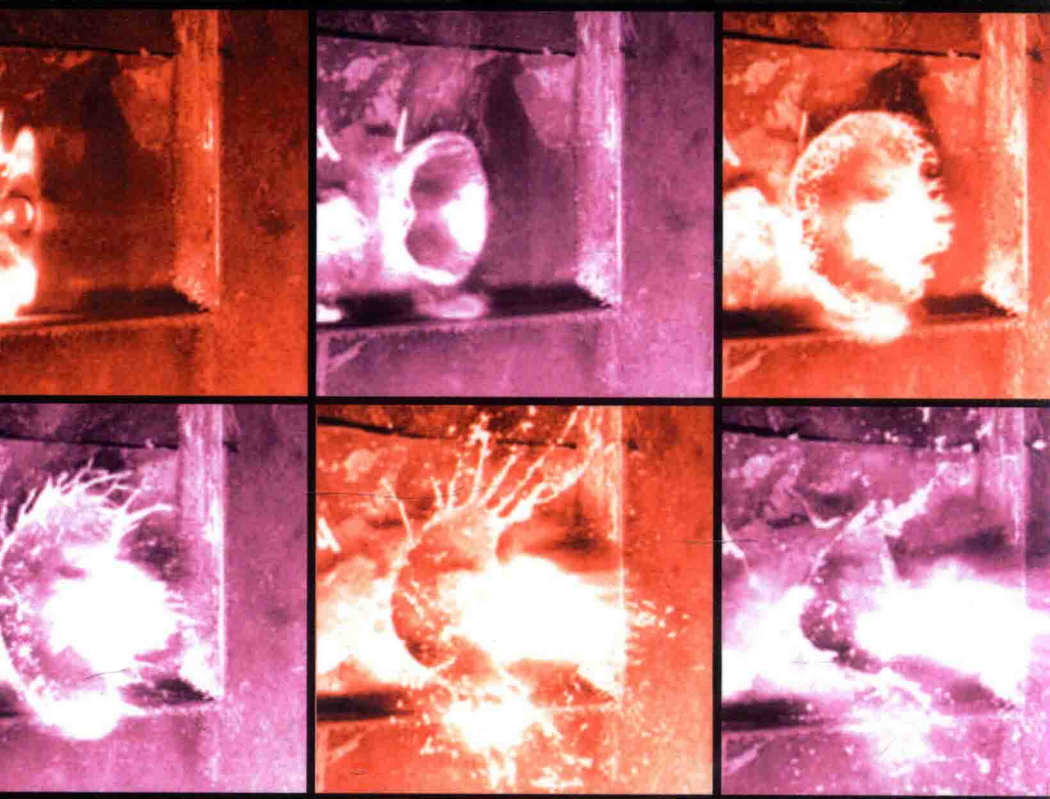
Fourth Edition

# The Science and Technology of Rubber



Edited by
James E. Mark, Burak Erman
and C. Michael Roland

# The Science and Technology of Rubber

## Fourth Edition

Edited by

**Burak Erman**
Department of Chemical and Biological Engineering
Koc University
Rumeli Feneri Yolu 34450 Istanbul, Turkey

**James E. Mark**
Department of Chemistry
University of Cincinnati
Cincinnati, OH 45221-0172, USA

**C. Michael Roland**
Naval Research Laboratory
Chemistry Division, Code 6120
Washington, DC, USA

常州大学
藏书章

ELSEVIER

AMSTERDAM • BOSTON • HEIDELBERG • LONDON
NEW YORK • OXFORD • PARIS • SAN DIEGO
SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Academic Press is an Imprint of Elsevier

Academic Press is an imprint of Elsevier
225 Wyman Street, Waltham, MA 02451, USA
The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK

© 2013 Elsevier Inc. All rights reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions.

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

**Notices**
Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

**Library of Congress Cataloging-in-Publication Data**
A catalog record for this book is available from the Library of Congress

**British Library Cataloguing-in-Publication Data**
A catalogue record for this book is available from the British Library.

