This book is an authoritative and comprehensive account of the principles and practice of modern NMR spectroscopy of solids as applied to polymeric materials.

NMR spectroscopy has been applied to the characterisation of polymers in the solid state for over 40 years. The past two decades have seen the development of many new NMR capabilities, including high-resolution techniques for solids, multidimensional methods, deuterium NMR and others. All of these developments have contributed to a dramatic increase in the power and applicability of NMR for the characterisation, at a molecular level, of the dynamics and structural organisation of polymeric solids.

This book is intended for polymer physicists, chemists and materials scientists. The emphasis of the applications chapters (5–8) is on polymer types and properties to make it more accessible to this audience. To help those with little knowledge of NMR the authors have included an introduction to the main principles of the technique involved in its application to solid polymers. Those more knowledgeable on the subject will find that rigorous and detailed analytical treatments are also available, often in appendices.

All research workers, whether graduate students beginning their studies or established professionals, with a concern for polymer characterisation and the relationship between structure, dynamics and function for these materials will find this book of value in their work.

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Cambridge University Press
978-0-521-03172-1 - Nuclear Magnetic Resonance in Solid Polymers
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NUCLEAR MAGNETIC RESONANCE IN SOLID POLYMERS

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CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

Cambridge University Press
The Edinburgh Building, Cambridge CB2 2RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521301404

First published 1993
This digitally printed first paperback version 2006

A catalogue record for this publication is available from the British Library

Library of Congress Cataloguing in Publication data

McBrierty, Vincent J.
Nuclear magnetic resonance in solid polymers/by Vincent J.
McBrierty and Kenneth J. Packer.
p. cm. – (Cambridge solid state science series)
Includes bibliographical references and indexes.
ISBN 0-521-30140-8 (hc)
1. Polymers – Analysis. 2. Nuclear magnetic resonance
spectroscopy. I. Packer, K. J. II. Title. III. Series.
QD139.P6M38 1993
668.4′2–dc20 92-45158 CIP

ISBN-13 978-0-521-30140-4 hardback
ISBN-10 0-521-30140-8 hardback

ISBN-13 978-0-521-03172-1 paperback
ISBN-10 0-521-03172-9 paperback

Dedicated to Kay and Christine for their
patience and support throughout

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Preface

Since its inception, nuclear magnetic resonance (NMR) has been used with remarkable success to investigate polymeric materials. However, application to solid polymers was for many years largely the province of physicists and physical chemists because of the need for specialised spectrometers to gain access to the broad spectra (usually ^{1}H) typical of solids, and because interpretation of these spectra and associated relaxation times required theoretical models of a strongly physical nature. The chemist, meanwhile, was more than satisfied to exploit the enormous potential provided by the increasing power of liquid-state NMR spectroscopy which had benefited considerably from the introduction of Fourier transform (FT) methods, the availability of higher fields generated by superconducting magnets with concomitant enhanced sensitivity, formidable on-line computing capabilities, and the added flexibility of multidimensional NMR. The rich site-specific information in high-resolution liquid-state NMR remained undetected in early solid-state spectra because of the dominant dipolar contribution. Sustained efforts to achieve comparable results for solids led to procedures to suppress dipolar contributions using high-power decoupling techniques, sample spinning and the application of ingenious pulse sequences. Today the full power of high-resolution one-, two- and three-dimensional NMR is available for solid materials, albeit requiring more sophisticated experimentation and analysis. Specifically, multidimensional NMR permits different spin interactions to be correlated or separated, exchange between different states of a resonant nucleus to be monitored over selected timeframes and the intricacies of complex molecular motions to be elucidated.

These developments initially centred on ^{13}C NMR, having circumvented difficulties of low natural abundance. Refinements in ^{2}H NMR have since added rich site-specific detail. The latest generation of spectrometers have access to a wide range of resonant nuclei and experiments on a relatively routine basis. Aside from constraints of time, high-resolution NMR of both liquids and solids may now be carried out on essentially the same spectrometer system.

