were stretched along the principal direction. Resultantly trans chains were slightly more spherical and cis chains were slightly less spherical with increasing chain length. At the same chain length, trans chains were slightly less spherical than cis chains. At long chain lengths, trans and cis chains have similar spherical shapes. The extent of stretching and compression was greater along the principal direction than the secondary directions. With increasing temperature, trans chains were slightly stretched along the principal direction whereas cis chains showed little or no change in shape. Thus trans chains were slightly less spherical with increasing temperature, while little or no variation in shape was computed for cis

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chains. Variations of the largest eigenvalue λ_1 of the radius of gyration matrix have the most significant effects on chain shapes: most changes in shapes arose from changes along the longest principal direction.

At longer chain lengths, both cis and trans chains showed similar asphericity. Little or no variation was computed in acylindricity for either cis or trans polybutadiene chains. Relative shape anisotropy followed the same trend as asphericity as functions of both chain length and temperature for cis and trans polybutadiene chains.

Joint correlation studies revealed that size and shape parameters are mutually dependent properties of chains. For asphericity, small size rod-like cis chains indicated anti-correlation between size and shape. Small size spherical chains showed high amount of correlation between size and shape. For medium size chains, notable anti-correlation between size and shape was observed for spherical chains whereas some correlation between size and shape was observed for near rod-like chains. Large rod-like chains showed correlation between size and shape. For acylindricity, round cross section small size chains showed good correlation between size and shape, whereas medium size chains showed correlation between size and shape for flattened cross section chains. Round cross section medium

size chains showed anti-correlation between chain size and shape. Large chains showed minor correlation between size and shape with being nearly round in cross section. Trans chains showed similar correlation and anti-correlation between size and shape as cis chains, yet to a greater extent.

Cis- and trans-1,4-polybutadiene show different size and shape probability density distributions, which imply different amounts of deformation work to alter chain shape and size. Quantifying this deformation work and its implications for mechanical properties, viscoelastic properties, and rolling resistance are the subject of ongoing work.