ISBN: 978-0-12-394584-6

For information on all Academic Press publications
visit our website at http://store.elsevier.com

Printed in the United States of America
13 14 15 9 8 7 6 5 4 3 2 1

# The Science and Technology of Rubber

Fourth Edition

# CONTENTS


**1. Rubber Elasticity: Basic Concepts and Behavior** 1

1.1 Introduction 1
1.2 Elasticity of a Single Molecule 1
1.3 Elasticity of a Three-Dimensional Network of Polymer Molecules 5
1.4 Comparison with Experiment 9
1.5 Continuum Theory of Rubber Elasticity 11
1.5.1 Stress-Strain Relations 12
1.6 Second-Order Stresses 19
1.7 Elastic Behavior Under Small Deformations 21
1.8 Some Unsolved Problems in Rubber Elasticity 24
Acknowledgments 25
References 25

**2. Polymerization: Elastomer Synthesis** 27

2.1 Introduction 27
2.2 Classification of Polymerization Reactions and Kinetic Considerations 28
2.2.1 Polyaddition/Polycondensation 29
2.2.2 Chain Polymerization 31
2.3 Polyaddition/Polycondensation 32
2.4 Chain Polymerization by Free Radical Mechanism 34
2.4.1 General Kinetics 34
2.4.2 Molecular Weight Distribution 38
2.4.3 Special Case of Diene Polymerization 39
2.4.4 Controlled Radical Polymerization 40
2.5 Emulsion Polymerization 43
2.5.1 Mechanism and Kinetics 43
2.5.2 Styrene-Butadiene Rubber 47
2.5.3 Emulsion Polymerization of Chloroprene 51
2.6 Copolymerization 54
2.6.1 Kinetics 54
2.6.2 Emulsion Copolymerization of Dienes 57
2.7 Chain Polymerization by Cationic Mechanism 60
2.7.1 Mechanism and Kinetics 60
2.7.2 Butyl Rubber 64
2.7.3 Living Cationic Polymerizations 65
2.7.4 Other Cationic Polymerizations: Heterocyclic Monomers 66
2.8 Chain Polymerization by Anionic Mechanism 68
2.8.1 Mechanism and Kinetics 68
2.8.2 Chain Microstructure of Polydienes 75




此为试读,需要完整PDF请访问: www.ertongbook.com

2.8.3 Copolymers of Butadiene 77
2.8.4 Terminally Functional Polydienes 78
2.9 Stereospecific Chain Polymerization and Copolymerization by Coordination Catalysts 79
2.9.1 Mechanism and Kinetics 79
2.9.2 Ethylene-Propylene Rubbers 83
2.9.3 Polydienes 85
2.9.4 Polyalkenamers 86
2.10 Graft and Block Copolymerization 89
2.10.1 Graft Copolymerization by Conventional Free Radical Reactions 89
2.10.2 Block Copolymers by Controlled Radical Mechanisms 92
2.10.3 Block Copolymers by Anionic Mechanism 93
2.10.4 Block Copolymers by Cationic Mechanism 97
2.10.5 Block Copolymers by Ziegler-Natta (Insertion) Mechanism 98
References 100

**3. Structure Characterization in the Science and Technology of Elastomers 115**

3.1 Introduction 115
3.2 Chemical Composition 116
3.3 Sequence Distribution of Repeat Units 119
3.4 Chain Architecture 122
3.4.1 Molecular Weight and Its Distribution 122
3.4.2 Branching 135
3.4.3 Gel 138
3.5 Glass Transition and Secondary Relaxation Processes 140
3.6 Morphology 145
3.6.1 Orientation 145
3.6.2 Blends 148
3.6.3 Crystallinity 154
3.6.4 Defects 157
Acknowledgments 159
References 159

**4. The Molecular Basis of Rubberlike Elasticity 167**

4.1 Introduction 167
4.2 Structure of a Typical Network 168
4.3 Elementary Molecular Theories 169
4.3.1 Elasticity of the Single Chain 170
4.3.2 The Elastic Free Energy of the Network 173
4.3.3 The Reduced Stress and the Elastic Modulus 174
4.4 More Advanced Molecular Theories 177
4.4.1 The Constrained Junction Model 177
4.4.2 Entanglement Models 179
4.4.3 Contribution of Trapped Entanglements to the Modulus 181

4.5 Phenomenological Theories and Molecular Structure 182
4.6 Swelling of Networks and Responsive Gels 183
4.7 Enthalpic and Entropic Contributions to Rubber Elasticity: The Force-Temperature Relations 185
4.8 Direct Determination of Molecular Dimensions 187
4.9 Single-Molecule Elasticity 188
4.9.1 Gaussian Versus Non-Gaussian Effects 188
References 190

