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Absolute Tacticity Assignments of Poly(vinyl chloride) via the Two-Dimensional NMR Spin-Lock RELAY Experiment

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ABSTRACT: A method is demonstrated for the unambiguous assignment of configurational sequences in the carbon-13 NMR spectrum of a homo vinyl polymer. This is achieved by elucidating the connectivity of carbons belonging to even- and odd-ad sequences along the polymer chain. A two-dimensional spin-lock RELAY experiment, involving magnetization pathways ^{a}H–^{b}H–^{b}C and ^{b}H–^{a}H–^{a}C, allows identification of neighboring carbons by recognition of shared protons. This approach has the distinct advantage of observing carbon while preserving the proton shift information which can aid in the identification of sequences by the equivalence or nonequivalence of the methylene protons. The method is demonstrated for poly(vinyl chloride) (PVC), whose tacticity has been well studied. The present report reevaluates carbon chemical shift assignments for PVC dissolved in 1,2,4-trichlorobenzene. By this approach, sequence assignments are made by direct experimental evidence, for both carbon and proton chemical shifts, and without dependence on propagation statistics.

Introduction

Tacticity, or the relative configuration of pseudoasymmetric centers in a vinyl polymer chain, may influence the physical and mechanical properties of a polymer. NMR is particularly useful in studying tacticity because chemical shift is sensitive to configurational sequences and intensities can be utilized to elucidate the propagation mechanism.[1,2] Carbon-13 NMR is advantageous because of the simplicity of proton-decoupled spectra and the large chemical shift range that allows long configurational sequences to be observed. Increased magnetic field strengths can be used to evaluate even longer configurational sequences which afford a more detailed description of tacticity but complicate spectral assignments. Another complication is the tendency of random propagation to produce sequence probabilities that are alike, limiting the use of peak intensities for the assignment to configurational sequences. An experimental method that would simply assignments and that is independent of the propagation statistics is desirable.

Recently, two-dimensional NMR has been used to make stereosequence assignments.[3-10] Bruch et al. have assigned fluorine NMR spectra on the basis of fluorine connectivities (through four-bond scalar coupling) of overlapping configurational sequences.[6] Likewise, Gippert and Brown have made proton chemical shift assignments based on proton connectivities and the necessary compositional relationships of triad and tetrad configurational sequences.[7] In this report, carbon chemical shift assignments are made on the basis of connectivities between the methine and methylene carbons of a homo vinyl polymer that belong to odd- and even-ad sequences, respectively.

Outline of Method. In the first step of our approach, a ^{1}H–^{13}C shift-correlated spectrum is obtained. In this experiment, an INEPT-type magnetization transfer occurs from a proton to a scalar-coupled carbon.[11-13] The amount of magnetization transferred depends upon the precession frequency of the attached proton and the length of the evolution period. The resultant carbon signal is modulated in amplitude, reflecting the proton chemical shift. Possible configurational sequence assignments for the carbon chemical shifts of the methylene can be reduced by the classification of sequences on the basis of correlation to one or two proton shifts. A single carbon shift correlated

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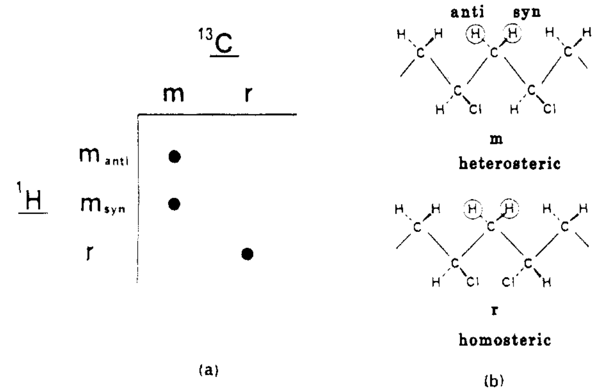

Figure 1. (a) Pattern resulting from ^1H–^{13}C correlations of diad (methylene) sequences. (b) Illustration of *m* and *r* diads with nonequivalent and equivalent methylene protons, respectively.

to a single proton shift indicates a sequence with equivalent or homosteric methylene protons. A single carbon shift correlated to two proton shifts indicates a sequence in which the methylene protons are nonequivalent or heterosteric. Figure 1a illustrates the chemical shift pattern that would occur from the correlation between carbon and proton diad sequences of a methylene. The protons of the *m* diad are nonequivalent (heterosteric) while the protons of the *r* diad are equivalent (homosteric) as shown in Figure 1b. This property, therefore, can be used to distinguish certain stereosequences.