Our intention is to provide the polymer scientist of whatever discipline with a view of what NMR is about, why and how it can be applied usefully to solid polymers and what practical information may be extracted from NMR experiments. The method has many unique attributes beyond merely complementing and supporting other methods in examining polymer properties such as chain chemistry, conformation, packing, orientation and dynamics; but NMR is a form of coherent spectroscopy and, as such, requires somewhat more investment of effort on the part of the newcomer to appreciate fully its scope and capability. Such effort will reveal a remarkable flexibility of application in diverse areas of science, not least those of polymer physics and chemistry.

The book primarily addresses the needs of the polymer scientist who is not a specialist in NMR and, consequently, the approach is more pedagogical than definitive. It does not focus exclusively on the most informative NMR experiments since they are often the most demanding and sophisticated and so are not readily accessible to the routine user. On the one hand, the various transitions in the polymer may be established using fairly conventional NMR methods to give much useful information of a practical nature. On the other, the maximum available information on the underlying molecular dynamics can require state-of-the-art procedures available only in the most advanced and specialist NMR laboratories.

With this in mind, Chapter 1 presents a broad overview of the versatility of the technique in the context of solid polymers while Chapters 2 and 4 introduce the reader to the prerequisite concepts and experimental procedures. For those who wish to delve more deeply into the fundamentals of NMR, Chapter 3 examines in more detail the key spin interactions used to probe the local structure and dynamics in solid polymers. The approach exploits the elegance of rotation matrices but in a way that does not compromise the needs of those merely interested in practical application. Expressions essential for data interpretation and analysis are cast in Cartesian representation in the main text and may be used directly without recourse to the formal derivations which are treated separately in the appendices. The remaining chapters are organised around polymer properties rather than the isotopes generally used in NMR experiments which often serve to delineate specific competences and interests in the published literature. This approach is more in keeping with the intended spirit of the book. These chapters cover structure and motion (Chapter 5), heterogeneity (Chapter 6), and orientation (Chapter 7). The final chapter 8 selects a number of specialist topics which demonstrate further the diversity of NMR applications. A glossary of NMR terms along with useful information on polymers referred to in the book are included.

Acknowledgements

It is a pleasure to acknowledge Dr Dean Douglass's sustained advice and inspiration. We are grateful also to Heather Browne, Elaine Kavanagh and Michelle Gallagher who typed the manuscript. Thanks are due to John Kelly and Vincent Weldon for the artwork and photography. Finally, the support and assistance of Edward and Gwen Morgan during the preparation of the book are gratefully acknowledged.

Glossary of terms

$90_{x'}, 180_{y'} \ldots$	rf pulses producing rotations of 90°, 180° etc., about the x', y' ... axes of the rotating reference frame
ADRF	Adiabatic demagnetisation in the rotating frame
ADC	Analogue-to-digital convertor
$\mathbf{B}_0$	Large, static, polarising magnetic field
$\mathbf{B}_{1i'}$	radiofrequency (rf) field along the i' axis of the rotating reference frame
$\mathbf{b}_{z'}$	effective z' magnetic field in the rotating reference frame
$\mathbf{B}_e$	effective rf field in the rotating reference frame
$\mathbf{B}_{loc}$	local magnetic field, for example, dipolar
β_0	angle between principal symmetry axis of spin coupling tensor and the external field $\mathbf{B}_0$
B_{1I}	amplitude of B_1 field applied to spins I
CP	cross polarisation: double irradiation method for magnetisation transfer between unlike spins
C	Curie constant
CW	Continuous wave: NMR detected by sweeping B_0/ω_0
CPMAS	Cross polarisation/magic-angle spinning experiment for obtaining high-resolution spectra from solids
CORD	Three-dimensional NMR experiment in solids which Correlates ORder and Dynamics
CRAMPS	Combined Rotation and Multiple Pulse experiments to determine (usually) isotropic chemical shift NMR spectra of homonuclear dipolar-coupled spins in solids
CSA	Chemical shift anisotropy
DD	Dipolar decoupling: strong resonant irradiation of one species of spin to remove its dipolar coupling effects from NMR spectra
$D(\Omega)$	Wigner operator
$D^{(l)}_{mn}(\Omega)$	Wigner rotation matrix elements
D_S	Spin diffusion coefficient
DRSE	Dipolar rotational spin echo experiment for determining heteronuclear dipolar lineshapes in solids
DSC	Differential scanning calorimetry
ΔE	Activation energy
eQ	nuclear electric quadrupole moment