**5. The Viscoelastic Behavior of Rubber and Dynamics of Blends 193**

5.1 Introduction 193
5.2 Definitions of Measured Quantities, $J(T)$, $G(T)$, and $G^*(\omega)$; and Spectra $L(\log \lambda)$ and $H(\log \tau)$ 198
5.2.1 Creep and Recovery 198
5.2.2 Stress Relaxation 199
5.2.3 Dynamic Mechanical Measurements 199
5.3 The Glass Temperature 202
5.4 Viscoelastic Behavior Above $T_g$ 203
5.4.1 Isothermal Measurements of Time or Frequency Dependence 203
5.4.2 Temperature Dependence 204
5.4.3 The Equilibrium Compliance $J_e$ 207
5.5 Viscoelastic Behavior of Other Model Elastomers 207
5.5.1 Fluorinated Hydrocarbon Elastomers ("Viton") 207
5.5.2 Urethane-Crosslinked Polybutadiene Elastomers (Plazek et al., 1988) 213
5.5.3 Comparisons Between Different Elastomers 215
5.5.4 Other Viscoelastic Measurements 216
5.6 Theoretical Interpretation of Viscoelastic Mechanisms and Anomalies 217
5.6.1 Breakdown of Thermorheological Simplicity of Low Molecular Weight Polymer 217
5.6.2 Thermorheological Simplicity of Elastomers 224
5.6.3 Changes of the Segmental Relaxation Time and the Johari-Goldstein Relaxation Time with Crosslink Density 225
5.6.4 Junction Dynamics 225
5.7 Component Dynamics of Highly Asymmetric Polymer Blends 229
5.7.1 Intermolecularly Coupled Segmental Relaxation and Interchain Coupled Chain Dynamics in Highly Asymmetric Polymer Blends 229
5.7.2 Anomalous Component Dynamics of Polymer Blends 233
5.7.3 Explanation of Properties (i)–(ix) 260
5.7.4 Summary 279
References 279

**6. Rheological Behavior and Processing of Unvulcanized Rubber** 285

6.1 Rheology 285
6.1.1 Introduction 285
6.1.2 Basic Concepts 286
6.2 Linear Viscoelasticity 289
6.2.1 Material Constants 289
6.2.2 Boltzmann Superposition Principle 294
6.2.3 Time-Temperature Equivalence 297
6.2.4 Molecular Weight Dependences 303
6.2.5 Stress Birefringence 307
6.3 Nonlinear Viscoelasticity 310
6.3.1 Shear Thinning Flow 310
6.3.2 Particulate Fillers 311
6.3.3 Blends 317
6.4 Engineering Analysis 319
6.4.1 Dimensionless Quantities 319
6.4.2 Empirical Rules 322
6.5 Practical Processing Considerations 325
6.5.1 Mixing 325
6.5.2 Die Swell 327
6.5.3 Tack 329
Acknowledgment 330
References 330

**7. Vulcanization** 337

7.1 Introduction 337
7.2 Definition of Vulcanization 338
7.3 Effects of Vulcanization on Vulcanizate Properties 339
7.4 Characterization of the Vulcanization Process 340
7.5 Vulcanization by Sulfur without Accelerator 343
7.6 Accelerated-Sulfur Vulcanization 345
7.6.1 The Chemistry of Accelerated-Sulfur Vulcanization 351
7.6.2 Delayed-Action Accelerated Vulcanization 353
7.6.3 The Role of Zinc in Benzothiazole-Accelerated Vulcanization 355
7.6.4 Achieving Specified Vulcanization Characteristics 356
7.6.5 Effects on Adhesion to Brass-Plated Steel 357
7.6.6 The Effect on Vulcanizate Properties 358
7.6.7 Accelerated-Sulfur Vulcanization of Various Unsaturated Rubbers 363
7.6.8 Selected Accelerated-Sulfur System Recipes 364
7.7 Vulcanization by Phenolic Curatives, Benzoquinone Derivatives, or Bismaleimides 364
7.8 Vulcanization by the Action of Metal Oxides 368
7.9 Vulcanization by the Action of Organic Peroxides 370

