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Analysis

Absolute Configurational Assignments for the ^{1}H-NMR Spectrum of Poly(Vinyl Alcohol) by Use of Two-Dimensional NMR Methods

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SUMMARY

FOCSY two-dimensional J-resolved NMR spectroscopy is used to resolve ^{1}H NMR resonances corresponding to triad and tetrad configurations of poly(vinyl alcohol). Two-dimensional auto correlation with ω_1-scaling NMR spectroscopy is used to observe connectivities between triad and tetrad ^{1}H NMR resonances. Comparison of these connectivities to the necessary compositional relationships at triad-tetrad level leads to absolute configurational assignments for the ^{1}H NMR spectrum of poly(vinyl alcohol).

INTRODUCTION

A major accomplishment of high resolution NMR studies of synthetic polymers has been the ability to study polymer structure at the molecular level. Thus, high resolution NMR has been used to investigate configurational sequences in homopolymers, head-to-tail inversions in polymers, branching of polymers, carbon skeletal arrangements in polymers such as polybutadiene, sequence distributions in copolymers, etc. However, even though high resolution NMR has become an essential tool and is widely used, there remains a variety of problems. For example, in recent years the use of ever higher magnetic fields has revealed dependence of the NMR spectrum on ever higher order configurational or compositional sequences. In the case of vinyl homopolymers such as poly(vinyl alcohol), observation of hexad or even higher configurational sequences is now quite common. To exploit the information in the NMR spectrum, there is now a critical need for improved methods of obtaining assignments of NMR resonances to specific configurational, compositional or structural features of a polymer. The purpose of the present paper is to demonstrate that two-dimensional (2D) NMR methods allow unambiguous assignments to be obtained directly from frequency relationships in the 2D NMR spectra.

EXPERIMENTAL

Poly(vinyl alcohol) of nominal molecular weight 14,000 was purchased from Scientific Polymer Products, Inc. This was exchanged once with ^2H_2O and then dissolved at 10% w/v in ^2H_2O for NMR experiments at 343°K. FOCSY 2D J-resolved NMR spectra (1) and 2D autocorrelation with ω_1-scaling NMR spectra (2) were recorded as described previously on a Bruker WM-360 NMR spectrometer. Chemical shifts are given relative to internal sodium 3-trimethylsilyl [2,2,3,3,-$^2H_4$] propionate.

RESULTS

To illustrate how 2D NMR methods can be used to obtain structural assignments in vinyl homopolymers, it is first useful to consider the necessary compositional relationships between different sequences of stereochemical configurations. At dyad-triad level, these relationships are shown schematically in Fig. 1A. Thus, a meso-meso (mm) triad contains only m

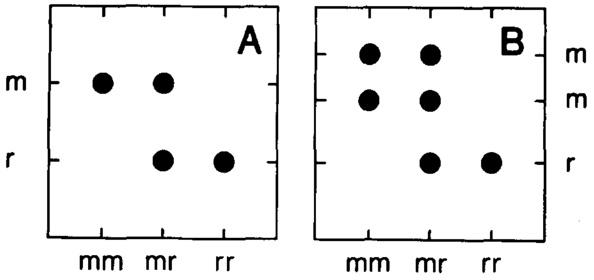

Fig. 1. Dyad-triad compositional relationships for vinyl homopolymers. (A) Compositional pattern which would be observed for ^{13}C-^{13}C 2D autocorrelation NMR. (B) Compositional pattern which would be observed for ^{1}H-^{1}H 2D autocorrelation NMR (see text).

