

Contents

Preface to the second edition	vii
Chapter 1	
Theory of polymer characterization	
Elements of polymer structure	1
Approach to polymer structure determination using probability considerations	3
Structure calculations using the probability distribution function	5
A simple example: degree of polymerization	5
Number-average molecular weights	7
Weight-average molecular weight measurements	8
Distributions of molecular weight	9
Chemical heterogeneity in the polymer chain	9
Characterization of polymer microstructure	11
Structural model of the polymer chain	11
Measurement of polymer structure using composition	12
Measurement of polymer structure using dyad units	13
Measurement of polymer structure using triad segments	14
Measurement of polymer structure using higher n-ad segments	15
Relationships between the various orders (lengths) of sequences	15
Calculation of polymer structural parameters from sequence measurements	16
Structural composition	17
Sequence order parameter	17
Number-average sequence lengths	18
Relating the polymer structure to the polymerization mechanism	20
Microstructure of terminal copolymerization model	20
Microstructure of the penultimate polymerization model	24
Higher order models of copolymerization and other complications	27
Differentiation between model mechanisms of copolymerization	27
Determination of polymerization mechanism for model copolymer	31
Determination of the polymerization parameters	32
Summary	32
The shape of things to come	33
References	33
Chapter 2	
Vibrational spectroscopy of polymers	35
Introduction to vibrational spectroscopy	35
Elementary theory of vibrational spectroscopy	36

Infrared spectroscopy	36
Raman spectroscopy	37
Vibrational spectroscopy as an identification tool	38
Basis of vibrational spectroscopy as a structural tool	39
Structural dependence of vibrational frequencies	39
Infrared selection rules	47
Raman selection rules	48
Infrared intensities	52
Raman intensities	54
Infrared dichroism in solids	58
Characteristic group frequencies in vibrational spectroscopy and interpretation of polymer spectra using group frequencies	63
Coupled infrared vibrations as a polymer structure probe	65
Vibrations of the infinite linear monatomic chain	65
Vibrations of the infinite diatomic chain	68
Vibrations of the infinite polymer chain in three dimensions	70
Vibrations of finite chains	73
Distribution of intensities for chain molecules	75
Summary	75
References	75
Chapter 3	
Experimental IR spectroscopy of polymers	77
Introduction	77
Infrared spectroscopic instrumentation	77
Dispersive infrared instrumentation	77
Multichannel dispersive instrumentation	78
Multiplex infrared instrumentation	79
Sampling methods for IR spectroscopy	85
Background	85
Transmission spectroscopy	88
Internal reflection spectroscopy (IRS)	90
External reflection spectroscopy	94
Diffuse reflectance FTIR spectroscopy (DRIFT)	96
Photoacoustic spectroscopy	100
Depth profiling using PAS	101
Emission spectroscopy	103
Microsampling techniques	108
Data processing of digitized IR spectra	109
Elimination of spectral backgrounds	110
Elimination of spectral distortion resulting from sampling technique	111
Spectral subtraction	113
Resolution enhancement using curve-fitting methods	122
Derivative spectroscopy.	122
Fourier self-deconvolution.	123
Maximum entropy method.	124
Quantitative IR spectroscopy of polymers	124

