Contents

Preface *xi*
Acknowledgements *xiii*

Part I Theories *1*

1 Single Polymer Chain *3*
Takamasa Sakai
1.1 General Features *3*
1.1.1 Conformation of a Polymer Chain *3*
1.1.2 Coarse-Graining of a Polymer Chain *4*
1.1.3 Free Rotation Model *5*
1.2 Statistics of a Single Polymer Chain *7*
1.2.1 End-to-End Distance of a 1D Random Walk *7*
1.2.2 End-to-End Distance of a 3D Random Walk *10*
1.2.3 Force Needed to Stretch an Ideal Chain *12*
1.3 Scaling of a Single Polymer Chain *15*
1.3.1 Stretching of an Ideal Chain *17*
1.3.2 Real Chains *18*
1.3.3 Stretching of a Real Chain *19*
Column 1: Miscible Gels and Immiscible Gels *21*
References *22*

2 Polymer Solution *23*
Takamasa Sakai
2.1 Polymer Chains in Solution *23*
2.1.1 Chain Swelling in a Good Solvent *23*
2.1.2 Existing Conditions of an Ideal Chain and a Real Chain *25*
2.2 Effect of Concentration on the Polymer Conformation *26*
2.2.1 Overlapping Concentration *26*
2.2.2 Semidilute Solution *28*
2.2.3 Blobs in Semidilute Solution *29*
2.3 Osmotic Pressure of a Polymer Solution *32*
2.3.1 Entropy Change in Mixing *33*

2.3.2 Enthalpy Change in Mixing *35*
2.3.3 Basic Equation of Osmotic Pressure *36*
2.3.4 Phase Separation of the Polymer Solution *37*
2.3.5 Scaling of Osmotic Pressure *40*
Column 2: Blob Size of a Polymer Gel *42*
References *43*

3 Definition of Polymer Gels and Rubber Elasticity *45*
Takamasa Sakai
3.1 Elasticity of Gels *45*
3.2 Definition of Polymer Gels *46*
3.2.1 Criterion for Gelation by Rheology *47*
3.2.2 Criterion for Gelation by Scattering *48*
3.3 Mesh Size of a Polymer Gel *49*
3.4 Elastic Modulus *51*
3.4.1 Affine Network Model *51*
3.4.2 Phantom Network Model *54*
3.5 Network Strands and Crosslinks *60*
3.5.1 Percolate Network Model *62*
3.5.2 Bethe Approximation *63*
3.6 Topological Interaction *67*
3.7 Sol–Gel Transition *69*
3.7.1 Gelation Threshold of Bethe Approximation *69*
3.7.2 Gelation Threshold from the Percolation Model *70*
3.8 Heterogeneity of Polymer Gels *71*
Column 3: Elastic Deformation and Plastic Deformation *73*
References *74*

4 Swelling and Deswelling *77*
Takamasa Sakai
4.1 Changes in the Elastic Modulus Due to Swelling/Deswelling *77*
4.1.1 Statistical Model for Networks Consisting of Ideal Chains *78*
4.1.2 Scaling for Networks Consisting of Nonideal Chains *79*
4.1.3 Scaling for Highly Deswollen Networks *82*
4.2 Equilibrium Swelling *85*
4.2.1 Scaling Prediction of the Equilibrium Swelling *86*
4.2.2 Statistical Mechanics of Equilibrium Swelling *87*
4.3 Volume Phase Transition *91*
4.3.1 Electrically Neutral Gels *91*
4.3.2 Electrically Charged Gels *94*
4.4 Swelling/Shrinking Kinetics *95*
4.5 Degradation of Polymer Gels *102*
4.5.1 Degradation by Cleavage of Specific Bonds *102*

4.5.2 Degradation by Cleavage of Nonspecific Bonds *104*
Column 4: Diffusions of Polymer Network During Swelling *105*
References *106*

5 Deformation and Fracture *109*
Takuya Katashima and Takamasa Sakai
5.1 Description of Deformation *109*
5.1.1 Displacement Vector *109*
5.1.2 Strain Tensor *110*
5.1.2.1 Normal Strain *110*
5.1.2.2 Shear Strain *111*
5.1.3 Principal Direction and Strain *113*
5.2 Phenomenological Description of the Strain Energy Density Function *115*
5.2.1 Estimation of the Strain Energy Density Function *116*
5.3 Molecular Models for the Strain Energy Density Function *120*
5.3.1 Neo-Hookean Model *120*
5.3.2 Inverse Langevin Model *121*
5.4 Scaling for Large Deformation *125*
5.5 Fracture Behavior of Polymer Gels *126*
5.5.1 Griffith Model *127*
5.5.2 Lake–Thomas Model *128*
5.6 Mesh Size Estimated from Elastic Modulus and Finite Extensibility *130*
Column 5: Linear Viscoelasticity and Nonlinear Viscoelasticity *134*
References *134*

6 Mass Transport in Polymer Gels *137*
Xiang Li and Takamasa Sakai
6.1 Thermal Motion and Brownian Motion *137*
6.1.1 Diffusion Coefficient and Relaxation Time *138*
6.1.2 Diffusion and Migration *139*
6.2 Diffusion in Dilute Polymer Solutions *139*
6.2.1 Diffusion of a Hard Sphere *139*
6.2.2 Rouse Model *140*
6.2.3 Zimm Model *141*
6.3 Diffusion in Semidilute Polymer Solutions and Polymer Gels *142*
6.3.1 Obstruction Model *142*
6.3.2 Hydrodynamic Model *144*
6.3.3 Free Volume Model *145*
6.3.4 Reptation Model *146*
6.3.5 Entropic Trapping Model *147*
Column 6: Effects of Mesh Sizes on Mass Transport *149*
References *149*