7.9.1 Peroxide Vulcanization of Unsaturated Hydrocarbon Elastomers 371
7.9.2 Peroxide Vulcanization of Saturated Hydrocarbon Elastomers 373
7.9.3 Peroxide Vulcanization of Silicone Rubbers 374
7.9.4 Peroxide Vulcanization of Urethane Elastomers 375
7.9.5 Recipes for Peroxide Vulcanization 376
7.10 Dynamic Vulcanization 376
7.10.1 EPDM-Polyolefin Compositions 377
7.10.2 NBR-Nylon Compositions 377
7.10.3 Other Elastomeric Compositions Prepared by Dynamic Vulcanization 378
7.10.4 Technological Applications 378
7.10.5 Extra-High-Performance TPVs 379
References 379

**8. Reinforcement of Elastomers by Particulate Fillers 383**

8.1 Introduction 383
8.2 Preparation of Fillers 384
8.2.1 Nonreinforcing Fillers 384
8.2.2 Reinforcing Fillers 384
8.3 Morphological and Physicochemical Characterization of Fillers 386
8.3.1 Filler Morphology Characterization 386
8.3.2 Dispersibility 392
8.3.3 Filler Physicochemistry 393
8.4 The Mix: A Nanocomposite of Elastomer and Filler 397
8.4.1 Dispersion, Aggregate Sizes, and Distances 397
8.4.2 Filler-Elastomer Interactions 400
8.5 Mechanical Properties of Filled Rubbers 402
8.5.1 Mechanical Properties in Green State 402
8.5.2 Mechanical Properties in Vulcanized State 404
8.5.3 Applications 411
References 413

**9. The Science of Rubber Compounding 417**

9.1 Introduction 417
9.2 Polymers 418
9.2.1 Natural Rubber 418
9.2.2 Synthetic Elastomers 420
9.3 Filler Systems 431
9.3.1 Carbon Black Properties 431
9.3.2 Silica and Silicates 438
9.3.3 Chemistry of Silane Coupling Agents 440
9.3.4 Other Filler Systems 443
9.4 Stabilizer Systems 444
9.4.1 Degradation of Rubber 444

9.4.2 Antidegradant Use 446
9.4.3 Antidegradant Types 447
9.5 Vulcanization System 449
9.5.1 Activators 450
9.5.2 Vulcanizing Agents 454
9.5.3 Accelerators 454
9.5.4 Retarders and Antireversion Agents 455
9.6 Special Compounding Ingredients 457
9.6.1 Processing Oils 457
9.6.2 Plasticizers 459
9.6.3 Chemical Peptizers 460
9.6.4 Resins 461
9.6.5 Short Fibers 461
9.7 Compound Development 462
9.8 Compound Preparation 463
9.9 Environmental Requirements in Compounding 465
9.10 Summary 469
References 470

**10. Strength of Elastomers 473**

10.1 Introduction 473
10.2 Initiation of Fracture 474
10.2.1 Flaws and Stress Raisers 474
10.2.2 Stress and Energy Criteria for Rupture 476
10.2.3 Tensile Test Piece 478
10.2.4 Tear Test Piece 480
10.3 Threshold Strengths and Extensibilities 481
10.4 Crack Propagation 485
10.4.1 Overview 485
10.4.2 Viscoelastic Elastomers 485
10.4.3 Strain-Crystallizing Elastomers 488
10.4.4 Reinforcement with Fillers 489
10.4.5 Repeated Stressing: Dynamic Crack Propagation 491
10.4.6 Thermoplastic Elastomers 494
10.5 Tensile Rupture 494
10.5.1 Effects of Rate and Temperature 494
10.5.2 The Failure Envelope 496
10.5.3 Effect of Degree of Crosslinking 497
10.5.4 Strain-Crystallizing Elastomers 499
10.5.5 Energy Dissipation and Strength 500
10.6 Repeated Stressing: Mechanical Fatigue 501
10.7 Failure Under Multiaxial Stresses 504
10.7.1 Critical Plane Hypothesis 504
10.7.2 Energy Density Available for Driving Growth of Crack Precursors 505
10.7.3 Compression and Shear 506
10.7.4 Equibiaxial Tension 506

