

MULTIDIMENSIONAL SOLID-STATE NMR AND POLYMERS

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Preface

Another book on NMR spectroscopy: why? As in other fields of science, NMR of polymers is divided into two major areas. From the chemist's point of view, high-resolution NMR provides detailed information about the chain microstructure in solution and is an indispensable tool of polymer chemistry. From the materials science point of view, many of the macroscopic properties of polymers arise from the organization of macromolecules in the bulk. Therefore, experimental techniques like solid-state NMR are needed that can characterize the behaviour of polymers on a molecular level and on mesoscopic scales in order to relate it to the macroscopic properties. However, contrary to the situation in liquids, where the detailed information about chain microstructure as available from high-resolution NMR is unique, solid-state NMR competes with well-established techniques, such as light, X-ray, or neutron scattering, electron microscopy, and dielectric or mechanical relaxation. In order to compete favourably with these techniques, the potential of solid-state NMR has to be fully exploited.

This calls for multidimensional methods, which increase the spectral resolution and, therefore, the selectivity, but also provide routes to new information not accessible from 1D spectra even in the limit of high resolution. Whereas excellent monographs exist on high-resolution NMR in liquids and in solids as well as on two-dimensional NMR in general, a book on multidimensional solid-state NMR is not available. Substantial progress has been achieved in this area in recent years, in particular as far as the elucidation of molecular dynamics of polymers is concerned. This provided the impetus for our endeavour. When thinking of an outline, it quickly became apparent that the book will address a heterogeneous audience with backgrounds in polymers and spectroscopy. Therefore, we expanded the scope to include basic and advanced material of solid-state NMR (Chapters 2 and 3), Fourier theory (Chapter 4), and polymer science (Chapter 5), before we systematically discuss multidimensional separation and correlation experiments in Chapter 6. The primary aim of our monograph is molecular dynamics and multidimensional NMR techniques designed to unravel its different aspects; these are treated in the central Chapters 7–11. The book is concluded by addressing two other important aspects of macromolecular organization in the solid state, namely chain alignment in partially ordered systems (Chapter 12) and domain sizes in heterogeneous polymers (Chapter 13).

Although we restrict ourselves to discussing applications of multidimensional NMR to synthetic polymers, it is obvious that the techniques described here are equally applicable to many problems in solid-state physics, chemistry, materials science and notably, biophysics. The reader will quickly find out that different chapters are written on rather different levels, descriptive and technical or mathematical ones. Our intention was to generate a text that, first of all, is useful for many. Applying sophisticated spectroscopic techniques in an interdisciplinary area like polymer science inevitably involves use of concepts from different fields of science. More specifically, rather subtle aspects of quantum mechanics, statistical mechanics, signal processing,

and chemistry are involved. It is our experience that newcomers to the field often are 'overqualified' concerning some but have severe difficulties in other aspects. It is for this reason that we have included details which will seem trivial to many but will hopefully be appreciated by others. For the same reason we sometimes use simplification which the specialists might find hard to accept, but will hopefully help readers with different backgrounds to follow. In all cases we emphasize those aspects which are most important for our specific applications at the expense of generality. Thus, we tried to give as many details as possible in order to provide a self-contained text which can be read without constantly being forced to consult the literature cited. However, this does not imply that our text should be taken as 'the last word' on the subjects treated.

The references are by no means intended to provide an exhaustive compilation of the relevant literature. In a rapidly developing area like multidimensional solid-state NMR this would be quickly outdated. Likewise, we often took the liberty of ignoring aspects of priority and did not cite pioneering work, if adequate descriptions are readily available in books or review articles. We apologize to all the authors affected by this procedure. For the reader's convenience we have included short titles of the papers in the citation, in order to indicate which aspect is actually treated in a particular reference. Moreover, at the beginning of each chapter keywords are listed as a guidance for the reader.

Our work on NMR of polymers has substantially benefited from the close contact and the advice of Professor Ulrich Haeberlen at the Max-Planck-Institute at Heidelberg and Professor Hans Sillescu at the University of Mainz. Therefore, special thanks are due to them for their continuous support and specifically for their helpful comments concerning individual chapters.