Part II Experiments *151*

7 Tetra Gel as a Near-Ideal Polymer Network *153*
Takamasa Sakai
7.1 Ideal Polymer Network *153*
7.2 Tetra-PEG Gel *155*
7.3 Structure Tuning of Tetra-PEG Gels *155*
References *158*

8 Sol-Gel Transition *161*
Takamasa Sakai
8.1 Determination of Sol–Gel Transition by Rheometry *161*
8.2 Phase Diagram *161*
8.3 Fractal Dimension at the Critical Point *163*
8.4 Critical Behavior of Elastic Modulus *165*
8.5 Reaction Kinetics of a Gelling System *166*
8.5.1 Hydrolysis Kinetics of Tetra-PEG–OSu *167*
8.5.2 Gelation Kinetics of Tetra-PEG Gel *167*
References *169*

9 Structural Analysis by Light and Neutron Scattering *173*
Takamasa Sakai and Xiang Li
9.1 Scattering Curves of Tetra-PEG Gels *173*
9.2 Scattering Curves of Stretched Tetra-PEG Gels *176*
References *177*

10 Elastic Modulus *179*
Takamasa Sakai and Yuki Yoshikawa
10.1 Effect of Connectivity *179*
10.2 Effect of the Polymer Concentration and Network Strand Length *180*
References *182*

11 Large Deformation *183*
Takamasa Sakai and Takuya Katashima
11.1 Estimation of Strain Energy Density Function *183*
11.1.1 Applicability of Neo-Hookean Model *184*
11.1.2 Finite Extensibility Effect *185*
11.1.3 Coupling Between Different Principal Axes *186*
11.1.4 Extended Gent Model *187*
11.2 Cross-Coupling *189*
11.2.1 Effects of the Fraction of Elastically Effective and Ineffective Chains *190*
11.2.2 Effects of Polymer Volume Fraction and Network Strand Length *191*
11.2.3 Effect of the Fraction of Guest Chains *193*
11.2.4 Conjecture on Origin of Cross-Coupling *196*
11.3 Stretchability in Uniaxial Stretching *196*
11.3.1 Kuhn Model *197*

11.3.2 Effect of Connectivity *197*
11.3.3 Effect of Polymer Concentration and Network Strand Length *198*
11.3.4 Semiempirical Model Based on Experiments *200*
References *201*

12 Fracture *205*
Takamasa Sakai and Takeshi Fujiyabu
12.1 Estimation of Fracture Energy *205*
12.2 Conversion-Tuned Tetra-PEG Gels *207*
12.3 Effects of Network Concentration and Strand Length *208*
12.4 Bimodal Tetra-PEG Gels *209*
12.5 Summary *210*
References *211*

13 Mass Transport *213*
Takamasa Sakai and Takeshi Fujiyabu
13.1 Diffusion of Water Molecules *213*
13.1.1 Estimation of Diffusion Coefficient of Water Molecules *213*
13.1.2 Effect of Structural Parameters *214*
13.1.3 Applicability of Theoretical Models *215*
13.1.4 Effect of Correlation Length on Diffusion *216*
13.2 Migration of Water Molecules in Hydrogels *217*
13.2.1 Water Permeation Through Hydrogel *217*
13.2.2 Effect of Structural Parameters on Friction Coefficient *219*
13.2.3 Effect of Correlation Length on Friction Coefficient *220*
13.3 Electro-Osmotic Flow in Electrically Charged Gels *221*
13.3.1 Electro-Osmosis in an Electrically Balanced System *221*
13.3.2 Electro-Osmosis in an Electrically Imbalanced System *222*
13.3.3 Sum Rule of Electro-Osmotic Flow and Electrophoretic Motion *224*
13.4 Migration of Small Double-Stranded DNAs *225*
13.4.1 Electrophoresis of dsDNA in Tetra-PEG Gels and Solutions *225*
13.4.2 Semiempirical Model *226*
13.4.3 Effect of Correlation Length on Electrophoretic Mobility *228*
13.4.4 Interaction Between Elastic Blobs and Contour of dsDNA *229*
13.5 Migration of Large Double-Stranded DNAs *229*
13.5.1 Electrophoresis of Large dsDNA in Tetra-PEG Gels and Solutions *230*
13.5.2 Transition of the Migration Mechanism *231*
References *233*

14 Osmotic Pressure *235*
Takamasa Sakai
14.1 Osmotic Pressure of Gels and Prepolymer Solutions *235*
14.2 Change in Osmotic Pressure During Gelation *235*
14.3 c^* Theorem at the Gelation Threshold *237*
References *239*

15 Swelling *241*
Takamasa Sakai and Takeshi Fujiyabu
15.1 Elastic Modulus of Swollen and Highly Deswollen Gels *241*
15.2 Equilibrium Swelling *243*
15.3 Swelling Kinetics *244*
15.3.1 Examination of Swelling Equation *244*
15.3.2 Cooperative Diffusion Coefficient *245*
References *246*

16 Degradation *249*
Takamasa Sakai and Takeshi Fujiyabu
16.1 Cleavage of a Specific Site *249*
16.2 Cleavage of Nonspecific Sites *253*
16.2.1 Initial Swelling Equilibrium *254*
16.2.2 Degradation Behavior of Tetra-PEG Gels *254*
16.2.3 A Model for Degradation *255*
16.2.4 Estimation of Degradation Rate Constants *257*
References *258*

17 Control Over Swelling of Injectable Gel *261*
Takamasa Sakai and Takeshi Fujiyabu
17.1 Nonswellable Gels *261*
17.2 Nonosmotic Gel *265*
17.3 Oligo-Tetra-PEG Gel *269*
References *275*

Index *277*