10.7.5 Triaxial Tension 507
10.8 surface Cracking by Ozone 508
10.9 Abrasive Wear 509
10.9.1 Mechanics of Wear 509
10.9.2 Chemical Effects 512
10.10 Computational Approaches to Failure Modeling 512
Acknowledgments 513
References 513

**11. The Chemical Modification of Polymers 517**

11.1 Introduction 517
11.2 Chemical Modification of Polymers within Backbone and Chain Ends 518
11.3 Esterification, Etherification, and Hydrolysis of Polymers 520
11.4 The Hydrogenation of Polymers 523
11.5 Dehalogenation, Elimination, and Halogenation Reactions in Polymers 524
11.5.1 Dehydrochlorination of Poly(vinyl chloride) 524
11.5.2 Thermal Elimination 525
11.5.3 Halogenation of Polymers 526
11.5.4 Cyclization of Polymers 527
11.6 Other Addition Reactions to Double Bonds 528
11.6.1 Ethylene Derivatives 528
11.6.2 The Prins Reaction 530
11.7 Oxidation Reactions of Polymers 530
11.8 Functionalization of Polymers 531
11.9 Miscellaneous Chemical Reactions of Polymers 531
11.10 Block and Graft Copolymerization 532
11.10.1 Effects on Structure and Properties of Polymers 532
11.10.2 Block Copolymer Synthesis 534
11.10.3 Examples 534
11.10.4 Other Methods of Effecting Mechanicochemical Reactions 535
11.10.5 Ionic Mechanisms 536
11.10.6 Graft Copolymer Synthesis 537
11.10.7 Base Polymer Properties 544
References 545

**12. Elastomer Blends 547**

12.1 Introduction 547
12.2 Thermodynamics and Solubility Parameters 552
12.2.1 Flory-Huggins Model 553
12.2.2 Solubility and Interaction Parameters 554
12.2.3 Other Models 556
12.3 Preparation 558
12.4 Miscible Elastomer Blends 559

此为试读,需要完整PDF请访问: www.ertongbook.com

12.4.1 Thermodynamics 559
12.4.2 Analysis 559
12.4.3 Compositional Gradient Copolymers 562
12.4.4 Distinct Polymers 565
12.4.5 Reactive Elastomers 566
12.5 Immiscible Elastomer Blends 567
12.5.1 Formation 567
12.5.2 Kinetics of Blend Morphology 567
12.5.3 Analysis 567
12.5.4 Interphase Distribution of Filler, Curatives, and Plasticizers 571
12.5.5 Analysis of Interphase Transfer 576
12.5.6 Compatibilization 577
12.5.7 Properties of Immiscible Blends 579
12.5.8 Applications 582
12.6 Conclusion 583
References 585

**13. Thermoplastic Elastomers 591**

13.1 Introduction 591
13.2 Synthesis of Thermoplastic Elastomers 597
13.2.1 Step-Growth Polymerization: Polyurethanes, Polyether-esters, Polyamides 597
13.2.2 Anionic Polymerization: Styrene-Diene Copolymers 599
13.2.3 Catalytic Polymerization 600
13.2.4 Free Radical Polymerization 600
13.2.5 Molecular Weight and Chain Structure 601
13.3 Morphology of Thermoplastic Elastomers 604
13.3.1 General Characteristics 604
13.3.2 Studies of Morphology 607
13.4 Properties and Effect of Structure 620
13.4.1 General Characteristics 620
13.4.2 Mechanical Properties 623
13.4.3 Thermal and Chemical Properties 627
13.5 Thermodynamics of Phase Separation 628
13.6 Thermoplastic Elastomers at Surfaces 633
13.6.1 General Characteristics 633
13.6.2 Studies of Surfaces 635
13.7 Rheology and Processing 641
13.8 Applications 644
References 647

