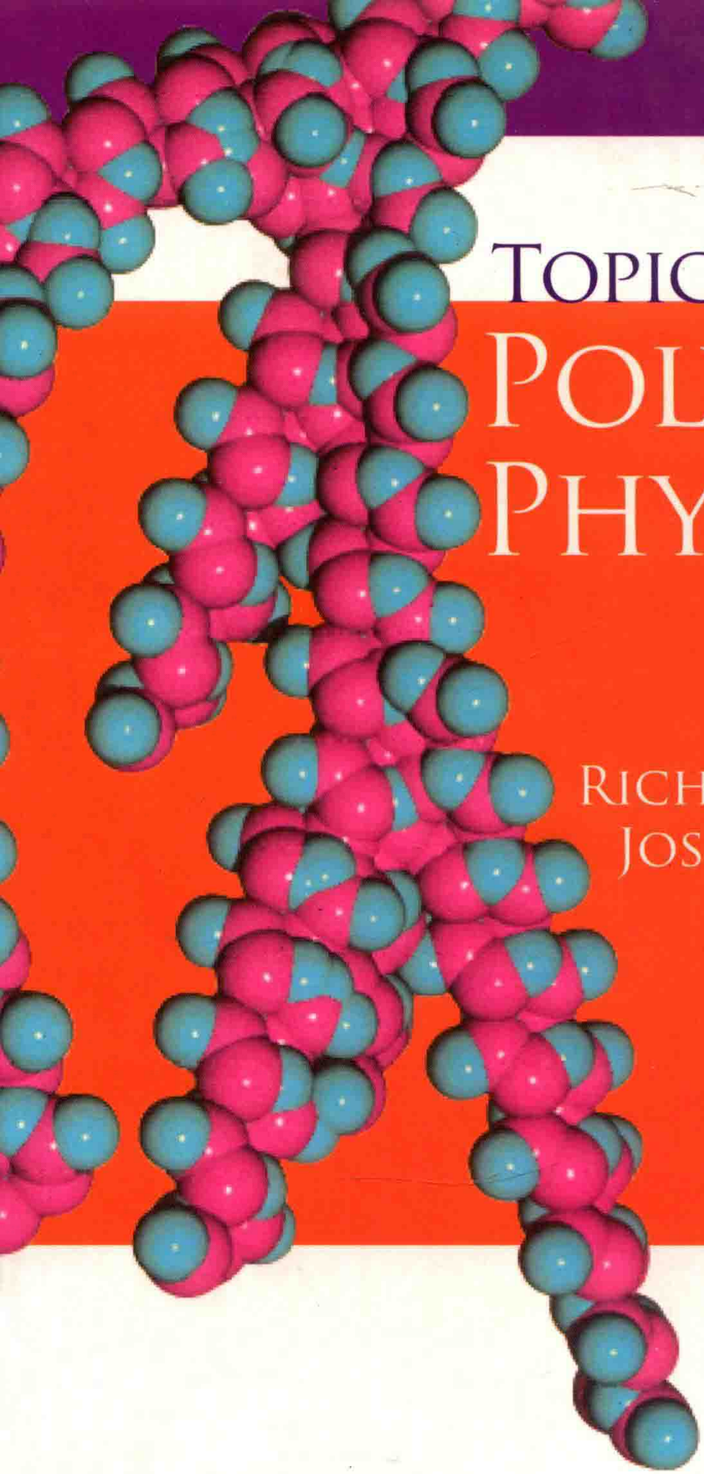
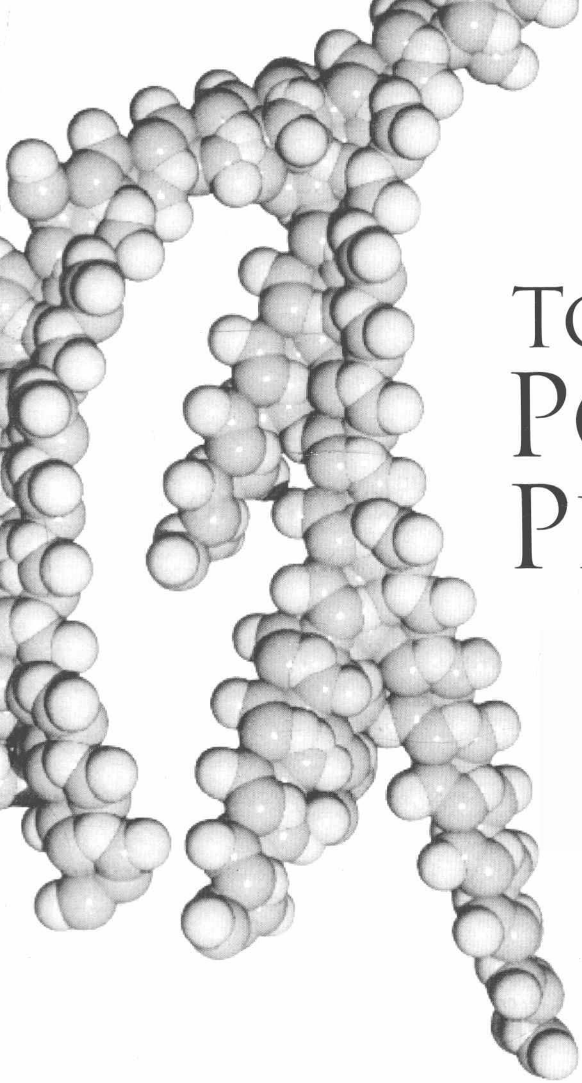


