
Foreword

The interaction of electromagnetic (EM) radiation with molecular systems gives rise to quantized transitions between the electronic, vibrational and rotational molecular energy states which may be observed by UV/visible and infra-red absorption spectroscopies at frequencies above about 1 THz (10^{12} Hz). These quantum spectroscopies for molecules in the gaseous, liquid and solid states form a large part of physical chemistry and chemical physics. However, if one asks a fellow scientist “what happens when EM radiation in the range 10^{-6} to 10^{12} Hz is applied to those systems” the answer is usually tentative and incomplete, which shows that a majority of scientists are unfamiliar with the dielectric dispersion and absorption phenomena that occur in this vast frequency range due to (i) dipole relaxation arising from the reorientational motions of molecular dipoles and (ii) electrical conduction arising from the translational motions of electric charges (ions, electrons). This is the domain of *Broadband Dielectric Spectroscopy* (BDS).

At frequencies below about 10^8 Hz a dielectric sample is regarded as a complex electrical impedance $Z^*(\omega)$, expressed in terms of the resistance $R(\omega)$ and capacitance $C(\omega)$, which are frequency-dependent *extensive* properties (here $\omega = 2\pi f/\text{Hz}$ where f is the measuring frequency). The *intensive* complex dielectric quantities of dielectric permittivity $\epsilon^*(\omega)$, electrical modulus $M^*(\omega)$, electrical conductivity $\sigma^*(\omega)$ and resistivity $\rho^*(\omega)$ are immediately derivable from $Z^*(\omega)$. Researchers traditionally use these different quantities to express BDS data for materials, which is a source of confusion when assessing the dielectric/electrical properties of a given material reported in the literature. Dipole relaxation behaviour is normally represented in terms of ϵ^* and electric conduction behaviour in terms of σ^* , Z^* , M^* or ρ^* .

Starting in the late nineteenth century, dielectric measurement techniques were developed for materials such as molecular liquids and solids and moderately-conducting materials such as electrolytes and semiconductors. Transient current methods were used for very low frequencies ($f < 1$ Hz) and a.c. bridges for power, audio, UHF and VHF frequencies (1 to 10^7 Hz). In the 1940s distributed circuit methods were introduced for microwave frequencies (10^8 to 10^{11} Hz) and in the 1970s novel spectroscopic methods were developed for far infrared frequencies (3×10^{11} to 3×10^{12} Hz). In the main, measurements were made point-by-point at each frequency in the range of interest, which was difficult, and time-consuming. This held back the use of dielectric spectroscopy as an investigative physical technique at times when rapid advances were being made in the related techniques of NMR, quasi-elastic light scattering and photon-correlation spectroscopy. Nevertheless extensive dielectric data for a host of organic and inor-

ganic materials were obtained prior to the early 1980s using these methods. Subsequently modern commercial impedance measuring devices for low frequencies and commercial network analysers, time-domain reflectometers and laser spectroscopies for high frequencies became available and were developed for broadband dielectric studies of materials. Automatic measurement and processing methods, made possible by on-line computers used in combination with the new instruments, transformed dielectric measurements of materials. Now it is possible to obtain accurate dielectric data quickly and efficiently over the entire frequency range 10^{-6} to 10^{12} Hz and means that BDS has now taken its rightful place alongside other modern investigative techniques for studying the structure and molecular dynamics of materials.