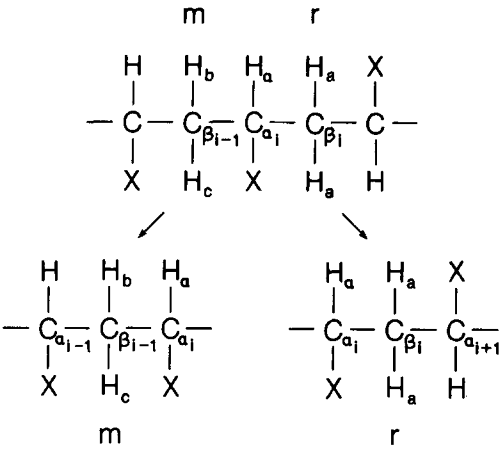

Fig. 2. Structure of a meso-racemic (mr) triad of a vinyl homopolymer showing the constituent meso and racemic dyads.

dyads, a racemic-racemic (rr) triad contains only r dyads and a meso-racemic triad (Fig. 2) contains one m dyad and one r dyad. Similar schematics of the necessary compositional relationships can be derived for higher configurational levels, e.g. pentad-hexad. The power of 2D NMR methods for obtaining structural assignments in vinyl homopolymers arises from the fact that exactly these types of compositional patterns can be observed directly in 2D NMR correlation spectra. For example, in a mr triad, the central carbon atom ($C_{\alpha,i}$, Fig. 2) is flanked by the central carbon atom of a m dyad ($C_{\beta,i-1}$) and the central carbon of a r dyad ($C_{\beta,i}$). Since directly bonded ^{13}C atoms show appreciable scalar couplings, for a polymer with dyad (C_β) -triad (C_α) resolution in the NMR spectrum, a ^{13}C -^{13}C correlation 2D NMR experiment (3) would show a pattern analogous to that in Fig. 1A. Comparison of the 2D NMR spectrum with Fig. 1A would then allow mr triad resonances to be uniquely identified, but absolute configurational assignments of resonances corresponding to mm and rr triads as well as m and r dyads could not be obtained from this experiment. This is because the pattern in Fig. 1A would not be altered by interchanging the m and r designations.

The ambiguity in the ^{13}C - ^{13}C 2D autocorrelation NMR experiment can be overcome by using ^{1}H-^{1}H 2D autocorrelation NMR (4). Because three bond ^{1}H-^{1}H scalar couplings are appreciable, this experiment can be used to detect pairs of hydrogens which are directly bonded to adjacent carbons, i.e. H_α and H_a as well as H_α and H_b and H_c in Fig. 2. In a vinyl homopolymer such as PVA, the two hydrogen atoms of the central CH_2 group of a m dyad are heterosteric (5), i.e. have different chemical environents, whereas the two hydrogens of the central CH_2 group of a r dyad have identical chemical environments (Fig. 2). The heterosteric nature of a m dyad may cause the two hydrogens (H_b and H_c) to have different chemical shifts. If so, this can be used to differentiate m and r dyads. For example, in a ^{1}H-^{1}H 2D autocorrelation NMR spectrum for a polymer with dyad-triad resolution in the ^{1}H NMR spectrum, the cross peaks between dyad and triad hydrogens would show the pattern in Fig. 2B if the two m dyad hydrogens have different chemical shifts. Absolute configurational assignments could then be obtained for all hydrogen atoms from the 2D NMR experiment.

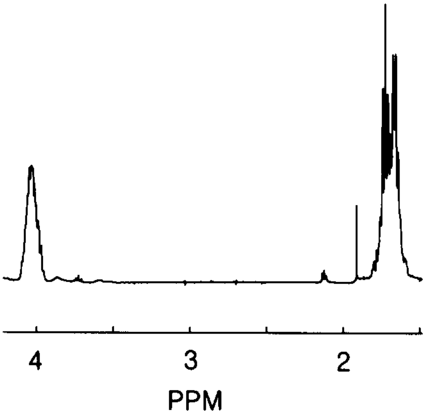

Fig. 3. One-dimensional 360 MHz ^{1}H NMR spectrum of 10% w/v poly(vinyl alcohol) in $^{2}H_2O$ at 343°K.