Multivariate linear regression	126
The K-matrix approach	126
Classical least-squares analysis using spectra of pure components	127
Inverse least-squares method.	128
Principal component analysis	128
Partial least-squares method	131
The ratio method for determination of component spectra	131
Factor analysis	132
Rank annihilation	139
Cross-correlation	141
Summary	142
References	143
Chapter 4	
Applications of IR spectroscopy to polymers	147
Structural applications of IR spectroscopy	147
Number-average molecular weight by using end-group analysis	147
IR analysis of the polymerization process	149
Chemical transformations in polymers	152
Copolymer analysis	154
Composition of copolymers	154
Microstructure of copolymers	154
Measurement of stereoregularity	162
Measurement of conformation	165
Measurement of branching in polymers	171
Characterization of polymer blends	173
Deformation of polymer systems	179
Dichroic IR measurements of orientation in polymers	179
Trichroic IR measurements of orientation	182
Mechanically stressed polymer systems	186
Dynamic IR linear dichroism spectroscopy	188
Dynamic two-dimensional IR spectroscopy	192
Measurement of morphological units in polymers	194
Intermolecular interactions in polymers	195
Structural changes and transitions as a function of temperature	198
Conformational analysis of polymers	198
Time-dependent phenomena in polymers	200
Kinetic studies of polymerization reactions	201
Characterization of surfaces	203
FT-IR studies of diffusion	204
Summary and conclusions	204
Where do we go from here?	204
References	205
Chapter 5	
Raman spectroscopy of polymers	207
The nature of Raman scattering spectroscopy	207

Spectral differences between IR and Raman spectroscopy	208
Raman and IR spectroscopy in combination to determine polymer conformation	212
Limitations of Raman spectroscopy resulting from fluorescence	215
Experimental Raman spectroscopy	217
Experimental conventional Raman spectroscopy	218
Raman illumination sources	219
Fourier transform Raman spectroscopy	227
Resonance Raman spectroscopy	229
Surface-enhanced Raman scattering	231
Sampling techniques in Raman spectroscopy	232
Fiber-optic sampling in Raman spectroscopy	234
Quantitative analysis using Raman spectroscopy	236
Chemical structure and composition	237
Monitoring of polymerization using Raman spectroscopy	238
Monitoring residual monomer in polymer dispersions	239
Degradation of polymers	239
Conformation of polymer chains in the solid state	242
Conformation of polymers in solution and in the melt	243
Conformation of polymers at interfaces	245
Crystalline dimensions	245
Measuring the crystalline chain segment length	245
Molecular orientation in polymers	247
Summary, conclusions and forecast	252
References	252
 Chapter 6	
High resolution NMR spectroscopy of polymers in solution	255
Elements of nuclear magnetic resonance spectroscopy	255
Pulsed NMR Fourier transform spectroscopy	261
Basis of the Fourier transform NMR experiment	261
Experimental considerations for the FT NMR experiment	263
Improved sensitivity in NMR	264
Nuclear spin relaxation	265
The spin–lattice relaxation time	265
The spin–spin relaxation time	266
Magnetic interactions between nuclei	268
Interactions between nuclei and their environments	269
Observation of chemical shifts in proton resonances	269
Origin of chemical shifts	270
Through-bond interactions with other nuclei	272
Through-space interactions with other nuclei	276
Experimental proton NMR spectroscopy	277
Experimental ¹³ C-NMR spectroscopy	277
Experimental NMR spectroscopy of polymers	280
NMR method of structure determination for polymers	281
The use of chemical shifts to determine polymer structure	282
Measurement of chemical shifts	282

Interpretation of chemical shifts	283
Spectral editing techniques for structural assignments	285
Spectral assignments using decoupling techniques	286
Determination of proton multiplicity of carbons	294
Two-dimensional NMR experiments	297
2D correlation via heteronuclear chemical shifts	300
2D correlation via homonuclear scalar coupling (COSY)	306
2D homonuclear J-resolved spectroscopy	307
Expectations	311
References	311

Chapter 7

Applications of high-resolution solution NMR 315

Introduction	315
Determination of structure of the repeating unit	316
Determination of end-group structure	318
Nomenclature for end-group resonances of α -olefin- <i>co</i> -ethylene copolymers	319
Identification of end groups in PMMA at high field	321
Determination of branching in polyethylene.	322
Nomenclature for branch carbon resonances	323
Determination of crosslinking in polyethylene	327
Determination of thermal oxidation in polyethylene	330
Determination of stereoregularity of polymers	332
Nomenclature for NMR resonances for stereoregular polymers	332
Determination of directional isomerism in polymers	341
Nomenclature for regioisomerism	341
Regio-isomerism studies	343
Determination of copolymer structure	345
Compositional heterogeneity of copolymers as determined by NMR	348
Summary	350
References	350