Debye (1927) established that *dielectric relaxation*, which is the dispersion of the real permittivity (ϵ') and the occurrence of dielectric absorption (ϵ'') in the f -domain for dipolar liquids and solids, was due to the reorientational motions of the molecular dipoles. Many dielectric studies followed, especially those by Smyth (Princeton) and Cole (Brown) that were started in the 1930s. Early areas of study included dipolar liquids (e.g. chlorobenzene, polar solutes in non-polar solvents), rotator-phase crystals (e.g. cyclohexanol, the polymorphs of ice), non-polar polymers (e.g. polyethylene, polypropylene), polar polymers (e.g. polyacrylates, nylons, polyamides). Knowledge of the low frequency permittivity allowed molecular dipole moments to be determined, which was useful for the elucidation of molecular structures prior to the use of modern spectroscopic techniques. The dielectric loss spectra characterized the reorientational dynamics of molecules in the different materials. Also dielectric studies were made for inorganic solids that have ferroelectric properties (e.g. barium titanate) or are semi-conducting (e.g. doped silicon, organic photoconductors and semi-conductors) which have important applications in solid state devices. In parallel, extensive BDS data were obtained for electrolytes, polyelectrolytes, organic and inorganic semi-conductors, giving information on electrical conductivity and hence the mobilities of the effective charge carriers. More recently many BDS studies have been made for novel polymers, glass-forming liquids, liquid crystals (e.g. alkylcyanobiphenyls), polymeric liquid crystals (e.g. polysiloxanes with mesogenic side chains), ferroelectric organic materials (e.g. chiral alkylcyanobiphenyls and their polymeric derivatives), electrolytes (e.g. KCl/H₂O), molten salts (e.g. Ca-K/NO₃) and polyelectrolytes (e.g. polyethylene oxide/salt solutions). Such researches were often motivated by the applications of these materials in devices for modern technology. For example (i) the dielectric anisotropy of the liquid crystal is the source of the optical switching process in liquid crystal displays while (ii) new thin-film solid-state electrolytes are sought for battery applications.

As the data-base for the broadband dielectric behaviour of different materials increased, phenomenological and molecular theories for dipole relaxation and charge conduction were developed. The molecular theories required the deduction of $\epsilon^*(\omega)$ or $\sigma^*(\omega)$ from the field-induced perturbation of the field-free reorientational and translational motions of molecular species. Such theories become extremely difficult for complex motions, e.g. as for multi-site motions of dipoles or ions in crystals or structured liquids. The situation changed completely when Kubo (1957), using linear response theory and time-dependent sta-

tistical mechanics, showed that $\sigma^*(\omega)$ was related, via Fourier transformation, to the field-free mean-squared displacement of charges with time $\langle \Delta R^2(t) \rangle$ or to their velocity correlation function $\langle v(0)v(t) \rangle$. For dielectric relaxation Glarum (1961) and Cole (1965) related $\varepsilon^*(\omega)$, via Fourier transformation, to the field-free dipole moment correlation function $\langle \mu(0)\mu(t) \rangle$ with time. Thus Fourier inversion of $\sigma^*(\omega)$ or $\varepsilon^*(\omega)$ gave direct determinations of these t -dependent molecular properties, which could in turn be fitted by chosen models for motions of molecules or charges. Research texts dealing with dielectric data (mainly for molecular liquids and solids) were published by Smyth (1955), Fröhlich (1958), Hill, Vaughan, Price and Davies (1969) and Böttcher and Bordewijk (1978) and for polymers by McCrum, Read and Williams (1967) and Runt and Fitzgerald (eds) (1997). Obviously the wide range of materials studied in different frequency bands for their dipole relaxation and conduction behaviour, the differing backgrounds of the researchers (physicists, chemists, materials scientists, electrical engineers, chemical engineers, theorists) and the publication of the researches in different journals of physics, physical chemistry/chemical physics, electrical engineering, polymer science and materials science made it increasingly difficult for scientists to monitor overall activities in dielectric spectroscopy. A great help to this effect have been the *International Discussion Meetings on Relaxations in Complex Systems* organized by K. L. Ngai and his associates held in Crete (1990), Alicante (1993) and Vigo (1997), published as special issues of *J Non-Crystalline Solids*, and that held in Crete (2001) where researchers in different areas of dielectrics science have been brought together along with a host of researchers that use related relaxation, scattering and spectroscopic techniques for the study of the dynamics of materials.

The stage has been reached where the foundations of broadband dielectric spectroscopy are well-established in terms of the large body of literature for the dielectric behaviour of dipolar materials and moderately-conducting electrolyte systems, phenomenological and molecular theories that relate $\varepsilon^*(\omega)$ and $\sigma^*(\omega)$ to empirical relaxation functions and to time-dependent molecular properties that give information on the reorientational and translational motions of molecules and charges in molecular liquids and solids. In this book the editors Friedrich Kremer and Andreas Schönhals have built on these foundations, through their own contributions and those of other leading scientists, taking the subject forward into those areas where BDS is making vital and new contributions to our understanding of the dynamics of complex systems. After a summary of the essentials of modern experimental techniques and dielectric theories (Chaps. 1–3) experimental data are shown over the entire frequency range for glasses, supercooled liquids, amorphous polymers (Chaps. 4, 5, 7), (polymeric) liquid crystals (Chap. 10) and semi-conducting disordered materials (Chap. 12) where multiple dipole relaxations are observed and are analysed in terms of particular motional processes. BDS provides a powerful method for studying the dynamics of molecules in confined spaces down to the mesoscopic and molecular levels (Chap. 6). Since the capacitance of a dielectric sample is inversely proportional to its thickness, BDS is highly suitable for studies of ultra-thin films, in contrast to NMR, light scattering and other spectroscopic techniques. The effects of film thickness on molecular dynamics in ultra-thin poly-