This book is based on the efforts of our research group during several years. It is our pleasure to acknowledge the contributions of a large number of co-workers, who participated in our program as staff members, PhD students, postdoctoral fellows or as visiting scientists, providing ideas, samples, hardware or software: Bernhard Blümich, Christine Boeffel, Ralf Born, Lothar Brombacher, Brad Chmelka, Joachim Clauss, Norbert Egger, Stefan Féaux de Lacroix, Ewald Günther, Alfred Hagemeyer, Michael Hansen, Gerard Harbison, Manfred Hehn, Jérôme Hirschinger, Sigmar Kaufmann, Julia Kornfield, Andrzej Kulik, Johannes Leisen, Volker Macho, Angela Ohlemacher, Ute Pawelzik, Claudia Schmidt, Jeremy Titman, Der-Lii Tzou, Stephan Wefing, Michael Werth, Manfred Wilhelm, Yuliang Yang, Karen Zemke. Two of our co-workers deserve special thanks: Haskell Beckham closely followed the actual writing and checked the manuscript at various stages. His advice on scientific and, not least, linguistic aspects was invaluable. Dieter Schaefer carefully proofread the whole work and removed inconsistencies both in the text and in the mathematics. Various sections have been improved after discussions with the Pines group in Berkeley, in particular Mei Hong thoroughly checked several chapters.

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NMR Acronyms and Abbreviations

List of NMR acronyms and abbreviations used in the text. Polymer acronyms are explained in Section 5.7.

Acronym	Full wording	Specific discussion: section(s)
ADC	Analog-to-Digital Converter	4.5
BR-24	pulse sequence by Burum and Rhim	3.3.1
CHF	Coupled Hartree-Fock technique	2.4.6
CORD	Correlation of ORder and Dynamics	12.6
СР	Cross polarization	3.2, 3.4.3
CRAMPS	Combined Rotation And Multiple-Pulse Spectroscopy	3.2
CS	Chemical Shift	2.4.1
CSA	Chemical-Shift Anisotropy	2.4.2
DANTE	Delays Alternating with Nutation for Tailored Excitation	3.8
DAS	Dynamic-Angle Spinning	3.10
DBM	Double-Balance Mixer	4.5.1
DD	Dipolar decoupling	6.2
DECODER	Direction Exchange with Correlation for Orientation-Distribution Evaluation and Reconstruction	12.7
deTOSS	time-reversed TOSS	3.9.4
DF	Director Frame	12.2
DFT	Discrete Fourier Transformation	4.2
DOR	DOuble Rotation	3.10
DRAMA	Dipolar Recovery At the Magic Angle	6.7.4
FFT	Fast Fourier Transformation	4.2
FID	Free Induction Decay	2.5.7
FT	Fourier Transformation	Chapter 4
fwhm	full width at half maximum	12.3.1
GIAO	Gauge-Invariant Atomic Orbitals	2.4.6
IGLO	Individual Gauge for Localized Orbitals	2.4.6
KWW	stretched exponential according to Kohlrausch, Williams, and Watts	8.1
LORG	Localized Orbitals/local oRiGin	2.4.6
LC	Liquid Crystal(line)	5.6
LF	Laboratory Frame	2.4.2

continued

Continued

Acronym	Full wording	Specific discussion: section(s)
MAS	Magic-Angle Spinning	2.4.4, 3.9
MF	Molecular Frame	12.2
MQ	Multiple-Quantum	3.12
NOE	Nuclear Overhauser Effect	3.13.2
OMAS	Off-Magic-Angle Spinning	2.4.4
PAS	Principal-Axes System	2.4.2, D.3
PASS	Phase-Altered Spinning Sidebands	6.5.3
REDOR	Rotational-Echo DOuble Resonance	6.6.5
RF	Rotor Frame	3.9, 12.2
rf	radio frequency	2.6
R^2	Rotational Resonance	13.5.7
SATRAS	SAtellite-TRansition Spectroscopy	3.10
SASS	Switching-Angle Sample Spinning	6.4.3, 6.6, 6.7.4
SAXS	Small-Angle-X-ray Scattering	13.3.4, 5.2
SELDOM	SELectivity by Destruction Of	3.8
	Magnetization	
SF	Sample(-fixed) Frame	2.4.2
SLF	Separated-Local-Field	6.6.1
S/N	Signal-to-Noise ratio	4.9
sync-MAS	rotation-synchronized MAS	12.4
$T_{ m g}$	Glass-transition temperature	5.3, 8.1
TOSS	TOtal Suppression of (Spinning) Sidebands	3.9.3
TPPI	Time-Proportional Phase Incrementation	4.5.1
VACSY	Variable-Angle Correlation SpectroscopY	6.4.3
VFT	temperature dependence according to Vogel, Fulcher, and Tammann	8.1
WHH-4	pulse sequence by Waugh, Huber, and Haeberlen	3.3.1
WAXS	Wide-Angle X-ray Scattering	12.7.3
WIM	Windowless Isotropic Mixing	3.4.3
WISE	WIdeline SEparations	6.6.2
WLF	temperature dependence according to Williams, Landel, and Ferry	8.1