In the second step, carbon–carbon connectivities are obtained via the heteronuclear RELAY experiment. The RELAY spectrum will contain the same resonances as in the previous experiment that arise from correlation of a carbon and directly attached proton(s). The shift-correlated experiment, however, is often necessary to identify these peaks. Additional peaks in the RELAY spectrum, due to correlation of a carbon and protons attached to a neighboring carbon, are the key to elucidating carbon–carbon connectivities. From the combination of relayed pathways, ^aH–^bH–^bC and ^bH–^aH–^aC, adjacent carbons ^aC and ^bC are identified by virtue of their shared protons. Magnetization transfer in the RELAY experiment occurs first along scalar-coupled protons as in the COSY experiment and then from the proton to an attached carbon as in the heteronuclear shift-correlated experiment.[13] Initial attempts using the traditional heteronuclear RELAY experiment[14,15] failed to give adequate sensitivity even after optimization of delays using the transfer functions obtained by product operator analysis.[16] The newly proposed heteronuclear RELAY experiment with spin-locking,[17] however, gives good results. With this method, magnetization transfer between protons is achieved via a homonuclear Hartmann–Hahn type cross polarization.[18] Proton magnetization decay during the transfer period occurs with $T_{1\rho}$ rather than T_2 as in the ordinary RELAY experiment. In addition, proton chemical shift information is retained as pure amplitude modulation so that magnitude calculation of spectra is not required and narrow absorption line shapes can be obtained.

Sequence assignments in a homo vinyl polymer can be made by correlation of adjacent methine and methylene carbons that belong to odd-ad (triad, pentad, ...) and even-ad (diad, tetrad, ...) sequences, respectively. In Figure 2b, for example, the methine carbon triad *rm* contains the *r* and *m* diads of the methylene carbon on the basis of its longer sequence length and hence is correlated to the methylene carbon as is shown in Figure 2a. As previously pointed out,[7] carbon connectivities alone do not provide absolute assignments due to the symmetry of the compositional pattern. For example, if every *m* label in Figure 2a were exchanged for an *r* and vice versa, the same pattern would result. The *m* and *r* diads of the methylene carbon, however, can be distinguished by the homo- or heterosteric property exhibited by the methylene protons as described earlier.

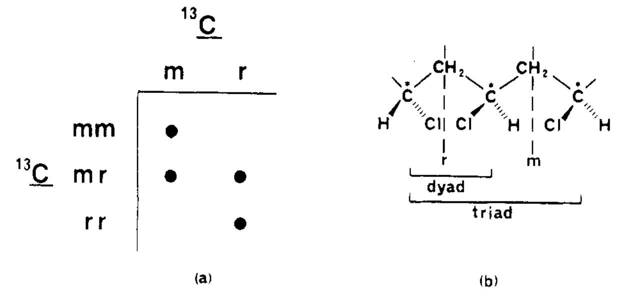

Figure 2. (a) Simulated pattern resulting from ^{13}C–^{13}C correlations of diad (methylene) and triad (methine) sequences. (b) Example of the *rm* triad and *r* and *m* diads that comprise it giving rise to the pattern shown in (a).

Tacticity assignment, using this methodology, is demonstrated for PVC, a commercially significant polymer whose tacticity has been well studied.[19-27] After Schaefer's first observation of microstructure in the carbon-13 spectrum,[19] triad and tetrad assignments were made by Inoue et al.,[20] using model compounds and comparison of intensities to those predicted by Bernoullian propagation statistics. Ando and co-workers attributed discrepancies between these assignments and those made by Carman,[21] to the sensitivity of the methylene shifts to solvent.[22,23] The observed relative chemical shifts, which are a function of the distribution of rotational conformations, were determined to be dependent upon configuration, temperature, and nature of the solvent. Calculated carbon-13 shifts by Tonelli et al.,[24] based on rotational probabilities and the γ shielding effect, were accurate for the methine region but not for the methylene carbons where solvent dependency was again observed. For this reason, there may be ambiguity in the methylene carbon shift assignments. In the following analysis, no previous knowledge of the sequence assignments is assumed.