For the reasons outlined above, we have first attempted to obtain absolute configurational assignments for the ^{1}H NMR spectrum of PVA. The one-dimensional ^{1}H NMR spectrum of PVA (Fig. 3) shows complex, overlapping resonances for both the *H*COH (3.9-4.1ppm) and CH_2 (1.6-1.8ppm) hydrogens. The complexity of this spectrum arises from ^{1}H-^{1}H scalar couplings. For example, a *H*COH hydrogen has three-bond scalar couplings to four different CH_2 hydrogens and the *H*COH NMR resonance may therefore consist of a multiplet with up to 16 individual frequencies. Consequently, resonances from different stereoconfigurations are heavily obscured by the multiplet splittings in the one-dimensional ^{1}H NMR spectrum. This problem can be overcome by use of 2D J-resolved ^{1}H NMR (1,6). As shown in Fig. 4, this type of experiment allows scalar couplings (J) and chemical shifts (δ) to be expressed along orthogonal frequency axes. Projection of the 2D J-resolved spectrum parallel to the J axis then gives a homonuclear broad-band decoupled spectrum (7). In the case of PVA, such a projection reveals three major resonances for the *H*COH hydrogens (Fig. 4A), which presumably correspond to mm, mr and rr triad configurations. In both the contour plot and the projections, there is some indication for further splitting of these three resonances along δ. This would correspond to higher level stereoconfigurations, i.e. pentads, but no attempt has been made to resolve the spectrum further.

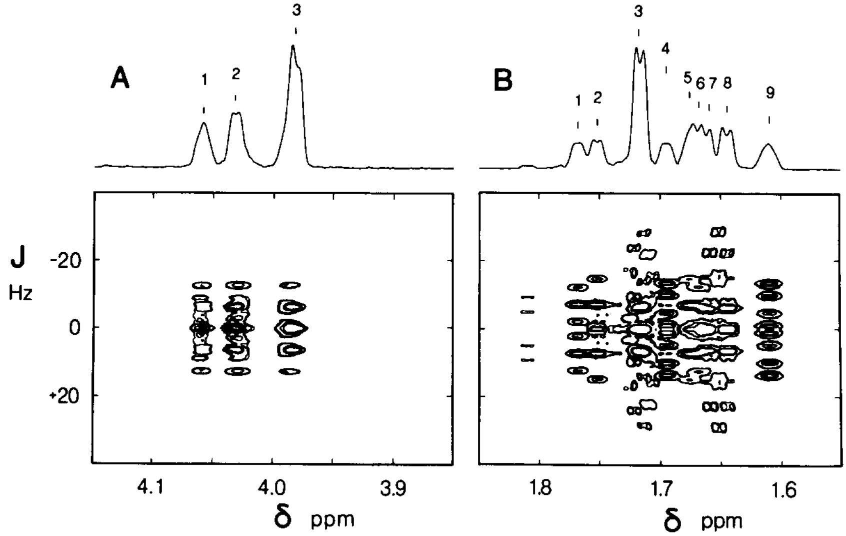

Fig. 4. Absolute value contour plot for a FOCSY 2D J-resolved NMR spectrum of poly(vinyl alcohol) recorded under the conditions noted in the caption to Fig. 3. The projections at the top correspond to a broad-band homonuclear decoupled ^1H NMR spectrum. The numbers shown on the projections correspond to different multiplet resonances arising from different stereoconfigurational sequences. (A) *H*COH resonances. (B) CH_2 resonances.

For the CH_2 hydrogens, a considerably more complex pattern is observed in the 2D J-resolved ^1H NMR spectrum (Fig. 4B). Careful examination of this spectrum has revealed that nine different individual multiplets are present, the chemical shifts of which are indicated in Fig. 4B. In addition, strong coupling between individual hydrogen atoms is evidenced by resonances at $|J| > 20$ Hz in Fig. 4 B. The strong coupling pattern at $\delta = 1.652$ ppm is centered on the chemical shifts of multiplets 4 and 9, which indicates strong coupling between the corresponding hydrogens. In the case of PVA, this requires that these two hydrogens correspond to a single CH_2 group. Similarly, two further strong coupling patterns centered at 1.712 and 1.721 ppm indicate that multiplets 2 and 6 as well as multiplets 1 and 5 also correspond to single methylene groups respectively. The remaining three multiplets, i.e. 3, 7 and 8, do not show strong coupling patterns. This suggests that these multiplets correspond to CH_2 groups for which both hydrogens have the same chemical shift. This would mean that the 9 different multiplets observed in Fig. 4B correspond to six different CH_2 groups. This would be consistent with resolution of the ^1H NMR spectrum at tetrad level for the CH_2 groups of PVA.