mer films are clearly demonstrated (Chap. 11) and provide severe tests of results for glass-forming materials obtained from other physical techniques. Inhomogeneous media (Chap. 13) give rise to interfacial polarization in addition to dipole relaxation and charge-conduction and this is particularly important in multi-phase liquids and polymers, emulsions and biological systems. The component structures of relaxation processes and the questions of dynamic heterogeneity in organic materials are further elucidated by the new, sophisticated techniques of pulsed and non-resonant dielectric hole-burning (Chap. 14). BDS studies provide evidence for the structure and molecular dynamics in all these systems, evidence is obtained on the molecular dynamics which complements that obtained using the related techniques of solvation dynamics (Chap. 15), dynamical mechanical spectroscopy (Chap. 16), multi-dimensional multi-nuclear NMR (Chap. 17) and neutron scattering (Chap. 18). While dielectric relaxation behaviour is usually studied over wide ranges of frequency and sample temperature, the relaxation strength, relaxation time and its distribution are all affected significantly by applied pressure. This 'forgotten variable' (G. Floudas, Chap. 8) can be used to separate overlapping relaxations or induce crystallization – which transforms the relaxation behaviour in crystallizable polymers. Modern techniques allow broadband dielectric measurements to be made in real time for polymerizing systems where a liquid mixture transforms to a glass or an elastomer during reaction (Chap. 9). These studies monitor changes in molecular dynamics during the polymerization reaction and demonstrate the role of diffusion-control on reaction rate when a glass is formed.

Thus the editors and contributors show in this remarkable book that modern BDS techniques, as applied to a wide range of amorphous, crystalline and liquid crystalline systems, can give new and vital information on the reorientational and translational motions of dipolar molecules or electric charges and how the characteristics of these motions vary with temperature and pressure and with the physical condition of the material (bulk or thin film, confined geometries, macroscopic orientation (e.g. for liquid crystals)). They show how the wide frequency range of BDS may be utilised to obtain a detailed knowledge of individual motional processes whose time-scale may be in a range from picoseconds to kiloseconds and show further how this information complements that obtained for the same materials using related relaxation, scattering and spectroscopic techniques. A new researcher, or one from a related field of study, will find this 'state-of-the-art' account of broadband dielectric spectroscopy to be invaluable since *inter alia* it provides clear examples of the power of the technique to elucidate the dynamics of condensed systems, many of which have applied interest. Most important of all, the information provided by the BDS researches described here will stimulate new lines of research, not only into the applications of modern dielectric techniques to new materials and to time-varying systems but also to the development of further novel techniques that will test and extend the conclusions reached presently from BDS, NMR, mechanical relaxation, light scattering, neutron scattering, optical relaxation and related techniques concerning the detailed nature of molecular dynamics in organic and inorganic materials.

Preface

The interaction of electromagnetic waves with matter in the frequency regime between 10^{-6} and 10^{12} Hz is the domain of broadband dielectric spectroscopy. In this extraordinarily extended dynamic range, molecular and collective dipolar fluctuations, charge transport and polarization effects at inner and outer boundaries take place, and determine the dielectric properties of the material under study. Hence broadband dielectric spectroscopy enables us to gain a wealth of information on the dynamics of bound (dipoles) and mobile charge carriers depending on the details of the molecular system. In recent years novel dielectric instrumentation has been developed which allows for automatic measurements in nearly the entire range from ultra low frequencies up to the Far Infra Red.

It is intended that this book be more than a monograph at the leading edge of research. Therefore in three introductory chapters written in the style of a textbook, broadband dielectric spectroscopy is described in its theoretical foundation, its experimental techniques, and in the way dielectric spectra have to be analyzed. In the chapters 4–13, examples are described where the dielectric method has made important contributions to modern scientific topics. This is, of course, far from being a comprehensive overview and corresponds to the research interests of the editors. In chapters 14 and 15, two novel experimental techniques are introduced which are closely related to dielectric spectroscopy. Special attention is given in chapters 16–18 to the comparison between dielectric and other spectroscopic techniques such as mechanical, NMR, and neutron scattering.

