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Volume 51

G. A. Webb

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Edited by

G. A. WEBB

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Preface

Applications of NMR are well established in all areas of science and new ones are being regularly reported. Annual Reports on NMR reflect developments in all areas of science. Contained within Volume 51 of this series are reviews from five different areas of interest.

'A Study of Conformational Stability of Polypeptide Blends by Solid State NMR Spectroscopy' is contributed by K. Murata, S. Kuroki, E. Katoh and I. Ando, D. Gudat reports on 'Applications of Heteronuclear X/Y-Correlation Spectroscopy in Organometallic and Organoelement Chemistry: Recent Developments', 'NMR Studies of Biomolecular Dynamics and Structural Plasticity using Residual Dipolar Couplings' is reviewed by J. R. Tolman and H. M. Al-Hashimi, R. H. Contreras, V. Barone, J. C. Facelli and J. E. Peralta cover 'Advances in Theoretical and Physical Aspects of Spin–Spin Coupling Constants' and 'High Resolution Magic Angle Spinning-Applications to Solid Phase Synthetic Systems and other Semi-Solids' is reviewed by W. P. Power.

Expressions of gratitude go to all of these reporters and to the production staff at Elsevier for their generous cooperation in the realisation of this volume.

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Contents

Advances in Theoretical and Physical Aspects of Spin–Spin Coupling Constants

High Resolution Magic Angle Spinning – Applications to Solid Phase Synthetic Systems and Other Semi-Solids

A Study of Conformational Stability of Polypeptide Blends by Solid-State NMR Spectroscopy

K. MURATA[1], S. KUROKI[1], E. KATOH[2] and I. ANDO[1]

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In polypeptide blends, the balance of intra- and intermolecular hydrogen bond interactions in two kinds of polypeptide chains play an important role for the conformational stability and the blend miscibility. The observation of the ^{13}C NMR chemical shifts and relaxation times, and the two-dimensional

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NMR spectrum leads to a deep understanding of the conformational stability and the miscibility. In this chapter, the most recent research works are introduced.

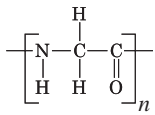
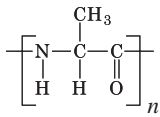
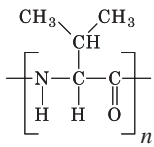
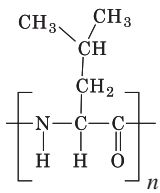
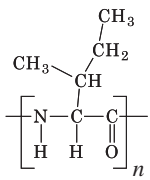
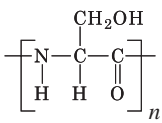
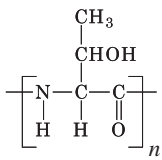
1. INTRODUCTION

Synthetic homopolypeptides consist of a repeated sequence of an amino acid. Although the structures of the homopolypeptides are not as complicated as those of proteins, homopolypeptides take some specified conformations such as the α-helix, β-sheet, etc., which appear in proteins. These conformational properties of homopolypeptides are shown in Table 1. The individual conformations are transformed into other conformations under certain conditions such as temperature and quenching.[1–7] For example, the main chain of poly (β-benzyl L-aspartate) takes on a right-handed $\alpha(\alpha_R)$-helix form within the temperature range from room temperature to 117°C and is transformed to the left-handed $\alpha(\alpha_L)$-helix form, the ω-helix form and the β-sheet form at temperatures above 117°C. On the other hand, copolymers of L-alanine (Ala) and glycine (Gly) [$(Ala, Gly)_n$] take the right-handed α-helix, β-sheet and the 3_1-helix forms in the solid state as obtained by changing the mixture ratio or by solvent treatment.[8–11] A scheme of conformational generation of polypeptides, copolypeptides and proteins is shown in Fig. 1.

These transformations arise from the energetical stability caused by intramolecular or intermolecular hydrogen bond (HB) interactions. Thus, by the balance of intramolecular and intermolecular HB interactions in polypeptide blends, it is expected that the strength of intermolecular interaction in the blends is different from those in homopolypeptides then new conformations can be formed by intermolecular HB interactions that do not exist originally in homopolypeptides. There are many studies on intermolecular HB interactions in homopolypeptides and copolypeptides in the solid state, but to the best of our knowledge there is little study on intermolecular HB interactions in polypeptide blends except for our previous studies.

