

Contents

1. Introduction	
By H. G. Kiess	1
References	5
2. An Overview of the Theory of π-Conjugated Polymers	
By D. Baeriswyl, D. K. Campbell, and S. Mazumdar (With 37 Figures)	7
2.1 Synopsis	7
2.2 Theoretical Concepts, Models and Methods	13
2.2.1 The Born-Oppenheimer Approximation	14
2.2.2 Ab Initio Calculations	15
2.2.3 Model Hamiltonians	18
2.3 The Hückel and SSH Models: Independent-Electron Theories	28
2.3.1 From Polyethylene to Polyacetylene	28
2.3.2 Bond Alternation	31
2.3.3 The Strength of the Electron-Phonon Coupling	34
2.3.4 Stability of the Dimerized State and the Phonon Spectrum	35
2.3.5 Spatially Localized Nonlinear Excitations: Solitons, Polarons and Bipolarons	36
2.3.6 Predictions of the Model	47
2.4 Hubbard Model: A Paradigm for Correlated Electron Theories	49
2.4.1 Ground State and Excitation Spectrum	50
2.4.2 Correlation Functions	53
2.4.3 Relevance for Conjugated Polymers	54
2.5 The One-Dimensional Peierls-Hubbard Model	56
2.5.1 The Model Hamiltonian and its Parameters	57
2.5.2 Methods	60
2.6 The Combined Effects of Electron-Phonon and Electron-Electron Interactions: Theory and Experiment	67
2.6.1 Ground State	67
2.6.2 Electronic Excitations and Excited States	82

2.6.3 Vibrational Excitation: Raman and Infrared Spectroscopy	102
2.7 Beyond Simple Models: Discussion and Conclusions	105
2.7.1 Effects of Disorder	105
2.7.2 Interchain Coupling and Three-Dimensional Effects	106
2.7.3 Lattice Quantum Fluctuations	108
2.7.4 Doping Effects and the Semiconductor–Metal Transition	109
2.7.5 Transport	111
2.7.6 Concluding Remarks	112
References	114
 3. Charge Transport in Polymers	
By W. Rehwald and H.G. Kiess (With 15 Figures)	135
3.1 Models for the Insulating and Semiconducting States	136
3.1.1 The Electronic Ground State	136
3.1.2 The Nature of the Charge Carriers	141
3.1.3 Disorder Along the Chains	146
3.1.4 Low and Intermediate Doping	147
3.2 Models for Transport Processes	149
3.2.1 Conduction in Extended States	149
3.2.2 Conduction in Localized States	150
3.2.3 Transport in One Dimension	152
3.2.4 Transport by Quasi-Particles	154
3.3 Experiments in the Insulating and Semiconducting State	157
3.3.1 Polyacetylene	157
3.3.2 Other Polymers	162
3.4 The Semiconductor–Metal Transition and the Metallic State	164
3.4.1 Models for the Highly Doped State	165
3.4.2 Experiments in the Highly Doped State	167
3.5 Summary	170
References	171
 4. Optical Properties of Conducting Polymers	
By H. G. Kiess and G. Harbeke (With 21 Figures)	175
4.1 Elementary Considerations	175
4.2 Dielectric Response Function and Band Structure	177
4.3 Band Gap and Band Structures of Undoped Conjugated Polymers	178
4.3.1 Results of Band Structure Calculations	178
4.3.2 Experimental Results	182
4.4 Photon–Phonon Interaction	185
4.4.1 General Remarks	185

4.4.2	Calculations of Vibrational Spectra of Polymers	186
4.4.3	Experimental Results	188
4.5	The Study of Elementary Excitations in Conjugated Polymers	191
4.5.1	General Considerations	191
4.5.2	The Electronic States of the Quasi-Particles	192
4.5.3	The Vibrational State of the Quasi-Particles	198
4.5.4	Experimental Results	198
4.6	Highly Conducting Conjugated Polymers	206
4.6.1	General Considerations	206
4.6.2	The Highly Conducting Phase of Trans-Polyacetylene	207
4.6.3	Polyacetylene: Experimental Results	209
4.6.4	Highly Conducting Polymers with Nondegenerate Ground State	211
4.6.5	Concluding Remarks	213
	References	214
5.	Magnetic Properties of Conjugated Polymers	
	By P. K. Kahol, G. C. Clark, and M. Mehring (With 46 Figures)	217
5.1	General Aspects of Magnetic Properties and Resonance Techniques	218
5.1.1	Susceptibility	218
5.1.2	Lineshapes, Linewidths and Lineshifts	220
5.1.3	Spin Relaxation (T_1 , T_2 , $T_{1\rho}$)	224
5.1.4	Double Resonance Techniques	228
5.1.5	High-Resolution NMR	231
5.2	Structure and Lattice Dynamics of Conjugated Polymers in the Non-Conducting Phase	233
5.2.1	Lattice Structure Determination from Dipole-Dipole Interactions	233
5.2.2	Bond Length Determination from Dipole-Dipole Interactions	238
5.2.3	Chemical Shift Tensor	240
5.3	Spin Dynamics of Conjugated Defects in the Non-Conducting Phase	245
5.3.1	ESR and ENDOR Lineshapes	245
5.3.2	Dynamic Nuclear Polarization	253
5.3.3	Nuclear Spin Lattice Relaxation	256
5.3.4	Electron Spin Relaxation	261
5.3.5	Light-Induced ESR	265
5.4	Magnetic Properties of Conjugated Polymers in the Conducting Phase	267
5.4.1	Susceptibility	267

5.4.2 ESR Lineshapes and Linewidths	272
5.4.3 NMR Results	278
5.5 Magnetic Properties of Polydiacetylenes (PDA)	281
5.5.1 Structure	281
5.5.2 Solid-State Polymerization	283
5.5.3 Quasi-Particle Excitation	289
5.6 Other Conjugated Polymers	291
5.7 Conclusions and Remarks	295
References	297
Subject Index	305