# TOPICS IN POLYMER PHYSICS

RICHARD S STEIN
JOSEPH POWERS

Imperial College Press



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# TOPICS IN POLYMER PHYSICS

TO OUR WIVES

JUDY BALISE STEIN

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## Preface

This book can serve as an introduction to students interested in learning the techniques used in developing mathematical models of physical phenomenon; or it can furnish the background information to the experienced professional desiring to broaden his/her knowledge of polymers.

The senior author presented material in this book to students interested in learning the fundamental mathematics underlying many areas of polymer physics and in lectures to audiences with varying backgrounds in polymer physics.

The material in this book should prove helpful to readers who have knowledge of introductory mathematics, chemistry and physics.

The text emphasizes the derivation of many equations used in Polymer Physics. The assumptions used in modeling, and in making the mathematical apparatus solvable in closed form, are presented in detail. Too many times, the basic equations are presented in final form in journal articles and books from either lack of space or the assumption that the derivation is widely disseminated and does not require repetition.

The fundamentals of any discipline have to be constantly tested against new findings. This book presents the assumptions and simplifications of the fundamentals of many areas of Polymer Physics so that the testing process can be expedited.

The authors have discussed this material with many colleagues and in return received many pertinent suggestions for improvement. These include Philip Wilson, Mohan Srinivasaro, Hiromichi Kawai, Shigeharu Onogi, Garth Wilkes, Takeji Hashimoto and Marion Rhodes, James J. Burke and many others who attended courses or collaborated with Professor Stein in research projects.

The improvements belong to our colleagues. The residual factual errors, typos and other problems belong to the authors.

For supplementary material, corrections and communications with us, please visit http://web.mac.com/rsstein1/iWeb

## Contents

Dedication .......... v
Preface .......... vii
Chapter 1 .......... 1
INTRODUCTION .......... 1
1.1. Background .......... 1
1.2. Linear Chain Molecules .......... 4
  1.2.1. Structure .......... 4
  1.2.2. Synthesis .......... 8
  1.2.3. Molecular Weight .......... 10
1.3. Network Molecules .......... 15
  1.3.1. Structure .......... 15
  1.3.2. Synthesis .......... 16
  1.3.3. Molecular Weight .......... 16
1.4. Rubber .......... 17
  1.4.1. Structure .......... 17
  1.4.2. Synthesis .......... 21
  1.4.3. Molecular Weight .......... 21
1.5. Multicomponent Systems .......... 21
  1.5.1. Copolymers .......... 21
  1.5.2. Polyblends .......... 25
  1.5.3. Composites .......... 25
  1.5.4. Ceramers .......... 26
References .......... 27
Appendix 1A - Derivation of the Most Probable Distribution 28
Reference .......... 30
Chapter 2 .......... 31
STATISTICS OF CHAIN CONFORMATIONS .......... 31
2.1. Introduction .......... 31
2.2. Small Molecules .......... 31
2.3. Larger Molecules, Statistical Variation of Molecular Conformations .......... 40
2.4. Statistical Segment Model .......... 41
2.5. Generalization to High Polymers .......... 44
2.6. Polymer Chains Containing Two Kinds of Atoms .......... 45