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CHAPTER ONE

Introduction

1.1 Overview

It is one of the key goals of materials science to establish structure-property relationships, in order to improve known and design new materials. This holds in particular for synthetic polymers, whose materials properties depend on both the molecular structure and the organization of the macromolecules in the solid state: their phase structure, morphology, molecular order and molecular dynamics (Flory, 1953; Kroschwitz, 1990). Macroscopic as well as microscopic parameters are influenced by the processing that follows the chemical synthesis. This calls for powerful analytical tools that can probe these aspects in the material as it is used, predominantly in the solid state. The structural aspects are studied mostly by scattering techniques or by microscopy. Information about dynamic aspects are deduced mainly from scattering or relaxation experiments (McCrum *et al.*, 1967). Various spectroscopic techniques are also applied to solid polymers, in particular for determining their electronic structure.

Nuclear magnetic resonance (NMR) (Abragam, 1961; Slichter, 1980) is well established in structural characterization of liquids or compounds in solution, but much less so of solids (Fyfe, 1983; Bovey, 1988). Moreover, NMR offers numerous ways to study dynamic aspects over a large range of characteristic motional rates. The main advantage of NMR is its unprecedented selectivity. Thus it is desirable to exploit this technique for studying structure and dynamics of solid polymers (Komoroski, 1986). However, due to the presence of angular-dependent anisotropic interactions, the spectral resolution of solid-state NMR spectra is orders of magnitude lower than that of high-resolution NMR in liquids. Important improvements were achieved in the 1970s by combining high-speed mechanical rotation of the sample with ingenious manipulations of the nuclear spins such as multiple-pulse irradiation, high-power decoupling and cross polarization (Mehring, 1983). Moreover, two-dimensional and higher-dimensional NMR techniques (Jeener, 1971; Müller et al., 1975; Aue et al., 1976; Ernst et al., 1987) have been introduced that offer fundamental advantages. First, as in liquids, the introduction of a new frequency dimension provides a means to increase the spectral resolution. Even more important, multidimensional spectroscopy also provides routes to new information, unavailable from 1D spectra even in the limit of high resolution. Experiments can be designed which correlate different spin interactions providing different structural information, or relate various states taken up by the molecular unit during different time periods by exchange and in this way probe dynamic processes in real time.

Progress in multidimensional solid-state NMR has been hampered by experimental and conceptual difficulties, which have now been overcome. This introductory chapter briefly outlines some of the main concepts and illustrates the information available about polymer structure and dynamics through selected experimental examples. Chapters 2–4 review the principles of Fourier transform solid-state NMR. The purpose of these chapters is twofold. They should enable the newcomer to follow the book without being forced to work through other monographs on NMR beforehand. For readers with a strong NMR background, these chapters emphasize the concepts that are particularly relevant for the experiments described later. These chapters also contain important details that should be appreciated by those who perform (or plan to perform) such experiments.

The advances in multidimensional NMR can be exploited in many fields of physics, chemistry, materials science, and, last but not least, biology. This book emphasizes applications of multidimensional solid-state NMR to synthetic polymers. This reflects the specific interest of the authors, the need for improved analytical tools in order to adequately characterize these complex materials, and the fact that ample experimental examples are already available. The rather short Chapter 5 reviews some background information on structure and dynamics of polymers that is needed to appreciate the remainder of the text. It is followed by an overview of experiments for separation and correlation of spectral patterns in Chapter 6, which also points out differences between the main objectives of multidimensional liquid- and solid-state NMR. Experiments are discussed which offer means to determine bond lengths and orientations within the molecular framework; others correlate molecular structure and mobility.

