

Cambridge University Press

978-0-521-03172-1 - Nuclear Magnetic Resonance in Solid Polymers

Vincent J. McBrierty and Kenneth J. Packer

Table of Contents

[More information](#)

Contents

<i>Preface</i>	page xv
<i>Acknowledgements</i>	xviii
<i>Glossary of terms</i>	xix
1 The NMR of solid polymers: an overview	
1.1 The nature of polymers	1
1.2 The role of NMR	2
1.3 Structural considerations: a model for the polymer	5
1.4 Molecular motion: an overview	8
1.5 Comparison with other relaxation experiments: transition maps	11
2 Basic concepts in NMR	
2.1 Nuclear magnetisation	16
2.2 The radiofrequency (rf) field	19
2.3 Rf pulses and nuclear magnetic relaxation	22
2.4 NMR signals: the free induction decay (FID)	23
2.5 Spin temperature	26
2.6 Spin couplings, lineshapes and motional averaging	29
2.6.1 Spin couplings	30
2.6.1.1 Magnetic dipole-dipole coupling	30
2.6.1.2 Magnetic shielding	33
2.6.1.3 Nuclear electric quadrupole coupling	35
2.6.2 Motional averaging	36
2.7 Spin-lattice relaxation and motion	38
2.7.1 Dipolar relaxation between like spins	39
2.7.2 Dipolar relaxation between unlike spins	44
2.7.3 Relaxation due to electric quadrupole interactions	48
2.8 Summary	49
3 Nuclear spin interactions	
3.1 General considerations	51

Cambridge University Press

978-0-521-03172-1 - Nuclear Magnetic Resonance in Solid Polymers

Vincent J. McBrierty and Kenneth J. Packer

Table of Contents

[More information](#)

x

Contents

3.2	Coordinate systems	52
3.3	General expression for the internal Hamiltonians	54
3.3.1	The chemical shift	54
3.3.2	Nuclear quadrupole interactions	55
3.3.3	Dipolar interactions	56
3.4	Spectral lineshapes	57
3.5	Moments of rigid spectral lineshapes	59
3.5.1	Moments expansion of the FID	62
3.6	Effects of motion on spectra	63
3.6.1	Rotation about an axis and magic-angle spinning	64
3.6.2	Rotational spin echoes in solids	65
3.6.3	Rapid rotation about an arbitrary molecular axis	66
3.6.4	Some idealised motions encountered in polymers	67
3.7	NMR relaxation in solids	69
3.7.1	Dipolar relaxation in solids	69
3.7.2	Distribution of correlation times	71
3.8	Spin diffusion	73
3.8.1	Off-resonance experiments	76
3.8.2	Dilute spin systems	76
3.8.3	Diffusion-limited relaxation	77
3.8.4	Geometrical considerations	78
3.8.5	Relaxation to paramagnetic centres	78
3.9	Overview and summary	81
4 Experimental methods		82
4.1	Spectrometer characteristics	83
4.2	NMR probes for solids	86
4.3	Sample-spinning devices	88
4.4	Pulse sequences	90
4.4.1	Single-resonance experiments	90
4.4.1.1	Single-pulse determination of spectra	90
4.4.1.2	Spectral moments	93
4.4.1.3	Spin-echo experiments	93
4.4.1.4	Spin-lattice relaxation experiments	95
4.4.2	Double-resonance experiments	102
4.4.2.1	Single-pulse excitation (SPE)	102
4.4.2.2	Cross polarisation (CP)	103
4.4.2.3	Dipolar dephasing/non-quaternary suppression (NQS)	106
4.4.2.4	Delayed contact and related experiments	108
4.4.2.5	Dilute-spin spin-lattice relaxation	109
4.4.2.6	Factors affecting resolution	110

Cambridge University Press

978-0-521-03172-1 - Nuclear Magnetic Resonance in Solid Polymers

Vincent J. McBrierty and Kenneth J. Packer

Table of Contents

[More information](#)