2.7. Model Chains with Restricted Rotation and No Interaction Among the $\phi$'s .......... 47
2.8. Rotational Isomeric State (RIS) Approximation .......... 49
2.9. Chains with Interactions between $\phi$ Values of Neighboring Monomers .......... 51
2.10. Asymmetric Barriers .......... 53
2.11. Comparison with Experiment .......... 56
2.12. Chain End-to-End Distribution Functions .......... 58
    2.12.1 One Dimensional Case .......... 58
    2.12.2. Extension to a Three Dimensional Chain .......... 61
    2.12.3. Extension to Non-Gaussian Case .......... 64
References .......... 71
Appendix 2A - Statistical Mechanics .......... 73
References .......... 80
Statistical Thermodynamics of an Ideal Monatomic Gas .......... 81
Appendix 2B - Vector Analysis .......... 83
    2B.1. Vector Addition .......... 83
    2.B.2 Scalar Product .......... 84
Reference .......... 85
Appendix 2C - Radius of Gyration .......... 86
Appendix 2D. Evaluation of $(\mathbf{a}_{m+n} \cdot \mathbf{a}_m)$ .......... 92
Appendix 2E. Restricted Rotation with Symmetrical Barrier .99
Appendix 2F. Rotational Isomeric State (RIS) Approximation .......... 103
    2F.1. Introduction .......... 103
    2F.2. The Conformational Partition Function .......... 104
    2E.3. Mean Square Distance .......... 106
References .......... 107
Appendix 2G. Random Walk of Gaussian Chains .......... 109
References .......... 113
Appendix 2H. Radius of Gyration, Size and Shape .......... 114
    Definition of $\langle \mathbf{r}_q^2 \rangle$ .......... 114
    $\langle \mathbf{r}_q^2 \rangle$ for a Rigid Rod .......... 115
    $\langle \mathbf{r}_q^2 \rangle$ for a Sphere of Radius R .......... 116

Determination of $\left\langle \mathbf{r}_q^2 \right\rangle$ from Scattering.......................... 117
Chapter 3 ........................................................................... 121
THERMODYNAMICS.......................................................... 121
3.1. Introduction.................................................................. 121
3.2 Thermodynamics of Elasticity ....................................... 121
3.3. Force on a Chain in the Presence of Energy Contributions to Elasticity ........................................................................ 129
3.4. Solution Thermodynamics.............................................. 134
3.4.1. Flory-Huggins Theory ............................................ 134
3.4.2. Calculation of $P_2$................................................... 138
3.3.3. Entropy of Mixing ............................................... 140
3.5. Polymer Miscibility...................................................... 145
3.6. Spinodal Decomposition............................................... 147
3.7. Heat Capacity ............................................................. 153
3.8. Thermodynamics of Crystallization .............................. 154
3.8.1 Polymer Structure – Melting Point........................ 155
3.8.2. Effect of Diluent and Impurities........................... 157
3.8.3. Crystallization Induced by Stretching .................. 164
References ........................................................................ 167
Appendix 3A Classical Thermodynamics ............................ 169
References ........................................................................ 175
Appendix 3B. Heat of Mixing ............................................ 176
Appendix 3C Osmotic Pressure........................................... 181
Chapter 4 ........................................................................... 185
OPTICS ............................................................................. 185
4.1. Introduction................................................................... 185
4.2. Nature of Electromagnetic Waves ................................ 186
4.3. Refraction ................................................................... 187
4.4. Scattering .................................................................... 191
4.4.1. Intensity of Light Scattering for an Isolated Atom or Molecule ......................................................................... 194
4.4.2. Effect of the Polarization of Light........................ 195
4.4.3. The Scattering Intensity for a Collection of Scattering Objects ............................................................ 196
4.5. Diffraction.................................................................... 205

4.5.1.The Reciprocal Lattice........................................205
4.5.2. Interpretation of the Vector Bragg Equation.........208
4.5.3. The Distance Between Crystal Planes ..................209
4.5.4. The Diffraction Phenomenon in One Dimension..211
4.6. Absorption ..............................................................215
4.7. Fluorescence ............................................................216
4.8. Birefringence.............................................................218
4.9. Scattering from Inhomogeneous Media ....................222
4.10. Quasi-elastic Light Scattering.................................228
4.11. Variation of Scattering with Electric Fields ..............229
4.12. Non-Linear Optics...................................................230
4.13. Piezo-Electric Materials ...........................................232
4.14. Kerr Effect ...............................................................233
References ....................................................................234
Appendix 4A Depolarization of Scattering.......................236
Appendix 4B Scattering from a Collection of Molecules.....239
Appendix 4D The Magnitude of the Reciprocal Vector H ...244
Appendix 4E Orientation Fluctuations.............................246
Appendix 4F Scattering from Concentration Fluctuations ...249
Evaluation of $(\partial\alpha/\partial c)$ ..................................................252
Evaluation of $\left[-(\partial\mu_1/\partial c)\right]$ ...............................................252
Molecular Weight from Light Scattering .......................253
Dealing with Large Molecules.......................................255
Extensions to Other Kinds of Radiation........................256
Extensions to Concentrated Solution and Bulk Polymers ..............................................................................257
Effect of Anisotropy and Orientation............................257
Appendix 4G Why Concentration Fluctuations Relate to Molecular Weight.........................................................257
How to Measure the Size of an Elephant .......................258
ANOTHER WAY OF LOOKING AT IT - ...................260
Chapter 5 ...........................................................................263
ELECTRICAL PROPERTIES ..........................................263
5.1 Introduction.................................................................263
5.2. Dielectrics...................................................................264