2.6 Acknowledgements

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CHAPTER 3

Supplementary Material

Supplementary material contains three dimensional visualizations of joint correlations between chain size and shape. The plots have been rotated at intervals of $60°$ about their azimuth angle (az) i.e rotated at intervals of $60°$ about their horizontal axes. The vertical elevation (el) of the plots is $15°$. All the plots are for 50 repeat unit cis-1,4-polybutadiene chains at 343 K. Trans-1,4-polybutadiene chains show similar correlation and anti-correlation behavior between chain size and shape as cis chains, yet to a greater extent.
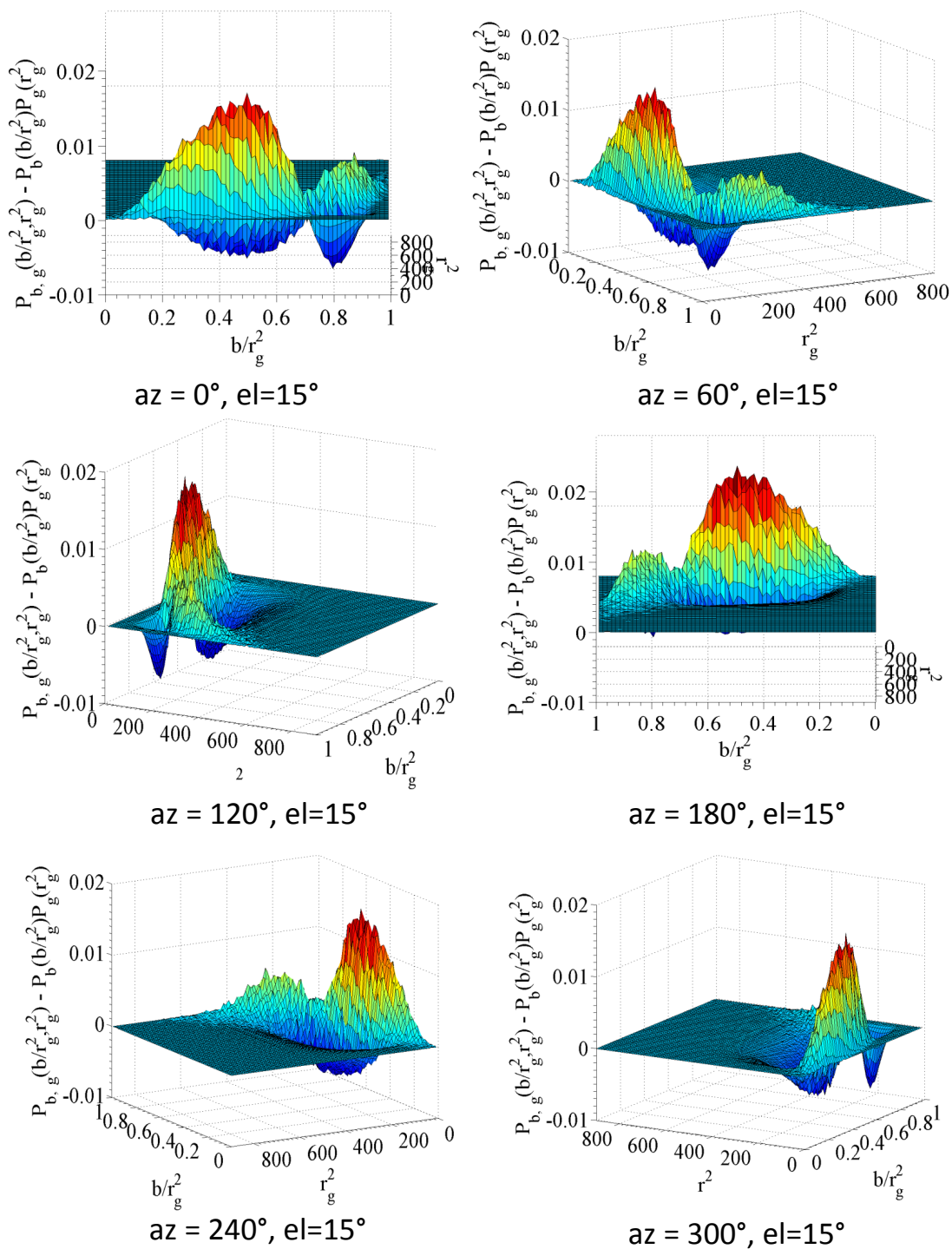
Figure 14. Joint correlations of probability density of chain size (P_g) and asphericity (P_b) for cis-1,4-polybutadiene chains of 50 repeat units at 343 K.
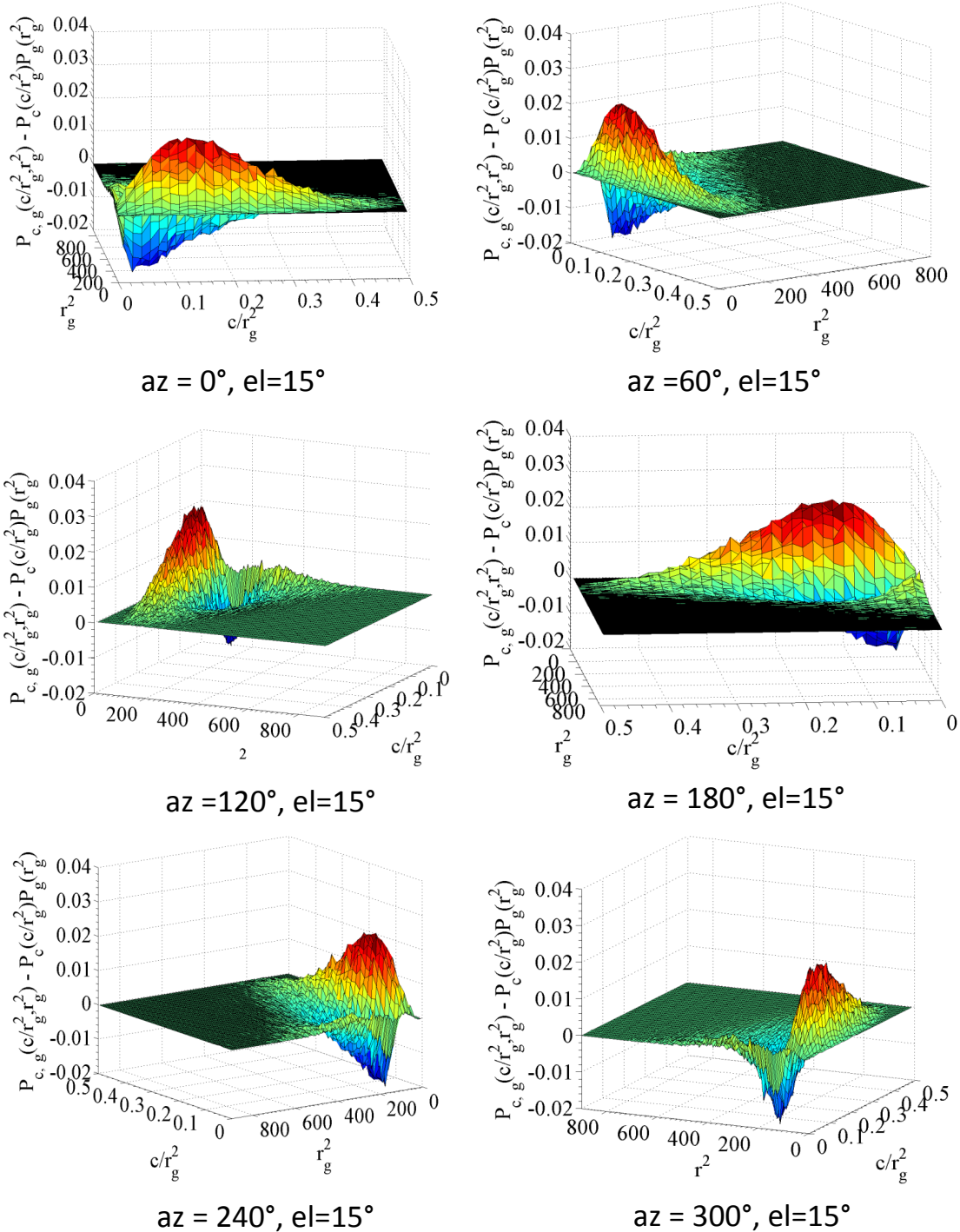
Figure 15. Joint correlations of probability density of chain size (P_g) and acylindricity (P_c) for cis-1,4-polybutadiene chains of 50 repeat units at 343 K.

