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SOLID STATE NMR
OF POLYMERS

Edited by
Isao Ando and Tetsuo Asakura

SOLID STATE NMR
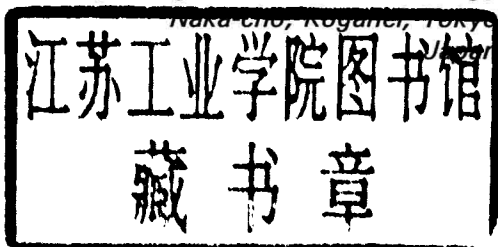# OF POLYMERS

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Preface

As materials polymers are almost always used as "solids". A structural and dynamic characterization of the polymers in question is necessary in order to understand the relations between properties and structure and, on the basis of these relations, to design new polymer materials. As is well known, the X-ray diffraction method has contributed to the structural determination of polymers with high crystallinity. However, most polymers have low crystallinity and so structural information about the noncrystalline region, which is the major component, cannot be obtained by X-ray studies. Therefore, the X-ray diffraction method has a limitation for the structural analysis of such systems. Further, it can be said that chain segments in the noncrystalline region are sometimes in a mobile state, so that the X-ray diffraction method provides no structural or dynamical information. On the other hand, the solid state NMR method provides information about the structure and dynamics of a sample irrespective of whether the region studied is crystalline or noncrystalline.

Recently, high resolution NMR studies of solids have been realized by using advanced pulse and mechanical techniques, and so have provided a variety of structural and dynamic information about polymer systems. Further, it can be said that solid state NMR has provided characteristic information that cannot be obtained by other spectroscopic methods, and that it has become a very powerful means for elucidating the structure and dynamics of polymer systems.

In polymer science and technology, the advanced development of various polymer materials with ideal properties and functions is desired. To achieve this, the close relationship between physical properties and molecular structure and dynamics must be clarified precisely. Therefore, powerful techniques are required for the elucidation of this relationship. One of these is solid state NMR spectroscopy.

This book is divided into two parts: the basic principles of solid state NMR and its application to polymer systems in the solid state. In the former part, the principles of NMR, important NMR parameters such as chemical shifts, relaxation times, dipolar interactions, quadrupolar interactions, pulse techniques and new NMR methods are covered. In the latter part, applications of NMR

to a variety of polymer systems in the solid state are discussed. The book is intended for graduate students and researchers in academic environments. It provides information relevant to beginners as well as those who are experts in solid state NMR applied to polymer science and technology, materials science, chemistry, biochemistry, physics, and so on.

We are delighted that so many active authors, who are leaders in the field of NMR spectroscopy and polymer characterization, have contributed to this work. We hope this book will be welcomed by the widespread NMR community and that all readers, from beginner to expert, everywhere will find the details of the various techniques and applications helpful.

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Introduction

Polymers generally form a variety of primary, secondary and higher-order structures in the solid state. This comes from the characteristic fact that a polymer chain is formed from an extremely large number of bonds and has sometimes irregular configurational structure and regiostructure. Due to such structural features some regions are found to be in the crystalline state and some in the noncrystalline state. In the former region, polymer chains are aligned like crystals and, on the other hand, in the latter region, they are randomly irregular in structure with and without molecular motion. The existence of these polymer structures is closely associated with their properties. For this reason, it becomes important to carry out precisely both structural and dynamic characterizations.

It has been demonstrated that solid state NMR spectroscopy provides useful information about the structure and dynamics of polymers in the bulk. At present, in polymer science, solid state NMR is recognized as one of the most powerful means for elucidating the structure and the dynamics of solid polymers in addition to X-ray diffraction. The history of solid state NMR, which has been used in polymer science, is very old. The appearance of new techniques in solid state NMR has certainly contributed to the development of polymer science and technology.

From such a background, the principles of solid state NMR and its applications to structural and dynamic characterization of polymers will be described.

Previously, many excellent books and periodical monographs on fundamental NMR and advanced NMR spectroscopies, have appeared. Also some excellent books of solid state NMR of polymers have appeared. Some of these books are mentioned for the convenience of readers below [1, 2].

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Contents

II. Applications of Solid State NMR

Chapter 1

NMR Chemical Shift and Electronic Structure

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1.1 Introduction

High-resolution solid-state NMR spectroscopy, combined with quantum chemistry, provides detailed information on the structure and electronic structures of solid polymers through the observation of the NMR chemical shift [1].

In the liquid and solution states, NMR chemical shifts of polymers are often the averaged values for all of the possible conformations because of rapid interconversion by rotations about bonds. However, in the solid state, chemical shifts are often characteristic of specific conformations because of strongly restricted rotation about the bonds. The NMR chemical shift is affected by a change of the electronic structure arising from structural changes. NMR chemical shifts in the solid state provide, therefore, useful information about the electronic structure of a polymer or polymers with a fixed structure. Furthermore, in the solid state, the components of the full chemical shift tensor can often be determined. The complete chemical shift tensor provides information on the local symmetry of the electron cloud around the nucleus and so provides much more detailed knowledge of the electronic structure of the polymer compared with the average chemical shift associated with the structure.