<i>Contents</i>	xi
-----------------	----

4.4.2.7 Factors affecting quantitative measurements	115
4.5 Multidimensional NMR in solids	118
4.5.1 Two-dimensional NMR in solids	118
4.5.2 Three-dimensional NMR in solids	122
5 Structure and motion in solid polymers	124
5.1 Introduction	124
5.2 High-resolution ^{13}C NMR spectroscopy of solid polymers	126
5.2.1 ^{13}C Chemical shifts in solid polymers	127
5.2.1.1 Conformational effects	127
5.2.1.2 Crystallographic effects	131
5.3 NMR structural investigations of solid polymers	133
5.3.1 Cellulose and its derivatives	133
5.3.2 Tacticity of solid poly(vinyl alcohol)	135
5.3.3 The structure of insoluble polymeric resins	137
5.3.4 Structural heterogeneity	145
5.3.5 Specialist methods for structure determination	150
5.4 Molecular motions in solid polymers	153
5.4.1 Poly(ethylene terephthalate) and related polymers	156
5.4.2 Polystyrenes	165
5.4.3 Polycarbonates	174
5.4.4 Polyethylene	179
5.4.5 Poly(vinylidene fluoride)	187
5.4.6 Epoxy polymers	188
6 Structural heterogeneity in polymers	191
6.1 Experimental probes of heterogeneity: an overview	191
6.2 NMR as a structural probe	194
6.2.1 Spin diffusion and structural heterogeneity	195
6.3 Nature of the interface	202
6.4 Heterogeneity in homopolymers	206
6.4.1 Polyethylene	207
6.4.2 Poly(ethylene terephthalate)	211
6.5 Amorphous–amorphous polymer blends	213
6.5.1 Modified polystyrene–methacrylate systems	214
6.5.2 Poly(vinyl chloride)–poly(methyl methacrylate)	216
6.5.3 Polystyrene–poly(vinyl methyl ether)	218
6.5.4 Poly(ethylene terephthalate)–bisphenol A polycarbonate	223
6.6 Amorphous–crystalline polymer blends	223
6.6.1 Poly(vinyl chloride)–poly(ϵ -caprolactone)	223
6.6.2 Poly(vinylidene fluoride)–poly(methyl methacrylate)	226

Cambridge University Press

978-0-521-03172-1 - Nuclear Magnetic Resonance in Solid Polymers

Vincent J. McBrierty and Kenneth J. Packer

Table of Contents

[More information](#)

xii

Contents

6.7	Crystalline–crystalline polymer blends	227
6.7.1	Polyethylene–polypropene	228
6.8	Block copolymers	228
6.8.1	Polystyrene–polybutadiene–polystyrene	229
6.8.2	Polyurethanes	231
6.9	Polymer–diluent systems	233
6.9.1	Plasticised poly(vinyl chloride)	234
6.9.2	Plasticised d ₈ -poly(methyl methacrylate)	235
	7 Oriented polymers	238
7.1	Introductory remarks	238
7.2	Nature of the distribution	240
7.2.1	Symmetry considerations	240
7.2.2	Theoretical distribution functions	243
7.3	NMR of oriented polymers	244
7.3.1	Dipolar linewidth studies	245
7.3.2	Chemical shift anisotropy	247
7.3.3	Quadrupole lineshape analysis	249
7.3.4	Analysis of two-dimensional MAS spectra	251
7.4	Orientation in polyethylene	251
7.5	Orientation in polytetrafluoroethylene	258
7.6	Orientation in poly(ethylene terephthalate)	262
7.7	Polymer liquid crystals	265
7.8	Secondary local probes of orientation	267
	8 Selected topics	269
8.1	Network systems	269
8.1.1	Filled elastomers	270
8.1.1.1	Siloxane–silica systems	270
8.1.1.2	Carbon black–elastomer systems	272
8.2	Water in polymers	277
8.3	Ionomers	284
8.4	Electrically active polymers	288
8.4.1	Conducting polymers	288
8.4.1.1	Doped and undoped polyacetylene	290
8.4.2	Piezoelectric polymers	291
8.4.3	Ferroelectric polymers	295
	<i>Appendix 1 Data on common polymers</i>	297
	<i>Appendix 2 The rotation operator</i>	303
	<i>Appendix 3 Rotation of tensors between coordinate frames</i>	307

Cambridge University Press

978-0-521-03172-1 - Nuclear Magnetic Resonance in Solid Polymers

Vincent J. McBrierty and Kenneth J. Packer

Table of Contents

[More information](#)

<i>Contents</i>	xiii
<i>Appendix 4 Spatial distribution of structural units in a polymer</i>	308
<i>Appendix 5 The internal Hamiltonian</i>	309
<i>Appendix 6 Spectral lineshapes</i>	312
<i>Appendix 7 Analysis of spinning sidebands</i>	314
<i>Bibliography</i>	316
<i>References</i>	320
<i>Author index</i>	337
<i>Subject index</i>	342