CHAPTER 4

Conclusions, Current Work and Future Work

Flory's Rotational Isomeric State approach was used to generate isolated single

chains of cis- and trans-1,4-polybutadiene over a range of temperatures and chain

lengths. 100,000 isolated single chains were generated under each condition of

chain length and temperature. Using a single chain is justified since a flexible

polymer surrounded by the same polymer takes on the same average shape as

a single random polymer chain. Probability density distributions of the chain

ensembles were quantified under unperturbed conditions (attractive and repulsive

forces balanced between polymer-solvent i.e. theta conditions).

4.1   Conclusions

Characteristic ratios were in good agreement with experimental [1, 2] and

prior computed values [3] (cis-1,4-polybutadiene), and slightly higher than prior

computed values [4] (trans-1,4-polybutadiene). Cis and trans chains characteristic

ratios were larger with increasing chain length. Higher characteristic ratios for

trans chains than cis chains indicated greater chain extension, which could poten-

tially be a result of greater distance spanned between the carbon atoms bonded

to the double bonded carbons. Characteristic ratios computed here increased with increasing temperature, with the increase being more prominent for trans chains than cis polybutadiene chains. Small absolute changes in chain size probability densities with temperature were observed. The increase in characteristic ratio can be attributed to a larger relative increase in probability density of larger size chains as compared to a smaller relative decrease in probability density of the smaller size chains with increasing temperature. This resulted in an increase in the average size of the chains with increasing temperature. The larger chains showed a much higher increase in characteristic ratios with temperature than smaller chains, and this effect was stronger for trans than for cis chains. Increase in characteristic ratios can be attributed to the size increase of the extended and taut chain conformations; hence we have named this effect as the *"taut conformation effect"*. Swelling of these polymer chains upon heating can thus be attributed to a size increase of the relatively few extended and taut conformations, rather than expansion uniformly across conformations of all sizes.

For limit of long chains, the mean squared radius of gyration $\langle r_g^2 \rangle_0$ should equal 1/6 of the mean squared end-to-end distance $\langle r^2 \rangle_0$ [5]. The ratio $\langle r^2 \rangle_0 / \langle r_g^2 \rangle_0$ was higher than 6 for shorter trans chains and decreased to 6 at longer lengths.

For cis chains, the ratio was slightly higher than 6 for all chain lengths.

The chain size probability density distributions of the cis- and trans-1,4-polybutadiene chains were compared to the Gaussian model [5, 6]. Gaussian model predicted higher probability than simulation results at shorter and longer chain sizes for both cis and trans chains. Simulation results predicted higher probability than the Gaussian model at certain regions of medium size chains for cis and trans chains while at other regions of medium size chains, simulation and Gaussian results were in agreement.