Experimental Section

Materials. The poly(vinyl chloride) used in this study is a commercial material from Monomer–Polymer Laboratories (No. 7649). The sample was dissolved in 1,2,4-trichlorobenzene at 15% (w/v) with approximately 15% benzene-d_6 added for lock.

NMR Spectroscopy. Experiments were performed on a General Electric GN-500 spectrometer operating at a temperature of 90 ± 3 °C. In the heteronuclear shift-correlated experiment, 128 carbon-13 spectra were obtained having 128 scans each with a ±1100-Hz sweep width and 2K complex data points. The evolution time was incremented with an increment size to give a proton sweep width of ±1 kHz and zero filling to give 256 data points. Time-domain signals in both dimensions were digitally filtered by a phase-shifted sine bell function. The resultant 2-D spectrum is displayed in absolute-value mode. Total time for the experiment was approximately 9 h. In the RELAY experiment, 128 carbon-13 spectra were obtained, each having 128 scans, ±1100-Hz sweep width, and 2K complex data points. Again, zero filling yielded 256 data points in the proton dimension. Time-domain signals in both dimensions were digitally filtered by a phase-shifted sine bell function. A total spin lock time of 18 ms was used and consisted of six 3-ms periods in which the transmitter phase was alternated by 180° to compensate for off-resonance effects.[18] The method of States et al., involving separate storage of real and imaginary components of evolved magnetization, was used to get a phase-sensitive 2-D spectrum.[28] Total time for the RELAY experiment was approximately 5 h.

Proton relaxation times T_1, T_2, and $T_{1\rho}$ were measured at 90 ± 3 °C and are summarized in Table I. T_1 was measured by

Table I

^{1}H Relaxation Times for PVC in 1,2,4-TCB at 90 °C

	T_1, s	T_2, s	$T_{1\rho}$, s
CH	0.78	0.016	0.083
CH_2	0.48	0.014	0.043

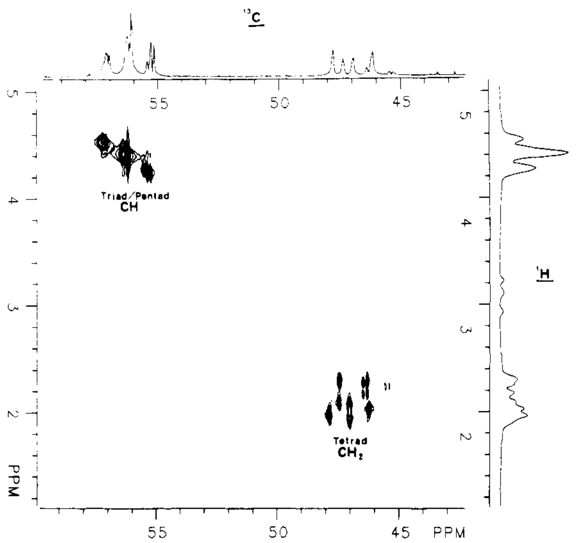

Figure 3. 500-MHz 2-D ^{1}H–^{13}C shift-correlated spectrum of a 15% solution of poly(vinyl chloride) in 1,2,4-TCB at 90 °C.

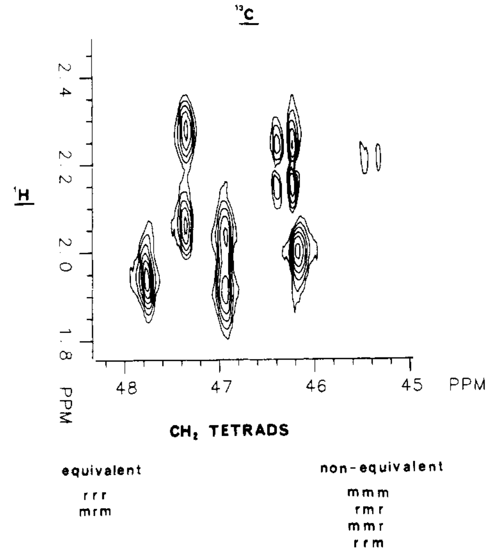

Figure 4. Expansion of the methylene region from Figure 3.

inversion–recovery, T_2 by a single-echo Carr–Purcell sequence, and $T_{1\rho}$ with an on-resonance spin-locking field having an intensity of 1800 Hz.