Such a situation applies to many polymers and, in order to establish the relationship between the NMR chemical shift and the electronic structure of polymers, it is necessary to use a sophisticated theoretical method which takes account of the characteristics of polymers.

Some methodologies for obtaining structures and the electronic structures of polymers, both in the solution and solid state, involve a combination of the observation and calculation of NMR chemical shifts. This approach has been applied to various polymer systems. Theoretical calculations of NMR chemical shifts for polymer systems have been achieved using two main approaches. One approach is that model compounds, such as the dimer,

trimer, etc., as a local structure of polymer chains, are used in the calculation by combining quantum chemistry and statistical mechanics. In particular, this approach has been applied to polymer systems in solution [2]. However, in solid polymer systems it should be recognized that the results of quantum chemical calculations on model compounds are not readily transferable to polymers because of differences in the electronic structure, including long-range interactions such as intrachain and interchain interactions. Electrons are constrained to a finite region of space in small molecules but this is not necessarily the case for polymers and, hence, some additional approaches are required. Another approach is to employ the tight-binding molecular orbital (TB MO) theory, which is well known in the field of solid-state physics, to describe the electronic structure of linear polymers with periodic structure within the framework of the linear combination of atomic orbitals (LCAO) approximation for the electronic eigenfunctions [3–11]. These approaches lead to the determination of the spatial structure and/or electronic structure of polymer systems including polypeptides in the solution and solid state. The essence of these two approaches are described below.

1.2   Approach using model compounds

1.2.1   *The origin of NMR chemical shift*

The chemical shift of an atom depends on its electronic and molecular environments [12]. Note that the chemical shift relative to a standard reference is expressed by δ and the chemical shielding by σ. The chemical shielding σ for atom A can be estimated by the sum of the following terms:

$$\sigma_A = \sigma^d + \sigma^P + \sigma' , \tag{1.1}$$

where σ^d is the diamagnetic term, σ^P is the paramagnetic term and σ' is another term which comes from the magnetic anisotropy effect, polar effect and ring-current effect. For nuclei with 2p electrons, such as ^{13}C, ^{15}N, etc., the relative chemical shift is predominantly governed by the paramagnetic term, and for the ^1H nucleus by the first and third terms in Equation (1.1).

The paramagnetic term is expressed as a function of excitation energy, bond order, and electron density according to the sum-over-states (SOS) method in the simple form as follows:

$$\sigma^P = -C\Sigma\langle r^{-3}\rangle_{2p}(E_m-E_n)^{-1}Q , \tag{1.2}$$

Table 1.1. Calculated ^{13}C chemical shieldings of hydrocarbons by FPT INDO method

Sample	Calculated[a] (ppm)				Experimental[c] (ppm)
	σ^d	σ^p	σ_A	δ (cal)[b]	δ (exp)
Methane CH_4	57.7	−129.3	−68.0	0	0
Ethane C_2H_6	57.4	−136.2	−75.7	7.7	8.0
Ethylene C_2H_4	57.9	−230.3	−169.3	101.3	124.9

[a] The negative sign means deshielding.
[b] Relative to CH_4.
[c] Relative to CH_4.

where E_m–E_n is the singlet–singlet excitation energy from the nth occupied to the mth unoccupied orbitals, and Q is a factor including the bond order and electron density. The quantity $\langle r^{-3} \rangle_{2p}$ is the spatial dimensions for a 2p electron while C is the coefficient incorporating universal constants. This term is calculated by semi-empirical MO or ab initio MO methods. The former has some features which give the substantial aspects of the chemical shift behavior associated with the spatial structure and/or the electronic structure. The diamagnetic term is estimated from the calculated electron density. Using these procedures, the chemical shielding σ_i of the model compound with any specified conformation is calculated. For example, the contributions of the paramagnetic term and diamagnetic term to the relative ^{13}C chemical shifts of small hydrocarbon molecules, such as methane, ethane and ethylene using the FPT (finite perturbation theory) with the INDO (semi-empirical MO) method, are calculated as shown in Table 1.1 together with the experimental data [13]. Note that the negative sign of the shielding constant σ indicates deshielding and, therefore, shielding variations can be compared with the observed chemical shift δ where a positive sign denotes deshielding. This table indicates that the paramagnetic term predominantly contributes to the relative ^{13}C chemical shift, and the contribution of the diamagnetic term is very small. These results show that it is very important to estimate exactly the paramagnetic term for the chemical shift calculations of nuclei with 2p electrons.

1.2.2 *Medium effects on NMR chemical shifts*

Most MO calculations of nuclear shielding relate to the case of a molecule in a vacuum. For nuclei forming the molecular skeleton, such as ^{13}C, and