The eigenvalues λ_1, λ_2, and λ_3 of the radius of gyration matrix used by Theodorou and Suter [7] indicate the extents of orthogonal principal axes that span the region occupied by a chain in primary and secondary directions (eigenvectors). Ratios of eigenvalues indicate if chains are being stretched or compressed. Two different shape comparisons were done for cis and trans chains: with increasing chain length and with increasing temperature. With increasing chain length, trans chains were slightly compressed along the principal direction while cis chains were slightly stretched. Resultantly trans chains were slightly more spherical with increasing chain length while cis chains were slightly less spherical. At the same chain length, trans chains were slightly less spherical than cis chains. At long chain

lengths, trans and cis chains have similar spherical shapes. The extent of stretching and compression was more along the principal direction than the secondary directions. With increasing temperature, trans chains were slightly stretched along the principal direction, whereas cis chains showed little or no change in shape. Thus trans chains were slightly less spherical in shape with increasing temperature while little or no variation in shape was computed for cis chains. Most changes in shapes arose from changes along the longest principal direction.

Ensemble averages of chain shape parameters such as asphericity (deviation from spherical shape), acylindricity (deviation from cylindrical shape) and relative shape anisotropy were studied based on the radius of gyration matrix for both cis and trans chains of different chain lengths and over different temperature ranges. Cis and trans chains showed similar asphericity behavior at longer chain lengths i.e. an asphericity value of 0.6. An asphericity of 0.6 corresponds to a chain with a contribution to the squared radius of gyration that is around 5.5 times larger in the longest direction than the secondary directions. At the longer chain lengths, the averaged ratio of the eigenvalues along the longest to the shortest direction was around 12, while at the same chain length, the averaged ratio of the eigenvalues along the secondary directions was around 2.5; this corroborates

that the contribution to the radius of gyration was around 5.5 times larger in the longest direction than the secondary directions.

The relative shape anisotropy followed the same trends as the asphericity as functions of both chain length and temperature. The acylindricity factor did not show much observable deviation with chain length and temperature for both cis and trans chains.

Joint correlation studies between chain size and shape showed that they are mutually dependent properties. For asphericity, rod-like small size and spherical medium size cis chains showed anti-correlation between chain size and shape. Spherical small size, near rod-like medium and large size chains showed correlation between chain size and shape.

For acylindricity, medium size chains of flattened cross section, and small and large size chains of round cross section showed correlation between chain size and shape. Round cross section medium size chains showed anti-correlation between chain size and shape. Trans chains showed similar behavior as cis chains with correlation and anti-correlation between chain size and shape occuring to a greater extent.

Probability densities are related to the work required to alter chain size and

shape. Cis- and trans-1,4-polybutadiene chains showed different probability density distributions, and thus different amounts of work would be needed to be done on them to bring about a change in their chain conformations. This deformation work can be quantified to determine mechanical properties, viscoelastic properties and rolling resistance. Thus it can be seen that changes in chain conformations directly impacts rolling resistance of vehicle tires.

4.2   Current Work

Currently I am looking at how cis- and trans-1,4-polybutadiene chain size and shape are affected under deformation. I am using the same ensemble of single isolated chains (100,000) under the same range of chain length and temperature, and applying deformation on them. Instead of squared end-to-end distance (r^2), I am using end-to-end distance vectors in the x, y, and z directions ($\mathbf{r}_x$, $\mathbf{r}_y$, and $\mathbf{r}_z$) to study the extent of deformation in each of those directions of the chains. Probability density distributions of the end-to-end distance vectors help quantify the deformation force acting on the chain ensembles. Deformation leads to changes in chain conformations which results in entropy losses of the chains (since entropy is related logarithmically to chain conformations [8]). These entropy losses lead to computing irreversible work, viscoelastic losses and ultimately rolling resistance.

4.3 Future Work

Future work includes introducing reinforcement fillers (carbon black, silica and their derivatives) in our system and seeing how elastomer-filler interactions impact rolling resistance of the elastomer-filler system and to what extent [9]. The results of deformation work and elastomer-filler interactions will be included in my PhD dissertation.