The editors would like to thank all the contributors to this volume for their efficient collaboration. Many chapters of the book were read by G. Williams who made numerous suggestions from which the book benefited a great deal. The patient help of Mrs. I. Grünwald in typing some of the manuscripts and managing the correspondence is thankfully acknowledged. The editors would also like to thank Dr. M. Hertel and Springer Verlag for the competent cooperation.

July 2002

*F. Kremer
A. Schönhalz*

Contents

1	Theory of Dielectric Relaxation	1
	<i>A. Schönhals, F. Kremer</i>	
1.1	Introduction	1
1.2	Electrostatics	3
1.3	Dielectric Relaxation (Dielectric Retardation)	10
1.3.1	Linear Response Theory and Fluctuation Dissipation Theorem	10
1.3.2	Theoretical Considerations (Models)	15
1.3.2.1	Debye Relaxation	17
1.3.2.2	Models for Non-Debye Relaxation	19
	Appendix 1.1 Linear Response Theory	24
	Appendix 1.2 Derivation of the Kramers/Kronig-Relationships	26
	Appendix 1.3 Fluctuation Dissipation Theorem	29
	References	32
2	Broadband Dielectric Measurement Techniques (10^{-6} Hz to 10^{12} Hz)	35
	<i>F. Kremer, A. Schönhals</i>	
2.1	Introduction	35
2.2	Measurements in the Frequency Domain from 10^{-6} Hz to 10^{11} Hz	37
2.2.1	Fourier Correlation Analysis	37
2.2.2	Dielectric Converters in Combination with Fourier Correlation Analysis	39
2.2.3	Impedance Analysis	41
2.2.4	Integrated Dielectric Analyzers	42
2.2.5	Samples and Sample Cells for Frequencies < 10 MHz	43
2.2.6	RF Reflectometry	43
2.2.7	Network Analysis	45
2.2.8	Impedance and Frequency Ranges Overview	46
2.3	Measurement Systems in the Time Domain from 10^{-6} Hz to 10^{10} Hz	48
2.4	Quasioptical Set-Ups in the Frequency Range from 10^{10} Hz to 10^{12} Hz	51
2.5	Conclusions	54
	References	56

3	Analysis of Dielectric Spectra	59
	<i>A. Schönhal's, F. Kremer</i>	
3.1	Introduction	59
3.2	Dipolar Fluctuations	60
3.2.1	Analysis of Dielectric Spectra – Model Functions	61
3.2.2	Analysis of Dielectric Spectra – Model Free	72
3.3	Fluctuations of Mobile Charge Carriers	81
3.4	Separation of Charges	87
3.4.1	Mesoscopic Scale: Maxwell/Wagner/Sillars Polarization	87
3.4.2	Electrode Polarization	91
3.5	Conclusion – How to Analyze Dielectric Spectra	93
	Appendix 3.1 Fit parameters	94
	References	96
 4	 The Scaling of the Dynamics of Glasses and Supercooled Liquids	 99
	<i>F. Kremer, A. Schönhal's</i>	
4.1	Introduction	99
4.2	Theories Describing the Scaling of the Dynamics in Glass-Forming Systems	101
4.3	Temperature Dependence of the Dynamic Glass Transition	108
4.4	Scaling of the Relaxation Time Distribution Function of the Dynamic Glass Transition	116
4.5	Scaling of the Dynamic Glass Transition and the Slow β -Relaxation in Poly(ethylene terephthalate) (PET)	120
4.6	Conclusions	125
	References	127
 5	 Glassy Dynamics Beyond the α-Relaxation	 131
	<i>P. Lunkenheimer, A. Loidl</i>	
5.1	Introduction	131
5.2	Dynamic Processes in Glass-Forming Materials	133
5.3	Broadband Dielectric Spectra of Glass-Forming Materials	136
5.4	The Excess Wing	142
5.4.1	Scaling and Divergent Susceptibility	143
5.4.2	The Excess Wing – a β -Relaxation?	146
5.5	The High-Frequency Response	149
5.5.1	The $\epsilon''(\nu)$ -Minimum	149
5.5.1.1	Phenomenological Description	150
5.5.1.2	Mode-Coupling Theory	152
5.5.1.3	Other Models	157
5.5.2	Comparison with Light and Neutron Scattering	158

