

Contents

1	Introduction	1
1.1	History of polymer science	1
1.2	Polymer microstructure	2
1.3	Homopolymers and heteropolymers	5
1.4	Fractal nature of polymer conformations	7
1.5	Types of polymeric substances	12
1.5.1	Polymer liquids	12
1.5.2	Polymer solids	15
1.5.3	Liquid crystal polymers	15
1.6	Molar mass distributions	16
1.6.1	Binary distributions	19
1.6.2	Linear condensation polymers	20
1.6.3	Linear addition polymers	25
1.7	Molar mass measurements	26
1.7.1	Measuring M_n by osmotic pressure	26
1.7.2	Measuring M_w by scattering	29
1.7.3	Intrinsic viscosity	33
1.7.4	Size exclusion chromatography	35
1.8	Summary	38
	Problems	39
	Bibliography	45

I Single chain conformations

2	Ideal chains	49
2.1	Flexibility mechanisms	49
2.2	Conformations of an ideal chain	51
2.3	Ideal chain models	54
2.3.1	Freely rotating chain model	55
2.3.2	Worm-like chain model	57
2.3.3	Hindered rotation model	59
2.3.4	Rotational isomeric state model	59
2.4	Radius of gyration	60
2.4.1	Radius of gyration of an ideal linear chain	62
2.4.2	Radius of gyration of a rod polymer	63
2.4.3	Radius of gyration of an ideal branched polymer (Kramers theorem)	64

Contents

2.5	Distribution of end-to-end vectors	66
2.6	Free energy of an ideal chain	70
2.6.1	Scaling argument for chain stretching	72
2.6.2	Langevin dependence of elongation on force	74
2.7	Pair correlations of an ideal chain	78
2.8	Measurement of size by scattering	79
2.8.1	Scattering wavevector	79
2.8.2	Form factor	81
2.8.3	Measuring R_g^2 by scattering at small angles	83
2.8.4	Debye function	85
2.9	Summary of ideal chains	88
	Problems	90
	Bibliography	96
3	Real chains	97
3.1	Excluded volume and self-avoiding walks	98
3.1.1	Mayer f -function and excluded volume	98
3.1.2	Flory theory of a polymer in good solvent	102
3.2	Deforming real and ideal chains	104
3.2.1	Polymer under tension	104
3.2.2	Polymer under compression	107
3.2.3	Adsorption of a single chain	110
3.3	Temperature effects on real chains	113
3.3.1	Scaling model of real chains	113
3.3.2	Flory theory of a polymer in a poor solvent	115
3.3.3	Temperature dependence of the chain size	117
3.3.4	Second virial coefficient	119
3.4	Distribution of end-to-end distances	121
3.5	Scattering from dilute solutions	122
3.6	Summary of real chains	125
	Problems	127
	Bibliography	133
II Thermodynamics of blends and solutions		
4	Thermodynamics of mixing	137
4.1	Entropy of binary mixing	137
4.2	Energy of binary mixing	140
4.3	Equilibrium and stability	146
4.4	Phase diagrams	150
4.5	Mixtures at low compositions	154
4.5.1	Osmotic pressure	155
4.5.2	Polymer melts	157
4.6	Experimental investigations of binary mixtures	159
4.7	Summary of thermodynamics	163
	Problems	165
	Bibliography	170

5	Polymer solutions	171
5.1	Theta solvent	171
5.2	Poor solvent	173
5.3	Good solvent	176
5.3.1	Correlation length and chain size	176
5.3.2	Osmotic pressure	181
5.4	Semidilute theta solutions	183
5.4.1	Correlation length	183
5.4.2	Osmotic pressure	184
5.5	The Alexander – de Gennes brush	186
5.6	Multichain adsorption	187
5.7	Measuring semidilute chain conformations	189
5.8	Summary of polymer solutions	190
	Problems	191
	Bibliography	196