Polymer dynamics is of central interest in our studies. Of the great variety of molecular motions possible in polymers (e.g. translations, rotations, vibrations), rotations have the most pronounced effects on NMR lineshapes and relaxation parameters. Thus, multidimensional NMR provides especially unique information about rotational motions. Their timescales are followed in real time over many orders of magnitude, covering in particular the regime of slow motions which govern the mechanical properties of polymers. Moreover, the higher-order correlation functions provided by multidimensional NMR yield previously inaccessible model-independent information about the geometry of rotational motions, the orientational memory of molecular units involved in complex dynamics, and the nature of nonexponential relaxation in disordered systems. This information collected for a variety of polymers should eventually lead to a better understanding of their mechanical and rheological behaviour, which is of interest not only for conventional but also for new advanced polymeric materials. The corresponding NMR techniques and examples concerning chain dynamics in crystalline and amorphous polymers are treated in Chapters 7-11 at various levels of sophistication. Chapters 7 and 8 address in particular readers with interest in polymers by giving a descriptive introduction to exchange NMR techniques, indicating their scope and presenting results on polymers, especially above the glass transition. In Chapter 9 the NMR techniques are explicitly compared to wellestablished scattering and relaxation experiments. Complex motions whose time dependencies cannot be described by single correlation times are treated in detail. Finally, the techniques for recording 2D exchange NMR spectra of solids as well as the algorithms developed for simulation and quantitative analysis of multidimensional NMR spectra are described in Chapters 10 and 11. Through numerous examples, these chapters should provide sufficient information not only to appreciate the unique information content of such spectra but also to actually perform the experiments.

Two other aspects are particularly important for establishing structure-property relationships for polymer materials, namely chain alignment in partially ordered systems and domain sizes in heterogeneous polymer materials. The orientation of macromolecular units is used to improve the properties of polymers for such different applications as high-tensile-strength fibres and nonlinear optical materials for information technology. Advanced polymer materials almost invariably consist of more than one component, which often leads to phase separation. Careful design of the molar ratios as well as size, composition, and morphology of the different phases offers a means to control the mechanical, electrical, and optical properties. Small domains that extend over only a few nanometers, as well as interfacial regions between the different phases, are particularly difficult to characterize. As described in Chapters 12 and 13, major advances have been achieved in these areas by introducing the concepts of multidimensional spectroscopy. The new solid-state NMR techniques nicely supplement well-established scattering and microscopic methods as demonstrated by various experimental examples and by explicit comparison.

The book addresses a heterogeneous audience with backgrounds in polymers and in spectroscopy. Therefore, most of its material is presented in two ways: a descriptive and a mathematical one. The text is self-contained in so far as most treatments start from obvious facts or first principles. More complex equations are followed by hints regarding the proofs or are at least justified in a heuristic fashion. Appendices are provided in which the mathematics and the physics needed to follow the derivations are collected. Also included is theoretical background which is readily available in principle but in practice often has been found to represent a problem to the beginner in solid-state NMR. Wherever possible, the discussion is based on geometric visualizations and principles rather than detailed analytical formulas. This applies for the various topics that are treated: the 'spin-operator gymnastics', the orientation dependencies of the NMR interactions, as well as the analysis of molecular dynamics, order, and structure. In many instances, analogies between multidimensional NMR spectroscopy and other techniques will be pointed out, and the information content of the corresponding spectra will be compared. For the study of dynamics, reference to relaxation techniques such as dielectric, dynamic-mechanical, or NMR relaxation is obvious. More surprisingly, 2D NMR exhibits a variety of analogies to scattering techniques such as quasielastic neutron scattering or wide- and small-angle scattering of neutrons and X-rays. It is hoped that these analogies will help the appreciation of the high information content of multidimensional solid-state NMR spectra.