eq	electric field gradient at nucleus
EFG	electric field gradient
η	asymmetry parameter of a tensor spin interaction
$\bar{\eta}$	effective asymmetry parameter after averaging over specific motions
FID	free induction decay signal
$F_n(t)$	time dependent function of lattice variables (n labels the component of the tensor)
FT	Fourier transformation
γ	nuclear magnetogyric ratio
$G(t)$	FID signal
$G^n(t)$	time correlation function of spin coupling interaction tensor (n labels the tensor component)
$\mathscr{H}_D$	dipole–dipole spin coupling Hamiltonian
$\mathscr{H}_{CS}$	magnetic shielding (chemical shift) Hamiltonian
$\mathscr{H}_Q$	nuclear electric quadrupole coupling Hamiltonian
$\mathscr{H}_{rf}$	rf field Zeeman coupling Hamiltonian
$\mathscr{H}_J$	indirect (scalar) spin coupling Hamiltonian
$\mathscr{H}_{SR}$	spin–rotation coupling Hamiltonian
$\mathscr{H}_Z$	Zeeman interaction Hamiltonian for $\mathbf{B}_0$
$\mathscr{H}'(t)$	zero-average, time-varying coupling Hamiltonian
I/I_Z	nuclear spin angular momentum quantum numbers
$\mathbf{I}/\mathbf{I}_Z$	nuclear spin angular momentum operators
$I(\omega)$	NMR spectrum
$\mathbf{I}^{+/-}$	raising/lowering spin angular momentum operators
I_{MN}	spinning sideband intensities in two-dimensional NMR spectra of solids
$I(\tau_c)$	distribution of correlation times τ_c
$J(\omega)$	power spectrum of a time-dependent spin coupling
$J^n(n\omega_0)$	power spectrum of the nth component of a fluctuating tensor coupling at frequency $n\omega_0$
LFSLR	laboratory frame spin–lattice relaxation
$\bar{\mathbf{M}}_n$	number average molecular weight
$\bar{\mathbf{M}}_w$	weight average molecular weight
MAS	magic-angle spinning
μ	nuclear magnetic moment
$\mathbf{M}$	nuclear magnetisation vector
M_0^I	equilibrium value of nuclear magnetisation of ensemble of I spins
$M_i^{eq}(i = x, y, z)$	laboratory frame components of $\mathbf{M}_0$
$M_{i'}(i = x', y', z')$	components of nuclear magnetisation in the rotating reference frame
m	quantum number for the z-component of spin (see I_Z)
$M_n(\omega)$	nth moment of a spectrum
$M(t)$	time-dependent nuclear magnetisation
MREV-8	an eight-pulse cycle sequence for obtaining high-resolution spectra from homonuclear dipolar-coupled spin systems in solids
ν_c	correlation frequency of a motion $(= 2\pi\tau_c)^{-1}$
NOE (F)	nuclear Overhauser enhancement (factor)
NQS	non-quaternary suppression (dipolar dephasing) experiment for obtaining NMR spectra in solids of dilute spins with weak