Chapter 8

High-resolution NMR spectroscopy of solid polymers 353

Introduction	353
The dipolar-decoupling experiment (DD)	354
Heteronuclear decoupling using spin-locking techniques	357
Homonuclear decoupling using multipulse methods	358
Limitations of the dipolar decoupling process	359
Chemical-shift anisotropy (CSA) in solids	359
Basis of chemical-shift anisotropy	359
Description of chemical-shift anisotropy	361
Effect of chemical-shift anisotropy on line shapes	362
Experimental determination of the chemical-shift anisotropy	364
CSA for hydrogen nuclei in various environments	367
CSA for carbon nuclei in various environments	367

Effect of motion on chemical-shift anisotropy	367
Structural applications of chemical-shift tensors	371
CSA analysis of coal samples	371
CSA determination of crystallinity	372
CSA determination of orientation	374
The magic-angle spinning (MAS) experiment	375
Utility of MAS	375
Removal of chemical-shift anisotropy	377
Experimental implementation of cross-polarization	380
Dynamics of the CP experiment	381
Factors influencing cross-polarization	383
Cross-polarization as a tool for resonance assignments	384
The interrupted-dephasing CP experiment	385
Quantitative aspects of cross-polarization spectra	386
Quantitative applications of cross-polarization	387
Use of cross-polarization for separation based on mobility	388
The cross-polarization experiment for the study of polymer blends	389
Contributions to line broadening in solids	390
Line shapes: chemical-exchange effects	392
The grand experiment (MAS-DD-CP)	392
References	394
Chapter 9	
Applications of high-resolution solid-state NMR spectroscopy to polymers	397
Chemical shifts in the solid state	398
Chemical shift studies of vulcanization of rubbers	399
Chemical-shift studies of polymer conformation	401
The γ -gauche effect	402
Polyethylene	403
Chemical-shift determination of helical conformation	404
Polypropylene	404
Poly(1-butene)	410
Poly(oxyethylene)	410
Poly(ethylene terephthalate)	412
Poly(butylene terephthalate)	412
Polyesters	415
Polypeptides	416
Analysis of crosslinked systems by solid-state NMR spectroscopy	417
Thermosetting systems	417
Elastomeric materials	418
Epoxide systems	429
Solid state NMR studies of polymer blends	432
Molecular interactions between components of polymer blends	432
NMR of liquid crystal-polymer interactions	433
NMR spectroscopy of surface species	434
Summary and conclusions	438
References	438

Chapter 10

Mass spectrometry of polymers	441
Introduction	441
Correlation of mass spectra with molecular structure	443
MS instrumentation — how to make macromolecules fly!	444
Ion sources	444
Electron impact	445
Chemical ionization	446
Static secondary ion mass spectrometry	447
Fast atom bombardment	447
Field desorption/field ionization	448
Electrospray ionization	448
Laser desorption	449
Matrix-assisted laser desorption ionization (MALDI)	450
Photoionization	451
Mass analyzer	452
Magnetic sector	452
Quadrupole analyzer	453
Quadrupole ion trap analyzer	453
Time-of-flight MS	453
Fourier transform MS	456
Electrical detection	457
Data stations	457
Tandem mass spectrometry (MS/MS)	458
Pyrolysis-MS of polymers	458
Direct pyrolysis mass spectrometry	458
Pyrolysis-GCMS of polymers	459
Applications of mass spectrometry to polymers	460
Identification of polymeric systems	460
Identification of polymeric additives	460
Mass spectrometric determination of molecular weight and molecular weight distribution	462
Determination of polymer structure using mass spectroscopy	464
End group determination in polymers using MS	465
Nature of linkages between monomers in polymers	467
Characterization of copolymers	467
Characterization of block copolymers	472
Characterization of macrocyclic polymers	476
Expectations for the future	479
References	479
Subject index	481