1.2 Examples

Before starting the systematic treatment, a number of experimental examples are presented which address the various aspects and advantages of multidimensional NMR. Details of the experiments designed to record multidimensional NMR spectra are not given here, but are left to the later chapters. However, basic knowledge of the concept of two-dimensional (2D) Fourier spectroscopy (Aue *et al.*, 1976; Ernst *et al.*, 1987) is needed to read this section: A 2D NMR spectrum is generated by recording a two-dimensional data set following pulsed irradiation as a function of two time variables t_1 and t_2 and subsequent double Fourier transformation, as indicated in

Figure 1.1. The development of the nuclear spin system in the *evolution period* with the incremented time t_1 at the beginning of the pulse sequence provides the basis for the first frequency dimension ω_1 . The NMR signal is detected in the *detection period* with time t_2 at the end of the pulse sequence, providing the basis for the second frequency dimension ω_2 . In many 2D experiments, a *mixing period* separates the evolution and detection times. This mixing period of duration t_m is particularly important in exchange experiments, allowing for dynamic processes to take place between the measurement of the correlated frequencies ω_1 and ω_2 (for details see Chapters 6 and 7). The concept of 2D spectroscopy is readily extended to three and higher dimensions by inserting additional evolution and mixing times.

Let us first consider experiments which increase the spectral resolution of solid-state NMR spectra in order to characterize polymer structure in terms of chemical moieties on the basis of isotropic chemical shifts. The information from isotropic chemical shifts represents the most important feature of standard NMR techniques. The corresponding spectra make up one or two dimensions of many multidimensional experiments in which the chemical structure is correlated with other molecular properties such as mobility or order. In the solid state, the tensorial nature of the chemical shift makes the NMR frequency also depend on the orientation of the molecular unit under study with respect to the applied magnetic \mathbf{B}_0 field. Since the orientational dependence of the NMR frequency is comparable to or even larger than the variation of the isotropic chemical shifts of different structural units, the powder patterns resulting from the anisotropic chemical shifts severely overlap in all but the simplest polymer structures. Thus, in many cases a quantitative analysis is virtually impossible. The effect of the anisotropy can be removed by rapidly spinning the sample about an axis inclined at the 'magic angle' of 54.7° (magic-angle spinning, MAS). However, this is accompanied by a loss of the information about the molecular orientation, which is the basis of structural and dynamic information typical of the solid state. Thus, experiments are desired that retain this information without sacrificing spectral resolution.

This can be achieved by extension to a second frequency dimension. For instance, in a 2D spinning experiment the angle of the rotor axis is set to 54.7° in the detection and to 90° in the evolution time (Bax *et al.*, 1983). As displayed in Figure 1.2(a), the powder patterns for the chemically distinct sites are then recorded along the frequency dimension ω_1 and separated according to their respective isotropic chemical shifts, recorded along the frequency dimension ω_2 . In standard MAS experiments the spinner axis is kept at the magic angle. For moderate spinning speeds in the range of a few kHz, the anisotropic chemical shift is not 'spun out', but leads



Figure 1.1 Schematic representation of the generic two-dimensional NMR pulse sequence, with evolution time t_1 , mixing period t_m , and detection time t_2 . The frequencies ω_1 and ω_2 are correlated in the corresponding two-dimensional spectrum obtained by Fourier transformation with respect to t_1 and t_2 .



Figure 1.2 Separation of anisotropic-chemical-shift patterns by the isotropic chemical shifts. (a) 2D ¹³C NMR spectrum of *p*-dimethoxybenzene, recorded with flipping of the spinner axis (adapted from Bax *et al.*, 1983), (b) 2D ¹³C sideband MAS spectrum of the amino acid Tyr-HCI (adapted from Kolbert and Griffin, 1990).

to sideband patterns which may again overlap considerably and hamper a quantitative analysis. By ingenious spin manipulations through multiple-pulse sequences these sideband patterns can be removed from the spectrum in one dimension and retained in the other (Kolbert and Griffin, 1990). As shown in Figure 1.2(b), the crowded sideband patterns can nicely be separated in a second frequency dimension and can then be exploited to provide structural and dynamic information.