Confirmation of the conclusions drawn from the 2D J-resolved ^1H NMR spectrum, as well as individual assignment of the ^1H NMR resonances, has been obtained by use of ^1H-^1H 2D autocorrelation NMR (Fig. 5). In this experiment, the usual one-dimensional ^1H NMR spectrum lies along the diagonal $\omega_1 = \omega_2$. Off diagonal peaks indicate scalar couplings between

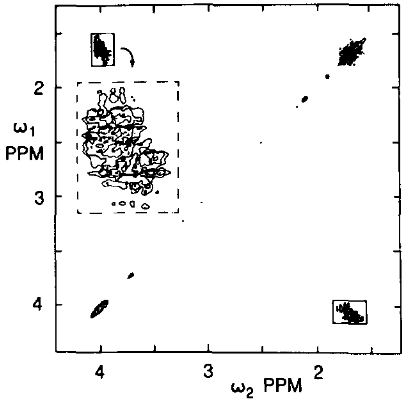

Fig. 5. Absolute value contour plot for a ^1H-^1H 2D autocorrelation NMR spectrum of poly(vinyl alcohol) recorded under the conditions noted in Fig. 3. The areas enclosed in solid rectangles contain all *H*COH-CH_2 cross peaks. The insert, enclosed by the dashed rectangle, shows an expansion of the cross peaks at upper left.

different hydrogen atoms. Thus, cross peaks between *H*COH and CH_2 hydrogens are contained in the spectral regions (ω_1 = 1.6-1.8 ppm, ω_2 = 3.9-4.1 ppm) and (ω_1 = 3.9-4.1 ppm, ω_2 = 1.6-1.8 ppm) in Fig. 5. As shown in the insert in Fig. 5, a very complex pattern is observed for these cross peaks. This is because cross peaks from three *H*COH multiplets and nine CH_2 multiplets overlap strongly even in the 2D spectrum. To simplify the pattern of cross peaks, a recently designed experiment, which allows differential scaling of chemical shifts and scalar couplings along ω_1 (2), was employed. Fig. 6A shows the pattern of cross peaks between *H*COH hydrogens and CH_2 hydrogens when chemical shifts were scaled up and scalar couplings were scaled down along ω_1. Twelve different multiplet cross peaks can be observed. The centers of the multiplets along ω_1 and ω_2, which are indicated in Fig. 6B, were in excellent agreement with the chemical shifts observed in the 2D J-resolved experiment. Furthermore, the spectral region of the ^1H-^1H autocorrelation experiment which contained *H*-C-*H* cross peaks between hydrogens of the same methylene group (not shown) confirmed that in PVA, resonances from three methylene groups show different chemical shifts for the two hydrogen atoms.