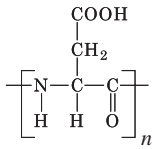
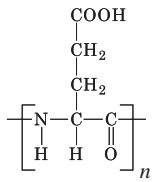
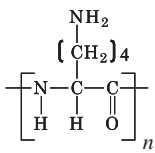
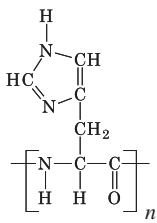
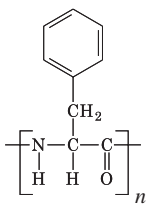
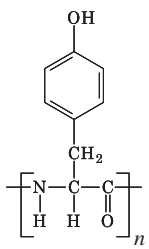
In order to understand the conformations or conformational changes of homopolypeptides and copolypeptides, solid-state NMR is a very useful method. After the first NMR experiment for obtaining high-resolution spectra of solids was carried out with the high-speed magic angle spinning (MAS) method,[12] the cross polarization (CP) procedure [13] was developed by Hartmann and Hahn.[14] On the basis of these methods a CP/MAS technique that combines MAS and CP has been conventionally used to obtain high-resolution solid-state NMR spectra.[15,16] In the solid-state, the NMR chemical shift is often characteristic of a specified conformation because of the highly restricted molecular motion. For example, it has been elucidated

Table 1. Preferred conformations of homopolypeptides in the solid-state

Amino acid residue		Conformation[a]		
		1	2	
Glycine		β-Sheet (PG-I)	3_1-Helix (PG-II)	Hydrophobic side chain Hydrophobic interaction
Alanine		α-Helix	β-sheet	Oligomers are β-sheet Hydrophobic side chain Hydrophobic interaction
Valine		β-Sheet		Hydrophobic side chain Hydrophobic interaction
Leucine		α-Helix		Hydrophobic side chain Hydrophobic interaction
Isoleucine		β-Sheet		Hydrophobic side chain Hydrophobic interaction
Serine		β-Sheet		Hydroxylic side chains of hydrogen bonding
Threonine		β-Sheet		Hydroxylic side chains of hydrogen bonding

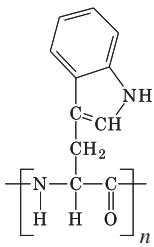
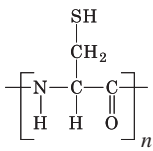
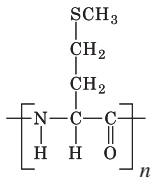
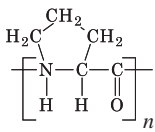
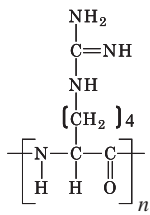
(*Continued*)

Table 1. Continued

Amino acid residue		Conformation[a]		
		1	2	
Aspartic acid[b]		α-Helix		Hydrophilic side chain
Glutamic acid[b]		α-Helix	(β-Sheet)	Hydrophilic side chain Salts Ca, Sr, Ba are β-sheet
Lysine[c]		α-Helix	β-Sheet	Hydrophilic side chain Salts, HPO_4 are β-sheet, Also Product from high pH, high temperature is β-sheet
Histidine		α-Helix		This residue is capable of hydrogen bonding and of other interaction.
Phenylalanine		α-Helix		Hydrophobic side chain Hydrophobic interaction
Tyrosine		β-Sheet		Hydroxylic side chains of hydrogen bonding

(*Continued*)

Table 1. Continued

Amino acid residue		Conformation[a] 1	Conformation[a] 2	
Tryptophan		α-Helix		Hydrophobic side chain
Cysteine		β-Sheet		
Methionine		α-Helix		
Proline		pP-II	pP-I	Hydrophobic side chain
Arginine		α-Helix		Hydrophilic side chain

[a] All β-sheet form are antiparallel.

[b] Polyaspartic acid and polyglutamic acid in the solid state are in the neutral carboxyl form. The conformational influence in solution at neutral pH where the side chain is ionized is one of α-helix disruption.

[c] Polylysine in the solid state is normally in the form of the HBr salt. The charged residue in solution at neutral pH would have an α-helix disruptive influence.