*5.2.1*. Dielectric Constant ........................................ 264
*5.2.2*. Orientation of permanent dipoles ........................ 269
*5.2.3*. Dielectric Loss ............................................ 269
5.3. Piezo- and Pyroelectric Effects ............................. 272
5.4. Piezo-Electric Coefficient ................................... 274
References ......................................................... 276
Appendix 5A. Lines of Flux ...................................... 278
5A.1. Electrical Field Strength ............................... 278
5A.2. Electric displacement and Flux Density ............... 278
5A.4. The Electrostatic Potential (Voltage) .................... 280
5A.5. The Field between Parallel Plates ........................ 280
Appendix 5B. Lorentz Calculation, Internal Field Correction ........................................................................ 282
Chapter 6 ............................................................ 285
SPECTROSCOPY ................................................... 285
6.1. Introduction ...................................................... 285
6.2. General Background ............................................ 286
6.3. Infrared ........................................................... 288
6.4. Raman ............................................................. 295
6.5. Ultraviolet and Visible ......................................... 299
6.6. Nuclear Magnetic Resonance ................................ 300
6.7. Neutron Inelastic Scattering (NIS) ......................... 301
References ......................................................... 303
Appendix 6A Fourier Transform Infrared (FTIR) ............... 305
References ......................................................... 307
Appendix 6B. Normal Coordinate Analysis ....................... 308
References ......................................................... 312
Appendix 6C. Spectrographic Notation ........................... 313
Chapter 7 ............................................................ 314
THE RUBBERY STATE ............................................. 314
7.1. Introduction ...................................................... 314
7.2. Force - Extension Relation for Rubbers ................... 316
7.2.1. Simple Case ................................................ 316
7.2.2. Consideration of Network Crosslinks .................. 318
7.3. Affine Transformation ......................................... 322
7.4. Uniaxial Stretching at Constant Volume ................... 329

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7.5. Biaxial Stretching at Constant Volume .......................... 331
7.6. Application to the Inflation of a Balloon .......................... 333
7.7. Network Defects -The Relationship between $N_C$ and ν . 334
7.8. Effect of Swelling on an Isotropic Network .......................... 336
7.9. Elastic Properties of Swollen Rubber .......................... 339
7.10. Elasticity of a Sample That is Swollen When Crosslinked. .......................... 341
7.11. Elasticity of Rubbers at Small Extensions .......................... 343
7.12. Guth-Smallwood Equations .......................... 347
References .......................... 348
Appendix 7A – Evaluation of Equation 7.30 .......................... 350
CHAPTER 8 .......................... 352
THE CRYSTALLINE STATE .......................... 352
8.1. Introduction .......................... 352
8.2. Evidence for Crystallinity .......................... 354
    8.2.1. X-Ray Diffraction .......................... 354
    8.2.2. Electron Microscopical Observations .......................... 358
    8.2.3. Optical Microscopy .......................... 359
    8.2.4. Thermodynamic Transitions .......................... 360
8.3. Determination of Degree of Crystalline .......................... 361
    8.3.1. Density Measurements .......................... 361
    8.3.2. X-Ray Diffraction .......................... 364
    8.3.3. Infrared (IR) and Raman .......................... 365
    8.3.4. Wide Line Nuclear Magnetic Resonance .......................... 366
    8.3.5. Thermal Measurements .......................... 368
8.4. Morphology .......................... 369
    8.4.1. Electron Microscope .......................... 369
        i) The observed pyramidal structure .......................... 369
        ii) Moiré Patterns .......................... 370
        i.) Density .......................... 370
        ii) nmr .......................... 371
        iii) X-ray diffraction .......................... 371
        iv) Kinetics .......................... 371
    8.4.2. Optical Microscopy .......................... 372
    8.4.3. Liquid Crystals .......................... 373
8.5 Mechanisms of Crystallization .......................... 375