**14. Tire Engineering 653**

14.1 Introduction 653
14.2 Tire Types and Performance 653
14.3 Basic Tire Design 656

14.3.1 Tire Construction 656
14.3.2 Tire Components 656
14.4 Tire Engineering 658
14.4.1 Tire Nomenclature and Dimensions 658
14.4.2 Tire Mold Design 661
14.4.3 Cord Tension 666
14.4.4 Tread Design Patterns 667
14.5 Tire Materials 671
14.5.1 Tire Reinforcement 671
14.5.2 Steel Cord 672
14.5.3 Mechanism of Rubber: Brass Wire Adhesion 674
14.5.4 Rayon 677
14.5.5 Nylon 677
14.5.6 Polyester 678
14.5.7 Fiberglass 679
14.5.8 Aramid 679
14.5.9 Tire Cord Construction 680
14.5.10 Fabric Processing 681
14.5.11 Function of Adhesive 683
14.5.12 Rubber Compounding 684
14.6 Tire Testing 685
14.6.1 Laboratory Testing 685
14.6.2 Proving Grounds 688
14.6.3 Commercial Evaluation 688
14.7 Tire manufacturing 688
14.7.1 Compound Processing 689
14.7.2 Calendering 691
14.7.3 Extrusion 691
14.7.4 Tire Building 692
14.7.5 Final Tire Inspection 693
14.8 Summary 694
References 694

**15. Recycling of Rubbers 697**

15.1 Introduction 697
15.2 Retreading of Tires 700
15.3 Recycling of Rubber Vulcanizates 700
15.3.1 Reclaiming Technology 700
15.3.2 Surface Treatment 703
15.3.3 Grinding and Pulverization Technology 704
15.3.4 Devulcanization Technology 708
15.4 Use of Recycled Rubber 722
15.4.1 General Remarks 722
15.4.2 Use in New Tires 723
15.4.3 Rubber-Recycled Rubber Blends 723
15.4.4 Thermoplastic-Recycled Rubber Blend 730
15.4.5 Concrete Modified by Recycled Rubber 742

15.4.6 Asphalt Modified by Recycled Rubber 745
15.4.7 Use of Crumb Rubber in Soil 750
15.4.8 Products Made from Recycled Rubber 751
15.5 Pyrolysis and Incineration of Rubber 753
15.5.1 Recovery of Hydrocarbon Liquid and Carbon Black 753
15.5.2 Tire-Derived Fuel 755
15.6 Concluding Remarks 755
Acknowledgment 756
References 756

**Index** **765**

Chapter 1

# Rubber Elasticity: Basic Concepts and Behavior

**A.N. Gent**
*The University of Akron, Akron, OH, USA*

## 1.1 INTRODUCTION

The single most important property of elastomers—that from which their name derives—is their ability to undergo large elastic deformations; that is, to stretch and return to their original shape in a reversible way. Theories to account for this characteristic high elasticity have passed through three distinct phases: (1) the early development of a molecular model relating experimental observations to the known molecular features of rubbery polymers; (2) generalization of this approach by means of symmetry considerations taken from continuum mechanics that are independent of the molecular structure; and (3) a critical reassessment of the basic premises on which these two quantitative theories are founded. In this chapter, the theoretical treatment is briefly outlined and shown to account quite successfully for the observed elastic behavior of rubbery materials. The special case of small elastic deformations is then discussed in some detail because of its technical importance. Finally, attention is drawn to some aspects of rubber elasticity that are still little understood.

## 1.2 ELASTICITY OF A SINGLE MOLECULE

The essential requirement for a substance to be rubbery is that it consist of long flexible chainlike molecules. The molecules themselves must therefore have a "backbone" of many noncollinear single valence bonds, about which rapid rotation is possible as a result of thermal agitation. Some representative molecular subunits of rubbery polymers are shown in Figure 1.1; thousands of these units linked together into a chain constitute a typical molecule of the elastomers listed in Figure 1.1. Such molecules change their shape readily and continuously at normal temperatures by Brownian motion. They take up random conformations in a stress-free state but assume somewhat oriented

**The Science and Technology of Rubber. http://dx.doi.org/10.1016/B978-0-12-394584-6.00001-7**
© 2013 Elsevier Inc. All rights reserved.