To obtain assignments of the ^1H NMR resonances to specific configurational sequences, the pattern in Fig. 6B has been compared to the necessary compositional relationships at triad-tetrad level (Fig. 6C). In Fig. 6C, these relationships have been augmented by showing two identical patterns for mmm, rmm, rmr and rrm tetrads. This allows for the fact that the central CH_2 group of all these tetrads is heterosteric and that the two hydrogen atoms may show different chemical shifts in the ^1H NMR spectrum. From Figs. 6B and 6C, it is immediately apparent that the central triad resonance at 4.037 ppm must correspond to mr. Assignment of the rr and mm triads as well as the rrr and mmm tetrads is then obtained as follows. Tetrad resonances at 1.769 and 1.675 ppm show cross peaks only to the triad resonance at 3.985 ppm. These cross peaks must be either rrr with rr or mmm with mm. Because the tetrad resonances clearly correspond to a heterosteric tetrad, these resonances are assigned to mmm and mm configurations. Similarly, a tetrad resonance at 1.647 ppm shows a cross peak only to the triad resonance at 4.062 ppm. The tetrad shows no evidence of heterostericity and these resonances are therefore assigned to rrr and rr configurations respectively. Since all triad resonances have now been assigned, assignents for the rrm and mmr tetrads follow immediately. The remaining two tetrads, mrm and rmr, show cross peaks only to the mr triad.

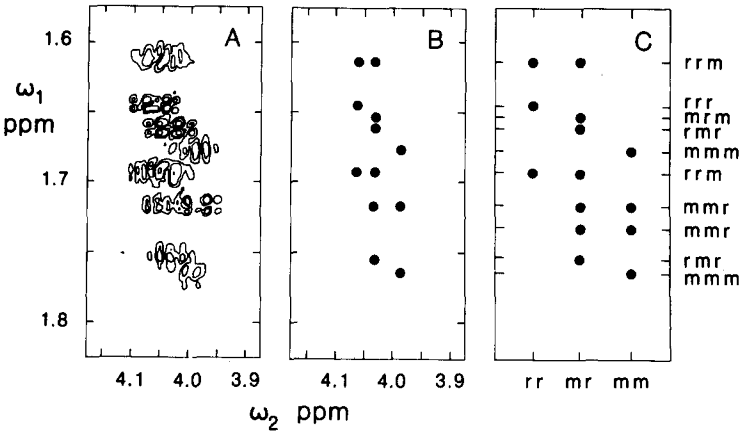

Fig. 6. Experimental data and compositional relationships used to assign the ^1H NMR spectrum of poly(vinyl alcohol). (a) absolute value contour plot for a ^1H-^1H 2D autocorrelation with ω_1 scaling NMR spectrum showing $\not{H}COH$-CH_2 cross peaks. Chemical shift frequencies were expanded 1.7 times and scalar couplings were reduced to 0.3 of the natural value. (b) Schematic representation of the data in (a) showing the chemical shifts of the multiplet resonances along ω_1 and ω_2. (c) Schematic representation of the necessary compositional relationships at triad-tetrad level assuming that the heterosteric tetrads mmm, mmr, rmr and rrm show two different ^1H resonances (see text).

In the NMR spectra, one of these tetrads is clearly heterosteric and is therefore assigned to rmr, whereas the other tetrad shows no evidence of heterostericity, which is consistent with assignment to mrm. The resulting assignments for the ^1H NMR spectrum of PVA are shown in Table 1. These assignments are consistent with triad assignments obtained earlier by examination of poly(vinyl alcohol) of varying tacticity (5). It is interesting to note that although the rmm tetrad is necessarily heterosteric, the two hydrogens of the central CH_2 group show the same chemical shift.

TABLE 1

Chemical shifts for the ^1H NMR Resonances of Poly(Vinyl Alcohol)

Configuration	δ (ppm)	Configuration	δ (ppm)
		mmm	1.769,1.675
		mmr	1.719
rr	4.062	rmr	1.754,1.670
mr	4.037	rrr	1.647
mm	3.985	mrr	1.696,1.610
		mrm	1.663