	dipolar couplings to abundant spins (for example, quaternary ^{13}C spins)
ω_0^I	precession frequency of nuclear spin I in field $\mathbf{B}_0$
Ω	apparent precession frequency of spins in the rotating reference frame
ω_e	precession frequency of spins about $\mathbf{B}_e$ in the rotating reference frame
ω_Q	quadrupole coupling energy expressed as a frequency
$\Omega_i(\alpha\beta\gamma)$	Euler rotation angles
ω_r	angular frequency of sample rotation
$\omega_1(=\gamma B_1)$	precession frequency of spins about on-resonance $B_1(\omega)$ field in the rotating reference frame
ω_{MAS}	angular frequency of sample rotation about an axis making an angle θ_m with respect to $\mathbf{B}_0$
PAS	principal axis system
$P_l(\cos\beta)$	Legendre polynomial of order l
$P(\Omega)$	orientation distribution in an oriented polymer
Q	quality factor of rf tuned circuit or component
r_{CH}	carbon–hydrogen internuclear distance
R_1	spin–lattice relaxation rate in the laboratory frame
$R_{1\rho}$	spin–lattice relaxation rate in the rotating reference frame
R_2	transverse spin relaxation rate
$R_1^{II/SS}$	homonuclear relaxation rates arising from dipole–dipole coupling
$R_1^{IS/SI}$	heteronuclear relaxation rates arising from dipole–dipole coupling
RFSLR	rotating frame spin–lattice relaxation (see $T_{1\rho}$, $R_{1\rho}$)
RAD	rotational angular distribution function for motions in solids
σ	magnetic shielding tensor
$\sigma_{ii}(i = 1, 2, 3)$	principal components of σ
$\sigma_{\parallel/\perp}$	principal components of σ for axial symmetry
$\tilde{\sigma}$	isotropic shielding constant
σ_{zz}	component of σ along the field $\mathbf{B}_0$
$\bar{\bar{\sigma}}$	shielding tensor in rotor frame
$\sigma^{(R)}$	shielding tensor averaged over fast motions about axis R
$S(\omega)$	NMR spectrum
$S(t)$	NMR signal in the time domain: FID (see $G(t)$)
$S(\Omega_1, \Omega_2)$	Two-dimensional NMR spectrum
$S(t_1, t_2)$	time domain signal which Fourier transforms to $S(\Omega_1, \Omega_2)$
SPE	single-pulse excitation: experiment which relies on dilute spin T_1 to produce magnetisation
SLR	spin–lattice relaxation (see T_1, R_1 etc.)
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SSB	spinning sideband
τ_c	correlation time
T_g	glass transition temperature
θ	angle of $\mathbf{B}_e$ with respect to z' axis in rotating reference frame
θ_p	rotation produced by an rf pulse
θ_m	magic angle $(\cos^{-1}(3)^{-\frac{1}{2}}) = 54.7°$
t_p	duration of rf pulse
T_2	transverse or spin–spin relaxation time

T_1	laboratory frame spin–lattice relaxation time
$T_{1\rho}$	rotating frame spin–lattice relaxation time
T_L	lattice temperature
T_S	spin temperature
T_{CR}	cross-relaxation time
$T_{CH}^{(SL)}$	cross-relaxation time between ^{13}C and ^{1}H spins under matched Hartmann–Hahn spin-locked cross polarisation
$T_{21t/ht}$	transverse relaxation times at temperatures below/above a linewidth transition
T_R	recycle (repetition) time of a pulse sequence
t_D	dwell time: interval between successive digitisation of a time-varying signal
T_{AQ}	acquisition time
τ	general time interval in an NMR pulse sequence
τ_D	dipolar dephasing time in an NQS experiment
TOSS	total sideband suppression experiment to eliminate spinning sidebands from MAS spectra
t_m	mixing time – often in a multidimensional NMR experiment or in studies of spin diffusion
$\langle T_j(^{13}C)\rangle$	average spin–lattice relaxation time ($j = 1, 1\rho$) for ^{13}C spins
X, Y, Z	axis labelling for the laboratory frame of reference
X_0, Y_0, Z_0	axis labelling for the sample-fixed coordinate system
x, y, z	axis labelling for the molecule-fixed coordinate system