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NMR Spectroscopy of Polymers

With 110 Figures and 43 Tables

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Preface

Nuclear magnetic resonance (NMR) spectroscopy is one of the most widely and frequently used methods for structure analysis in chemical research. So many books and monographs on NMR spectroscopy have been published aiming at the fundamental understanding as well as the practical applications especially to organic chemistry and biochemistry. Polymer chemistry has also been benefited from NMR spectroscopy but in a somewhat different and specialized manner, such as tacticity determination, monomer sequence analysis of copolymers, analysis of end groups and irregular linkages, and chain dynamics of polymers and so on. Therefore another NMR book which is oriented to practical use of the spectroscopy in polymer chemistry should be added to the list of NMR text books.

This book places emphasis on the practical use of NMR spectroscopy in polymer chemistry rather than on the theoretical treatments. In the first chapter, after the description of fundamental aspects of NMR spectroscopy, experimental problems such as preparation of sample solutions, selection of the solvent, internal standards and tubing, and contaminants in the sample solution are discussed. The second chapter is devoted to discussion on the accuracy and precision of NMR measurements, since a much higher degree of accuracy and precision is required in the analysis of polymer structures, such as tacticity, copolymer composition, and chain-end structures. This chapter also includes the explanation of the coaxial tubing method, which is very useful for quantitative analysis and determination of volume magnetic susceptibility by NMR.

Chapters 3–5 describe structural analysis of polymers, dealing with the stereochemistry of polymer chains (Chap. 3), chemical composition and comonomer sequence distribution in copolymers including diene polymers (Chap. 4), and end groups and irregular linkages (Chap. 5). The analysis of polymerization reactions by NMR and the relationship between chemical shift and reactivity for vinyl monomers are also described in Chap. 5. This information is quite useful for the understanding of polymerization reaction, and is discussed in this connection.

Two-dimensional NMR spectroscopy is introduced in Chap. 6 with examples of the application to polymer and oligomer analysis, including conformational analysis of methyl methacrylate oligomers.

NMR spectroscopy is also a powerful tool for the investigation of polymer chain dynamics in solution by the aid of NMR relaxation parameters, including T_1 and nuclear Overhauser enhancement (NOE). The problem is discussed in Chap. 7,

in which the precision and effect of experimental conditions in the determinations of relaxation times and NOE are discussed.

Combined use of spectroscopy and chromatography is one of the promising trends in analytical chemistry and thus we add one chapter (Chap. 8) describing on-line coupled size-exclusion chromatography (SEC)/NMR spectroscopy in which an NMR spectrometer is set in the SEC system as a detector. The system allows fast and facile determinations of the molecular weight dependence of polymer characteristics, such as tacticity and copolymer composition as well as the molecular weight itself.

The authors strongly hope that the basics in NMR measurements described in this book will be helpful and useful for many NMR users as well as newcomers to the field of NMR. An well-ordered index and a list of abbreviations are appended for the reader's convenience.

The contents of this book largely come from the authors' experiences in research work in polymer chemistry carried out at the Faculty of Engineering Science, Osaka University, where one of the authors (K.H.) first encountered a 100 MHz NMR spectrometer in 1965. The NMR research in the Faculty of Engineering Science has been cultivated by collaboration with the faculty members who have been actively involved in obtaining high-quality NMR data from time to time: Mr. Yoshio Terawaki (since 1965), Mr. Hiroshi Okuda (since 1968), and Dr. Koichi Ute (since 1985). Thus our most sincere thanks should be extended first to these people. We are particularly grateful to Mr. Terawaki, who has devoted himself to collecting NMR data for this book and also in assisting in the preparation of the manuscript.

The authors are also indebted to people who participated in round-robin tests on polymer samples which were organized by the Research Group on NMR, the Society of Polymer Science, Japan, the outcomes of which constitute important parts of several chapters in this book. K.H. is particularly grateful to Professor Riichiro Chûjô and Professor Yasuyuki Tanaka, who were the cofounders with K.H. of the research group, for their continuous encouragement and friendship.

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K. Hatada
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List of Symbols and Abbreviations

ADC	analogue-to-digital converter
AIBN	azobis(isobutyronitrile)
AN	acrylonitrile
B_0	static magnetic field
B_1	radio frequency field
BF	broadening factor
BPO	benzoyl peroxide
BuMA	*n*-butyl methacrylate
COM	complete decoupling condition
COSY	correlation spectroscopy
CW	continuous wave
DEPT	distortionless enhancement of polarization transfer
DMSO	dimethyl sulfoxide
DP	degree of polymerization
DQF-COSY	double-quantum filtered correlation spectroscopy
DSS	4,4-dimethyl-4-silapentane sulfonate
EMA	ethyl methacrylate
EPDM	ethylene–propylene–(2-ethylidene-5-norbornene) terpolymer
$Eu(fod)_3$	tris[1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctanedionato(4,6)]-europium(III)
$Eu(tfmc)_3$	tris[(3-trifluoromethylhydroxymethylene)-(+)-camphorato]-europium(III)
FID	free induction decay
FT	Fourier transform
GPC	gel permeation chromatography, size exclusion chromatography (SEC)
h	Planck constant
HETCOR	heteronuclear chemical shift correlation spectroscopy
HFA	hexafluoroacetone
HMBC	heteronuclear multiple-bond correlation spectroscopy
HMDS	hexamethyldisiloxane
HMDS'	hexamethyldisilane
HMQC	heteronuclear multiquantum correlation spectroscopy
HPLC	high-performance liquid chromatography
HSC	heteronuclear shift correlation spectroscopy
HSQC	heteronuclear single-quantum correlation spectroscopy
I	nuclear spin
INADEQUATE	incredible natural abundance double quantum transfer experiment
J	spin–spin coupling constant
k	Boltzmann constant

M	magnetization vector
m	magnetic quantum number
m diad	meso diad
MMA	methyl methacrylate
Mn	number-average molecular weight
MWD	molecular weight distribution
N	number of data points
NMR	nuclear magnetic resonance
NNE	gated decoupling mode with suppression of NOE
NOE	nuclear Overhauser enhancement
NOESY	2D nuclear Overhauser enhancement spectroscopy
$N_\alpha(N_\beta)$	number of α spins (β spins) (α: lower-energy state, β: upper-energy state)
OMTS	octamethylcyclotetrasiloxane
PEMA	poly(ethyl methacrylate)
PMMA	poly(methyl methacrylate)
PMVE	poly(methyl vinyl ether)
ppm	parts per million
r	racemo diad
RF	radio frequency
r_1, r_2	monomer reactivity ratios
RI	refractive index
S/N	signal-to-noise ratio
SEC	size-exclusion chromatography, gel permeation chromatography (GPC)
SPSJ	Society of Polymer Science, Japan
T_1	spin–lattice relaxation time
T_2	spin–spin relaxation time
THF	tetrahydrofuran
TMS	tetramethylsilane
TSP-d_4	sodium [2,2,3,3-d_4]3-trimethylsilylpropanoate
VPO	vapor pressure osmometry
WET	water suppression enhanced through T_1 effects
wt/vol%	weight of sample (g)/volume of solution (ml) %
γ	gyromagnetic ratio
δ	chemical shift (ppm)
μ	nuclear magnetic moment
υ	frequency
σ	shielding constant
σ	standard deviation
τ_c	correlation time
χ	volume magnetic susceptibility
ω	angular frequency

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