DISCUSSION

The first, fundamental step in any NMR study is the assignment of the NMR resonances to specific structural features of the compound under investigation. For polymers, most previous structural assignments have been based on one or more of the following methods: (1) comparison of resonance intensities with predicted intensities calculated on the basis of assumed polymerization kinetics and statistical models; (2) synthesis of polymers with specific structural or compositional features including, for example, synthesis of stereoregular polymers, epimerization of stereoregular polymers, and synthesis of copolymers with known, usually low, proportions of one component; (3) comparison with low molecular weight model compounds; and (4) calculation of chemical shifts, particularly for ^{13}C resonances, using additivity parameters to account for structure and often including parameters which depend on polymer conformation. Each of these methods suffers from disadvantages and/or ambiguities. For example, resonance intensities are often used to study polymerization kinetics. However, measurements of resonance intensities in 1D NMR spectra of polymers are often not very accurate because of spectral overlap and because line shapes are not known. Particularly in the case of high order configurational or compositional sequences, assumption of a certain type of kinetics to obtain resonance assignments, which are then used to confirm the proposed kinetics, can become a very ambiguous procedure. Similarly, synthesis of polymers or model compounds with specific structures should resolve any ambiguities in assignments. However, considering that even a vinyl homopolymer already contains 20 different hexad configurational sequences, synthetic methods may often be a very time consuming and inefficient procedure for obtaining reliable NMR assignments. Compared to these methods, the ability to obtain assignments from frequency relationships in 2D NMR spectra, which can be directly related to specific structural features, represents a much preferable procedure. As shown by the present experiments, a major advantage of the 2D NMR methods is that assignments can be obtained for highly atactic polymers. Indeed, for assignment of homopolymer configurational sequences, it is advantageous to use atactic polymers since the availability of complete compositional relationships in the 2D NMR spectra avoids any ambiguities in assignments.

Although the present experiments have been confined to obtaining assignments for homopolymer configurational sequences, it is readily apparent that the direct correlations between 2D NMR spectra and polymer structural features should permit unambiguous NMR assignments to be obtained in other situations. Sequence distribution in copolymers and the nature of branching in polymers are two obvious candidates. Two-dimensional NMR methods can also yield information on the conformational states of polymers. Scalar coupling constants, which give information on the population distribution of different rotational isomers in the polymer backbone, as well as nuclear Overhauser effects, which give information on interatomic distances, are both conveniently measured by 2D NMR methods. In the case of PVA, it is already apparent in Fig. 4A that the multiplet patterns for mm, mr and rr triads are quite different, which is indicative of different conformational states for these configurations. Actually, by taking different cross sections through the rr triad resonance in Fig. 4A, it is possible to show that at least three different splitting patterns are present (Fig. 7). This means that the ^{1}H NMR spectrum of PVA reflects different conformational states for different pentad configurational sequences. More efficient experiments for observation of ^{1}H-^{1}H scalar couplings and interpretation of these couplings will be presented elsewhere.

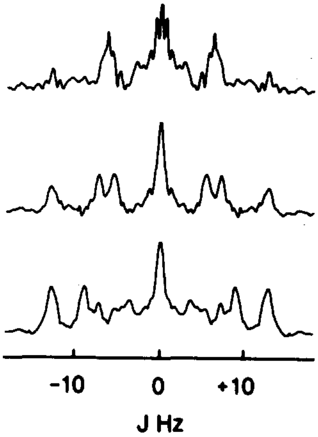

Fig. 7. Cross-sections through the rr triad multiplet (multiplet 1, Fig. 4A) parallel to the J axis at δ= 4.047, 4.053, and 4.069 ppm showing higher order (pentad) ^1H-^1H coupling patterns.

Despite the obvious promise of 2D NMR experiments for analysis of polymer structure and conformation, it should be noted that the broad resonances and spectral overlap characteristic of polymer spectra can present considerable practical difficulties even with 2D NMR methods. In general, many of the elegant 2D NMR methods designed for use with small molecules are not efficacious for macromolecular applications. For this reason, we have developed FOCSY 2D J-resolved ^1H NMR methods (1) and ^1H-^1H 2D autocorrelation with ω_1 scaling NMR methods (2). The absolute configurational assignments of ^1H NMR resonances obtained from these experiments can then be extended to ^{13}C NMR resonances by ^1H-^{13}C cross correlation 2D NMR experiments. Experimental procedures which are efficient for use with macromolecules will be presented elsewhere.

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