5.5.3	The Boson Peak	161
5.6	Conclusions	162
	References	165
6	Molecular Dynamics in Confining Space	171
	<i>F. Kremer, A. Huwe, A. Schönhals, S.A. Różański</i>	
6.1	Introduction	171
6.2	H-Bond Forming and van-der-Waals Liquids in Zeolitic and Nanoporous Media	172
6.2.1	Glycols in Zeolites and Nanoporous Sol-Gel Glasses	172
6.2.2	Salol in (Lubricated) Nanoporous Sol-Gel Glasses	188
6.3	Polymers in Zeolitic and Nanoporous Media	199
6.3.1	Poly(vinylether) in Mesoporous MCM	199
6.3.2	Poly(propylene glycol) in Nanoporous Sol-Gel Glasses	202
6.3.3	Poly(dimethyl siloxane) in Nanoporous Sol-Gel Glasses	207
6.4	Liquid Crystals in Confining Space	210
6.4.1	Nematic Liquid Crystals in Mesoporous Membranes	210
6.4.2	Ferroelectric Liquid Crystals in Mesoporous Membranes	216
6.5	Conclusions	220
	References	222
7	Molecular Dynamics in Polymer Model Systems	225
	<i>A. Schönhals</i>	
7.1	Introduction	225
7.2	Theoretical Considerations	227
7.2.1	Conformations of Polymeric Chains	227
7.2.2	Dipole Moments of Polymeric Chains	230
7.2.3	Motional Processes in Isolated Chains	233
7.2.3.1	Segmental Motion	233
7.2.3.2	Chain Motion	234
7.3	Dielectric Properties of Polymers in Solution	236
7.3.1	Dilute Solutions	236
7.3.1.1	Segmental Motion	236
7.3.1.2	Chain Motion	238
7.3.2	Concentrated Solutions	238
7.3.2.1	Segmental Motion	238
7.3.2.2	Chain Motion	239
7.3.3	Rod-Like Systems	240
7.4	Dielectric Properties of Polymeric Systems in the Bulk State	241
7.4.1	Amorphous Polymers	241
7.4.1.1	β -Relaxation	242
7.4.1.2	Dynamic Glass Transition (α -Relaxation)	244
7.4.1.3	Relationship Between the β - and the α -Relaxation – the ($\alpha\beta$)-Process	251

7.4.1.4	Normal Mode Relaxation	254
7.4.2	Semicrystalline Polymers	261
7.4.2.1	Morphology of Semicrystalline Polymers	263
7.4.2.2	Polymers with a Medium Degree of Crystallinity	264
7.4.2.3	Polymers with a High Degree of Crystallinity – Polyethylene	271
7.4.3	Polymer Blends	272
7.4.3.1	General Considerations	273
7.4.3.2	Miscible Blends – Concentration Fluctuations	273
7.4.3.3	Immiscible Blends	276
7.4.4	Novel Polymeric Architectures	277
7.4.4.1	Rings	277
7.4.4.2	Stars and Block Copolymers	277
7.4.4.3	Dendrimers	282
7.4.4.4	Networks	283
7.5	Conclusion	283
	Appendix	284
	References	286
8	Effect of Pressure on the Dielectric Spectra of Polymeric Systems	295
	<i>G. Floudas</i>	
8.1	Introduction	295
8.2	Theoretical Background	296
8.2.1	Transition State Theory	296
8.2.2	Models Based on Free Volume Theories	296
8.2.3	Model of Constant Free Volume Compressibility	298
8.2.4	Models of Variable Free Volume Compressibility	299
8.2.5	Problems Related to Free Volume Theories	300
8.2.6	Scaling of the α -Process: an Example	301
8.3	Effect of Pressure on the Separation of the α - and β -Processes	302
8.4	Effect of Pressure on the Local and Global (Chain) Dynamics	305
8.5	Effect of Pressure on the Miscibility of Blends/Copolymers	315
8.5.1	The PI- <i>b</i> -PVE Athermal Diblock Copolymer	317
8.5.2	The PS/PVME Homogeneous Blend	321
8.6	Effect of Pressure on Polymer Crystallization	326
8.6.1	Crystallization Kinetics	338
8.7	Conclusion	344
	References	346
9	Dielectric Spectroscopy of Reactive Network-Forming Polymers 349	
	<i>J. Mijovic</i>	
9.1	Introduction	349
9.2	Polarization Mechanisms	350
9.3	Experimental	351