The dipole-dipole coupling, for instance between ¹H and ¹³C, or ¹H and ¹⁵N, provides valuable structural information. Since the C-H bond lengths are known, the measurements of dipolar splittings can be interpreted in terms of angles between individual bonds and the applied magnetic fields. For proteins, measurements of N-H bond lengths are of considerable interest because they vary due to hydrogen bonding and therefore contain important structural information. In order to be useful, the dipolar patterns have to be separated, however, according to the chemically distinct sites in a molecule or monomer unit as identified by their ¹³C or ¹⁵N chemical shifts. Since the dipolar couplings correspond to local fields, such experiments are often named 'separated local field' (SLF) experiments. Figure 1.3 displays two examples of SLF spectroscopy, both obtained by sample spinning techniques. In Figure 1.3(a), 13 C chemical shift/¹³C-¹H dipolar powder patterns for the three carbons of isotactic polypropylene are correlated in the 2D plane (Nakai *et al.*, 1989). From a quantitative analysis of such patterns, bond lengths and bond angles, as well as the orientations of the principal axes of the chemical-shift tensor in relation to structural units such as CH_2 groups can be determined. Such information is needed for a quantitative analysis of other experiments exploiting anisotropic chemical shifts. As shown in Figure 1.3(b), similar patterns can be generated based on MAS sidebands reflecting the dipolar couplings.

As stated above, multidimensional NMR provides especially interesting information about polymer dynamics. A long-standing method for a qualitative characterization of



Figure 1.3 Separated local field spectroscopy correlating heteronuclear dipole-dipole coupling with chemical shifts. (a) 2D ¹³C/¹H spectrum of isotactic poly(propylene) (adapted from Nakai *et al.*, 1989), (b) 2D ¹⁵N/¹H MAS sideband spectrum of the amino acid [¹⁵N]acetylvaline (adapted from Roberts *et al.*, 1987).

molecular mobility is ¹H wideline NMR spectroscopy. There, large-amplitude motions are detected through the reduction of the dipolar line width. However, 1D proton lineshapes leave many questions open, since they typically represent superpositions of broad and narrow lines and their relation to different structural units is often not obvious. In a straightforward combination of ¹H wideline NMR, cross polarization (CP), and ¹³C MAS spectroscopy in a 2D experiment (Schmidt-Rohr et al., 1992), it is possible to separate the dipolar patterns for the different structural units (wideline separation, WISE). This is demonstrated in Figure 1.4, where a WISE NMR spectrum of a 50:50 wt% blend of poly(styrene) (PS) and poly(vinyl methylether) (PVME) is presented. The ¹H wideline spectrum, Figure 1.4(a), consists of a rather featureless superposition of components with different dipolar linewidths, which are nicely separated in the second frequency dimension (Figure 1.4(b)) and related to structural units according to their ¹³C chemical shifts. Substantial motional heterogeneities, PVME being more mobile than PS, are detected despite the fact that the spectrum is recorded about 60 K above the caloric glass transition of this blend, which appears homogeneous by most classical techniques. Such information about the mobility of the different structural units is highly valuable for many practical applications.

For a thorough understanding of the chain motions in polymers, qualitative information provided by ¹H wideline spectra is not sufficient. In order to relate chain motions to the structure of the polymer itself or to the packing of the macromolecular chains, knowledge is required concerning the geometry of the motion, for example the angles about which a molecular unit rotates during individual motional steps. This information, which is hard to get otherwise, is indeed provided by 2D exchange NMR as applied to rotational motions. In simple cases the 2D spectra exhibit elliptical ridge patterns from which the angle about which the molecules have rotated can be directly read off with a ruler (Schmidt *et al.*, 1986). As a specific example, Figure 1.5(a) displays such a ²H 2D exchange spectrum for poly(vinylidene fluoride) (PVF₂), a polymer of considerable technological interest because of its electric properties. The geometric information from 2D NMR, together with knowledge of the dipole-moment change generated by the motion, allowed the identification of the conformational



Figure 1.4 2D WISE NMR separating ¹H wideline spectra for different structural units according to their ¹³C chemical shifts. (a) Conventional ¹H wideline spectrum of a blend of poly(styrene) (PS) and poly(vinyl methylether) (PVME), (b) 2D ¹H/¹³C WISE NMR spectrum indicating different mobilities of the two components (adapted from Schmidt-Rohr *et al.*, 1992).



Figure 1.5 Multidimensional exchange NMR spectra elucidating slow molecular motions. (a) 2D ²H NMR spectrum of crystalline poly(vinylidene fluoride) reflecting chain motions through defect diffusion (adapted from Hirschinger *et al.*, 1991), (b) 3D ¹³C exchange spectrum of oriented poly(oxymethylene) reflecting helical jumps in the crystalline regions.