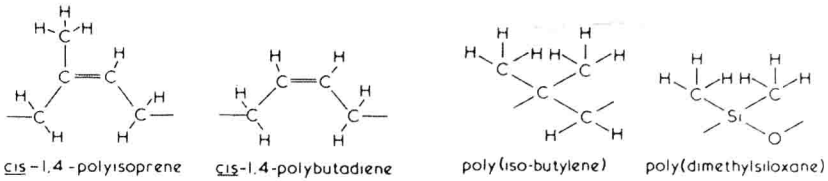



**FIGURE 1.1** Repeat units for some common elastomer molecules.

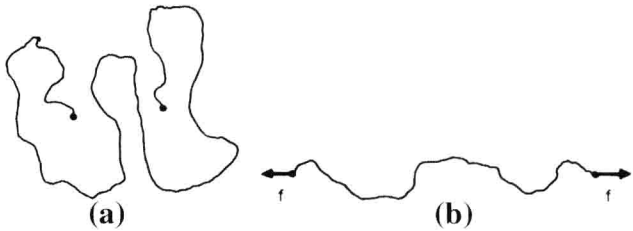



**FIGURE 1.2** (a) Random chain and (b) oriented chain (from Gent, 1958).

conformations if tensile forces are applied at their ends (Figure 1.2). One of the first questions to consider, then, is the relationship between the applied tension $f$ and the mean chain end separation $r$, averaged over time or over a large number of chains at one instant in time.

Chains in isolation take up a wide variety of conformations,[1] governed by three factors: the statistics of random processes; a preference for certain sequences of bond arrangements because of steric and energetic restraints within the molecule; and the exclusion of some hypothetical conformations that would require parts of the chain to occupy the same volume in space. In addition, cooperative conformations are preferred for space-filling reasons in concentrated solutions or in the bulk state.

Flory (1969) has argued that the occupied-volume exclusion (repulsion) for an isolated chain is exactly balanced in the bulk state by the external (repulsive) environment of similar chains, and that the exclusion factor can therefore be ignored in the solid state. Direct observation of single-chain dimensions in the bulk state by inelastic neutron scattering gives values fully consistent with unperturbed chain dimensions obtained for dilute solutions in theta solvents[2] (Cotton et al., 1972), although intramolecular effects may distort the local randomness of chain conformation.

---

[1] Although the terms *configuration* and *conformation* are sometimes used interchangeably, the former has acquired a special meaning in organic stereochemistry and designates specific steric structures. *Conformation* is used here to denote a configuration of the molecule, which is arrived at by rotation of single-valence bonds in the polymer backbone.

[2] These are (poor) solvents in which repulsion between different segments of the polymer molecule is balanced by repulsion between polymer segments and solvent molecules.

Flory has again given compelling reasons for concluding that the chain end-to-end distance $r$ in the bulk state will be distributed in accordance with Gaussian statistics for sufficiently long chains, even if the chains are relatively stiff and inflexible over short lengths (Flory, 1969). With this restriction to long chains it follows that the tension-displacement relation becomes a simple linear one,

$$f = Ar, \tag{1.1}$$

where $f$ is the tensile force, $r$ is the average distance between the ends of the chain, and $A$ is inversely related to the mean square end-to-end distance $r_0^2$ for unstressed chains,

$$A = 3kT/r_0^2, \tag{1.2}$$

where $k$ is Boltzmann's constant and $T$ is the absolute temperature.

If the real molecule is replaced by a hypothetical chain consisting of a large number $n$ of rigid, freely jointed links, each of length $l$ (Figure 1.3), then

$$r_0^2 = nl^2. \tag{1.3}$$

In this case $r_0^2$ is independent of temperature because completely random link arrangements are assumed. The tension $f$ in Eq. (1.1) then arises solely from an entropic mechanism; that is, from the tendency of the chain to adopt conformations of maximum randomness, and not from any energetic preference for one conformation over another. The tension $f$ is then directly proportional to the absolute temperature $T$.

For real chains, consisting of a large number $n$ of primary valence bonds along the chain backbone, each of length $l$,

$$r_0^2 = C_\infty nl^2, \tag{1.4}$$

where the coefficient $C_\infty$ represents the degree to which this real molecule departs from the freely jointed model. $C_\infty$ is found to vary from 4 to 10, depending on the chemical structure of the molecule and on temperature, because the

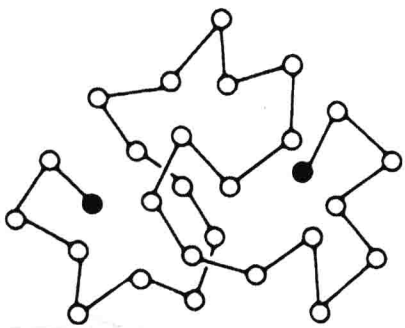


**FIGURE 1.3** Model chain of freely jointed links.

此为试读,需要完整PDF请访问: www.ertongbook.com