    8.5.1. Nucleation and Growth ........................................ 375
8.6. Kinetics of Crystallization ............................................ 376
    8.6.1. Temperature Dependence of the Nucleation Rate . 376
    8.6.2. Nucleation and Growth ........................................ 379
    8.6.3. Experimental Determination of n and k ................ 384
        i. Slope-Intercept Method ........................................ 384
        ii. Half-life Method .................................................... 385
    8.6.4. Temperature Dependence of the Rate of Homogeneous Crystallization ........................................ 386
References ........................................................................ 387
Glossary of Symbols Arranged by Chapters ......................... 389
    Chapter 1 ....................................................................... 389
    Chapter 2 ....................................................................... 389
    Chapter 3 ....................................................................... 392
    Chapter 4 ....................................................................... 396
    Chapter 5 ....................................................................... 398
    Chapter 7 ....................................................................... 402
    Chapter 8 ....................................................................... 403
Index .................................................................................. 407

## Chapter 1

# INTRODUCTION

### 1.1. Background

The concept of long chain molecules in which the atoms forming the backbone are bonded by strong primary valence forces, usually covalent in nature, is the foundation of polymer science. Until relatively recently, chemistry, which is the study of molecules in all their ramifications, emphasized the study of small molecules. These could be readily purified to yield materials with constant composition and well characterized properties. Naturally occurring polymers, such as natural rubber or cellulose, did not fit into this framework of small well-characterized molecules [1]. Many investigators considered that the naturally occurring polymers constituted a fourth state of matter, essentially colloidal in nature, because these materials did not seem to obey the laws derived for gases, liquids, or solids as these laws were then understood. The assertion that, since rubber and cellulose were the products of living organisms, a vital principle, not amenable to physico-chemical laws, was involved reinforced this viewpoint.

Based on chemical evidence, Staudinger [2], in the early 1920s, was the first investigator to strongly advocate long, linear chain structures for polystyrene, polyoxymethylene, and natural rubber. During this time span, x-ray diffraction developed as a tool for determining the structure of molecules. The diffraction photographs of natural rubber and cellulose taken by Meyer and Mark were interpreted as showing that these polymers did have long chain structures [3]. Carothers furnished a key argument, based on purely chemical reasoning, in favor of the view that polymers, in the main, were composed of long linear chains. By the late

1920s, organic chemists had accumulated a large store of knowledge on the reaction conditions, products, yields and structures of many small monomeric molecules involved in organic chemical reactions. For example, the reaction between an amine and an organic acid was known to produce an amide with the elimination of a molecule of water:

$$R_1NH_2 + HOOCR_2 \rightarrow R_1NHCOR_2 + H_2O$$

($R_1$, $R_2$ being typically methyl, ethyl or other aliphatic radicals). Carothers reasoned that, if both molecules were difunctional (i.e., two amine groups on $R_1$ and two organic acid groups on $R_2$), sites would be available for further reactions:

$$H_2NR_1NH_2 + HOOCR_2COOH \rightarrow H_2NR_1NHCOR_2COOH + H_2O$$

The reaction would continue until the starting materials (difunctional amines and organic acids) were exhausted. Thus, a long chain polymer structure could be synthesized using a well known and well understood organic chemical reaction. In a classic series of investigations [4], Carothers and a small group of co-workers were able to demonstrate that this and similar chemical reactions produced long linear chain molecules. As a point of interest, Carothers produced nylon 66 by using $C_6H_{12}$ (hexamethylene) for $R_1$ and $C_4H_8$ for $R_2$. Carothers [4] coined the term condensation polymers for the long chain molecules produced by these reactions because the elimination of small molecules such as water condensed the length of the polymer repeat unit compared to that of the starting molecules. Conversely, Carothers called polymers such as polystyrene and polyoxymethylene addition polymers because the monomer units add through the opening of double bonds. Thus, these latter polymers added monomers during formation with no elimination of small molecules.