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APPENDIX

Discussion on statistical weights, statistical weight matrices, partition function and transformation matrices

A.1   Statistical weights and statistical weight matrices

Statistical weights are relative probabilities of occurence for bonds in rotational isomeric states. Statistical weights are dependent on the torsional energy around the bonds,

$$\alpha = \exp(-E_\alpha/k_B T) \qquad (A.1)$$

In eqn A.1, α is a statistical weight based on the torsional energy E_α. The statistical weights are arranged in statistical weight matrices with the row and column elements being statistical weights for successive torsional bonds. Row elements are statistical weights around bond i and column elements are statistical weights around bond $i+1$ as shown in figure 2 of chapter 2 [1].

As mentioned in chapter 2, Mark chose to use six discrete rotational isomeric states (based on location of potential energy minima) for each torsional bond [2]. These correspond to ϕ = -120°,-60°, 0°,60°,120°,180°. The angles -120°,-60°,60°,120° correspond to gauche states and the angle 0° corresponds to trans

state. The bond pairs $\pm60°,\pm60°$ or $\mp60°,\pm60°$ have the same probability and were assigned the statistical weight γ. These were gauche-gauche bond pairs. The gauche-trans bond pairs were $\pm60°,0°$ or $\pm120°,0°$, and so on. These were assigned a statistical weight of 1. Further, $\pm120°$ based gauche-gauche bond pairs were assigned the statistical weight σ [2]. Equations A.2 and A.3,

$$\gamma = \exp(-E_\gamma/k_B T) \tag{A.2}$$

$$\sigma = \exp(-E_\sigma/k_B T) \tag{A.3}$$

show the statistical weights suggested by Mark. The torsional energies are $E_\gamma = $ -1600 cal/mol and $E_\sigma = $ -200 cal/mol.

Since there are six discrete rotational isomeric states, the statistical weights were arranged in 6×6 statistical weight matrices. Since each repeat unit of polybutadiene has three torsional bonds, three statistical weight matrices were used in our work (as suggested by Mark). These were

$$U_i = \begin{pmatrix} 1 & 0 & \sigma & 0 & \sigma & 0 \\ 1 & 0 & \sigma & 0 & \sigma & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \sigma & 0 & \sigma & 0 \end{pmatrix} \tag{A.4}$$

$$U_{i+1} = \begin{pmatrix} 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{A.5}$$

$$U_{i+3} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & \gamma & 0 & 0 & 0 & \gamma \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & \gamma & 0 & 0 & 0 & \gamma \end{pmatrix} \tag{A.6}$$

These statistical weight matrices (U_i, U_{i+1}, U_{i+3}) were the same as (U_c, U_a, U_b) as used by Mark [2].

A.2 Partition function

Partition function (z) can be defined as the sum of the unnormalized probabilities for all possible discrete rotational isomeric states. It is used in the computation of bond pair probability (as stated in chapter 2) as

$$z = J^\star U_{i+1} U_{i+3} (U_i U_{i+1} U_{i+3})^{n-2} U_i J \tag{A.7}$$

$$J^\star = (1, 0, 0, 0, 0, 0) \tag{A.8}$$

$$J = col(1, 1, 1, 1, 1, 1) \tag{A.9}$$

n is the degree of polymerization or number of repeat units in a polymer chain.

$J^\star$ and J are row and column matrices for chain start and end respectively [2].

Carrying out the matrix multiplication in equation A.7 provides one term in z for each possible combination of rotational isomeric states. The probability of a single conformation equals its contribution to z, divided by z.

A.3   Transformation matrices

Transformation matrices are used to transform bond vectors from one reference state to another one. According to Flory [1], the transformation matrix used to transform bond vectors from $i+1$ frame to i frame (refer figure 2 from chapter 2) can be given as

$$T_i = \begin{pmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i \cos\phi_i & -\cos\theta_i \cos\phi_i & \sin\phi_i \\ \sin\theta_i \sin\phi_i & -\cos\theta_i \sin\phi_i & -\cos\phi_i \end{pmatrix} \tag{A.10}$$

where θ_i = bond angle supplements (as given in Table 1) and ϕ_i = torsional angles. For the double bond $i+2$ (refer figure 2 from chapter 2), the transformation matrix reduces to

$$T_{i+2} = \begin{pmatrix} \cos\theta_{i+2} & \sin\theta_{i+2} & 0 \\ \sin\theta_{i+2} & -\cos\theta_{i+2} & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{A.11}$$

since $\phi_{i+2} = 0°$ (as no rotation is allowed around double bonds).

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