9.3.1	Principles of Measurements	351
9.3.2	Instrumentation	351
9.3.3	Cells and Sensors	351
9.3.4	In Situ Real Time Monitoring of Cure	352
9.4	Polarization Due to Migrating Charges	353
9.4.1	Modeling Concepts – Equivalent Circuits	353
9.4.2	Graphical Representation and Evaluation of Characteristic Parameters	356
9.4.3	Examples of In Situ Dielectric Cure Monitoring	358
9.5	Polarization by Dipole Orientation	360
9.5.1	Dipolar Relaxation Processes – Classification Scheme	360
9.5.2	Changes in Relaxation Time (τ) During Network Formation	363
9.5.3	Correlation Between Chemical Kinetics and Molecular Dynamics During Network Formation	366
9.5.4	Changes in Relaxation Strength During Network Formation	372
9.5.5	Changes in Relaxation Spectrum During Network Formation	375
9.6	Conclusions	379
	References	381
10	Molecular and Collective Dynamics of (Polymeric) Liquid Crystals	385
	<i>F. Kremer, A. Schönhalz</i>	
10.1	Introduction	385
10.2	Molecular and Mesomorphic Structures of Liquid Crystals	385
10.2.1	Low Molecular Weight Systems	385
10.2.2	Polymeric Systems	388
10.3	Theoretical Considerations	388
10.4	Molecular Dynamics	392
10.4.1	Low Molecular Weight Systems	392
10.4.2	Polymeric Systems	396
10.4.2.1	Side Chain Polymers	396
10.4.2.2	Main Chain Polymers	411
10.5	Collective Dynamics in Ferroelectric Liquid Crystalline Systems	412
10.5.1	Low Molecular Weight Systems	412
10.5.2	Polymeric Systems	422
10.6	Conclusions	428
	References	430
11	Molecular Dynamics in Thin Polymer Films	433
	<i>L. Hartmann, K. Fukao, F. Kremer</i>	
11.1	Introduction	433
11.2	Preparation and Methodical Aspects	434
11.2.1	Preparation of Thin Polymer Films	434
11.2.2	Thermal Expansion Spectroscopy	436

11.3	Thin Films of Glass Forming Polymers	438
11.3.1	Poly(methyl methacrylate) (PMMA)	438
11.3.2	Atactic Polystyrene (a-PS)	452
11.4	Thin Films of Grafted Polymers: Poly(γ -benzyl-L-glutamate) (PBLG)	462
11.5	Conclusions	469
	References	472
 12	 The Dielectric Properties of Semiconducting Disordered Materials	 475
	<i>F. Kremer, S.A. Róžański</i>	
12.1	Introduction	475
12.2	Similarities in the a.c. Conductivity of Semiconducting Disordered Materials	480
12.3	Relaxation and Charge Transport in Mixtures of Zwitterionic Polymers and Inorganic Salts	483
12.4	Conclusions	492
	References	493
 13	 Dielectric Properties of Inhomogeneous Media	 495
	<i>P.A.M. Steeman, J. van Turnhout</i>	
13.1	Introduction	495
13.2	Theory	496
13.2.1	Two-Phase Heterogeneous Materials	496
13.2.2	Heterogeneous Materials Containing More than Two Phases	501
13.2.3	Heterogeneous Materials with an Interfacial Layer	502
13.3	Experimental Results	503
13.3.1	Polymeric Blends	503
13.3.2	Filled Polymers	508
13.3.3	Semi-Crystalline Polymers	512
13.3.4	Effect of Processing on Material Homogeneity	516
13.4	Conclusions	519
	References	520
 14	 Principles and Applications of Pulsed Dielectric Spectroscopy and Nonresonant Dielectric Hole Burning	 523
	<i>R. Böhmer, G. Diezemann</i>	
14.1	Introduction	523
14.2	Theoretical Concepts	525
14.2.1	Macroscopic Linear Response	525
14.2.2	Microscopic Reorientation Models	527