III Networks and gelation

6	Random branching and gelation	199
6.1	Introduction	199
6.1.1	Percolation around us	202
6.1.2	Percolation in one dimension	205
6.2	Branching without gelation	206
6.2.1	Hyperbranched polymers	206
6.2.2	Regular dendrimers	211
6.3	Gelation: concepts and definitions	213
6.4	Mean-field model of gelation	215
6.4.1	Gel point	216
6.4.2	Sol and gel fractions	217
6.4.3	Number-average molar mass below the gel point	218
6.4.4	Weight-average molar mass below the gel point	219
6.4.5	Molar mass distribution	220
6.4.6	Size of ideal randomly branched polymers	224
6.5	Scaling model of gelation	227
6.5.1	Molar mass distribution and gel fraction	227
6.5.2	Cutoff functions	231
6.5.3	Size and overlap of randomly branched polymers	234
6.5.4	Vulcanization universality class	237
6.6	Characterization of branching and gelation	241
6.7	Summary of branching and gelation	244
	Problems	247
	Bibliography	252

7	Networks and gels	253
7.1	Thermodynamics of rubbers	253
7.1.1	Flory construction	255
7.2	Unentangled rubber elasticity	255

Contents

7.2.1	Affine network model	255
7.2.2	Phantom network model	259
7.2.3	Finite extensibility	263
7.3	Entangled rubber elasticity	264
7.3.1	Chain entanglements and the Edwards tube model	264
7.3.2	The Mooney–Rivlin model	268
7.3.3	Constrained fluctuations models	269
7.4	Swelling of polymer gels	274
7.4.1	Swelling in θ -solvents	276
7.4.2	Swelling in athermal solvents	277
7.4.3	Swelling in good solvents	278
7.5	Networks in the gelation regime	280
7.6	Linear viscoelasticity	282
7.6.1	Stress relaxation after a step strain	284
7.6.2	The Boltzmann superposition principle	285
7.6.3	Steady shear	286
7.6.4	Creep and creep recovery	288
7.6.5	Oscillatory shear	290
7.7	Summary of networks and gels	294
	Problems	295
	Bibliography	305

IV Dynamics

8	Unentangled polymer dynamics	309
8.1	Rouse model	311
8.2	Zimm model	312
8.3	Intrinsic viscosity	314
8.4	Relaxation modes	319
8.4.1	Rouse modes	319
8.4.2	Zimm modes	323
8.5	Semidilute unentangled solutions	325
8.6	Modes of a semiflexible chain	330
8.6.1	Bending energy and dynamics	330
8.6.2	Tensile modulus and stress relaxation	333
8.7	Temperature dependence of dynamics	334
8.7.1	Time–temperature superposition	334
8.7.2	Transition zone of polymer melts	339
8.7.3	Short linear polymer melts	340
8.8	Randomly branched polymers	341
8.9	Dynamic scattering	345
8.10	Summary of unentangled dynamics	350
	Problems	352
	Bibliography	360

9	Entangled polymer dynamics	361
9.1	Entanglements in polymer melts	361
9.2	Reptation in polymer melts	363
9.2.1	Relaxation times and diffusion	363
9.2.2	Stress relaxation and viscosity	364
9.3	Reptation in semidilute solutions	367
9.3.1	Length scales	367
9.3.2	Entanglement concentration	369
9.3.3	Plateau modulus	370
9.3.4	Relaxation times and diffusion	370
9.3.5	Stress relaxation and viscosity	372
9.4	Dynamics of a single entangled chain	374
9.4.1	Chain in an array of fixed obstacles	374
9.4.2	Entangled star polymers	376
9.4.3	H-polymers and combs	380
9.4.4	Monomer displacement in entangled linear melts	381
9.4.5	Tube length fluctuations	383
9.5	Many-chain effects: constraint release	387
9.5.1	Relaxation times and diffusion	388
9.5.2	Stress relaxation	389
9.6	Computer simulations in polymer physics	391
9.6.1	Molecular dynamics	392
9.6.2	Monte Carlo	395
9.7	Summary of entangled dynamics	402
	Problems	403
	Bibliography	422
	Notations	423
	Index	433