Many of these linear chain polymers have the advantage for characterization that they are soluble in organic solvents. This has aided greatly, as will be shown later, in the analysis of chain structures and reaction mechanisms and the determination of molecular weight. Most linear polymers, both condensation and addition, also reversibly soften and flow on heating and conversely harden and become rigid on cooling. These materials are sometimes called thermoplastics because they flow at sufficiently high temperatures. This thermal characteristic is used to advantage in reprocessing these polymers. The thermoplastics did not become commercially available, with a few exceptions such as cellulose acetate, polystyrene, poly(methyl methacrylate), until after World War II. A second class of polymeric materials (thermosets) had been introduced earlier (ca. 1910) starting with the phenol-formaldehyde polymers developed by Leo Baekeland [5]. Thermosets are composed of non-linear polymer chains (based on a functionality of 3 or more) that combine chemically to form three dimensional network polymers. They are soluble and fusible only up through the intermediate stages of polymerization. Once polymerization is complete, the thermosets form hard infusible insoluble structures that soften on heating over a temperature range. The average temperature for the range is called the glass temperature. On heating to higher temperatures, thermosets decompose because of their network structure. The lack of solubility and general intractability rendered thermosets difficult to study from a fundamental standpoint.

Elastomers or rubbers represent an intermediate stage in terms of functionality between thermoplastics and thermosets. Elastomeric behavior in polymers originates from a special type of chain structure. This point is discussed more fully in Chapter 7. Elastomers to be useful articles of commerce require a controlled number of crosslinks (chemical bonds between neighboring chains). Natural rubber (and its progeny, the synthetic rubbers, spawned during and after World War II) elongates readily to several times its original length on the application of a small force and readily retracts with release of the applied force. But, unless it is crosslinked, rubber will tend to flow on being held at high elongations and gradually lose its ability to retract. Goodyear [6] found in the 1830s that, upon adding sulfur to natural rubber latex and heating, the coagulated latex changed from a flowable gum to a retractive elastic material. He also observed that the hardness of natural rubber ranged from a soft crepe rubber (essentially thermoplastic) on small sulfur additions to hard infusible rubber (or thermoset) with large sulfur additions.

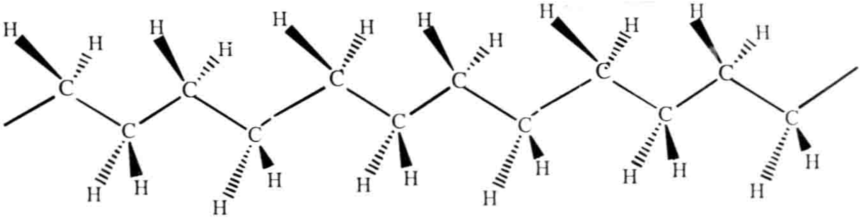

Figure 1.1a. Linear Polyethylene.

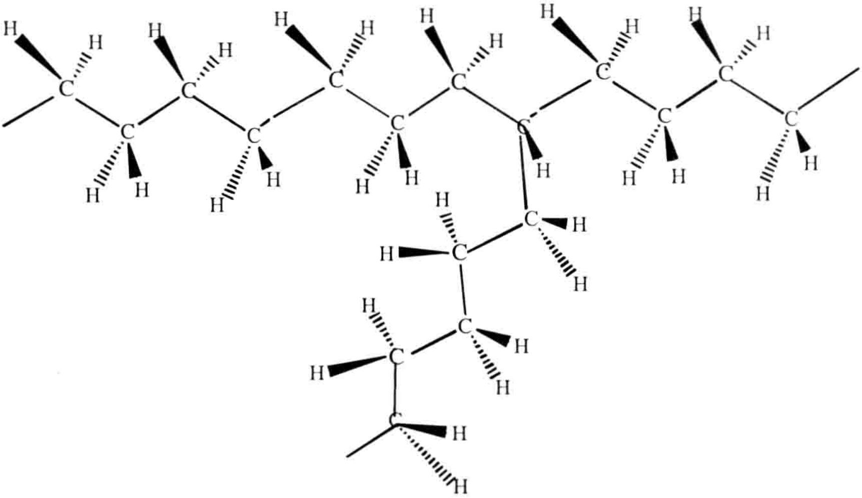

Figure 1.1b. Branched Polyethylene.

## 1.2. Linear Chain Molecules

### 1.2.1. Structure

Polyethylene, the prototype or model chain for linear addition polymers, is composed of ethylene monomer units linked by covalent bonds to form long chains (Figure 1.1a.) But, this linear chain was only produced in the mid 50's by the Ziegler–Natta catalysts. Before this, the Fawcett process that required high pressure and temperature produced a polyethylene chain that contained many small side chains or branches attached by covalent bonds to the main chain (Figure 1.1b). Nuclear

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