14.2.3	Stochastic Dynamics in Moderately Large Electric Fields	533
14.2.3.1	The Model of Asymmetric Double Well Potentials	534
14.2.3.2	The Box Model	540
14.3	Experimental Aspects	542
14.4	Applications	545
14.4.1	Supercooled Liquids and Plastic Crystals	545
14.4.1.1	Pulsed Dielectric Spectroscopy	545
14.4.1.2	Nonresonant Spectral Hole Burning	548
14.4.2	Ion Conducting Glasses	552
14.4.3	Crystals with Frozen-In Disorder	556
14.5	Related Experimental Methods	559
14.6	Conclusions	562
	Appendix 14.1	563
	Appendix 14.2	564
	References	566
 15	 Local Dielectric Relaxation by Solvation Dynamics	 571
	<i>R. Richert</i>	
15.1	Introduction	571
15.2	Experimental Techniques	572
15.3	Dielectric Aspects of Solvation	576
15.4	Solvation Dynamics	580
15.4.1	Dynamic Heterogeneity	583
15.4.2	Confined Systems	587
15.5	Summary	592
	References	594
 16	 Dielectric and Mechanical Spectroscopy – a Comparison	 597
	<i>T. Pakula</i>	
16.1	Introduction	597
16.2	Principles of Mechanical Analysis	600
16.3	Linear Viscoelastic Behaviour	602
16.4	Experimental Procedures and Typical Data Analysis	606
16.5	Differences in Data Treatment	610
16.6	Typical Behaviour of Polymeric Materials	612
16.6.1	Melts of Linear Polymers	612
16.6.2	Block Copolymer Systems	614
16.6.3	Highly Branched Polymers	618
16.7	Suggested Analysis of Modulus Spectra	619
16.8	Concluding Remarks	620
	References	623

17	Dielectric Spectroscopy and Multidimensional NMR – a Comparison	625
	<i>R. Böhmer, F. Kremer</i>	
17.1	Introduction	625
17.2	Selected NMR Methods	626
17.2.1	Spin-Relaxation Techniques	627
17.2.2	Stimulated Two-Time Echo Spectroscopy	631
17.2.2.1	Translational Displacements	632
17.2.2.2	Reorientational Dynamics	636
17.2.3	Multidimensional Techniques	638
17.2.3.1	Frequency-Domain Spectroscopy	638
17.2.3.2	Multiple-Time Correlations	641
17.3	Combined Dielectric and NMR Studies: Recent Experimental Examples	646
17.3.1	Dynamics in ‘Simple’ Glass Formers: Glycerol vs Toluene	646
17.3.2	Motional Processes of a Triphenylene-Based Discotic Liquid Crystal	652
17.3.3	α - and β -Relaxations in Poly(methyl methacrylate)	657
17.3.4	Dynamic and Spatial Heterogeneity in Poly(vinyl acetate)	662
17.3.5	$2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{MNO}_3$ as an Example for an Ion Conductor	668
17.3.6	Self-Diffusion in Polymeric Systems	671
17.4	Concluding Remarks	674
	Appendix 17.1	675
	Appendix 17.2	676
	References	679
 18	 Polymer Dynamics by Dielectric Spectroscopy and Neutron Scattering – a Comparison	 685
	<i>A. Arbe, J. Colmenero, D. Richter</i>	
18.1	Introduction	685
18.2	Quasielastic Neutron Scattering	686
18.2.1	Neutron Cross Sections and Correlation Functions	686
18.2.2	Neutron Instrumentation	688
18.2.2.1	Time of Flight Spectrometer	688
18.2.2.2	Backscattering Instrument	689
18.2.2.3	Spin Echo Spectrometer	690
18.2.3	Relation to Dielectric Spectroscopy	692
18.3.	Dynamic Structure Factors for the α - and β -Process	695
18.3.1	Local Processes	695
18.3.2	Diffusive (Q Dispersive) Processes	697
18.3.3	Merging of the α - and β -Processes	699
18.4.	Experimental Examples	699
18.4.1	Polybutadiene as a Showcase	699

18.4.2	Combined Dielectric and Neutron Investigations of the β -Process	703
18.4.3	α -Process on Polybutadiene	705
18.4.3.1	Temperature Dependence	705
18.4.3.2	Q-Dependence	706
18.4.3.3	Merging of α - and β -Processes	707
18.5.	Conclusions	714
	References	717
	For Further Reading	719
	Subject Index	721

Broadband Dielectric Spectroscopy

Kremer, F.; Schönhals, A. (Eds.)

2003, XXI, 729 p., Hardcover

ISBN: 978-3-540-43407-8