Results and Discussion

Two distinct regions are observed in the ^{1}H–^{13}C shift-correlated spectrum of PVC (Figure 3). In the methine region, there are three resonances that correspond to triad sensitivity with internal splitting along the carbon axis due to pentad structure. The center triad can be assumed to be the *mr* sequence since its shift is expected to be an average of the *mm* and *rr* triads. In the methylene region, there are at least six distinct carbon resonances. Figure 4 shows an expanded view of this region and the six tetrad sequences grouped according to the homosteric or heterosteric environment of the methylene protons. A single carbon resonance correlated to two proton resonances is attributable to a configurational sequence with nonequivalent methylene protons. For the case where a single proton resonance is correlated to more than one carbon resonance (45.4 and 46.3 ppm), hexad structure can be assumed since carbon is more sensitive to tacticity than proton. Only the *rrr* and *mrm* tetrad sequences should exhibit the homosteric property (single proton shift), yet there appears to be three such tetrads, including the very weak resonance upfield.

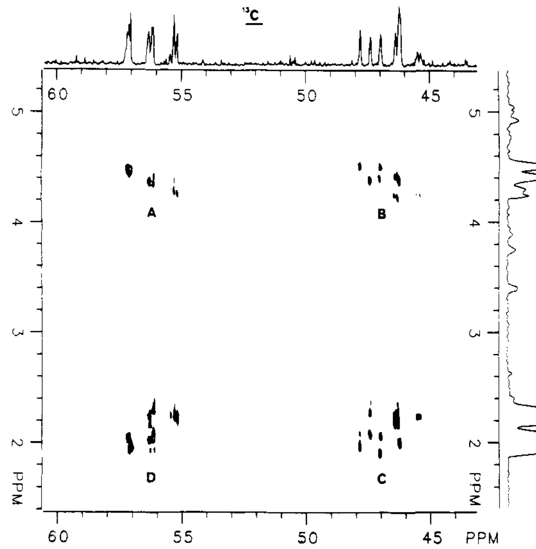

Figure 5. 500-MHz 2-D heteronuclear spin-lock RELAY spectrum of a 15% solution of poly(vinyl chloride) in 1,2,4-TCB at 90 °C. Regions A and C appear in the shift-correlated spectrum (Figure 3) while regions B and D result from relayed magnetization.

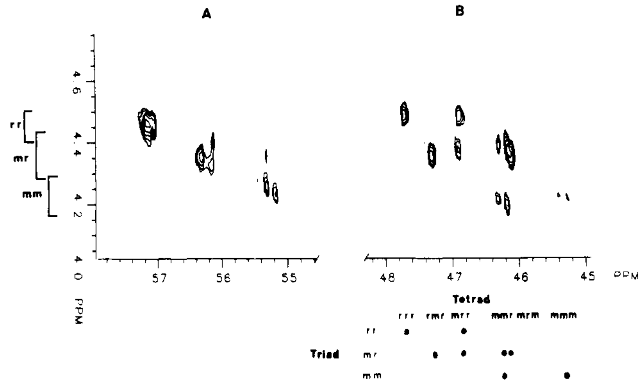

Figure 6. Expansion of regions A and B from Figure 5. The table below illustrates the necessary order of tetrad resonances to achieve a pattern that simulates the experimental spectrum.

Four distinct regions are observed in the spin-lock RELAY spectrum (Figure 5). Regions A and C are the methine and methylene carbons correlated to their own protons as in the heteronuclear shift-correlated experiment. In region B the methylene carbon is correlated to the methine proton, and in region D the methine carbon is correlated to the methylene protons. An expanded view of regions A and B is shown in Figure 6. The tetrads *mmm* and *rrr* in region B are distinguished from other tetrads as being the only sequences *not* correlated to the *mr* triad in region A. This limits the *rrr* and *mmm* tetrads to the two outermost resonances. Since the downfield resonance is clearly not heterosteric, as observed in the shift-correlated experiment, this is assigned to the *rrr* tetrad and the upfield resonance to the *mmm* tetrad. The methylene *mmm* tetrad in region B correlates to the methine triad *mm* in region A, and hence the last triad is the *rr* assignment. The tetrad assignments in region B can be completed on the basis of correlation to the triad sequences which comprise them. This is represented by the

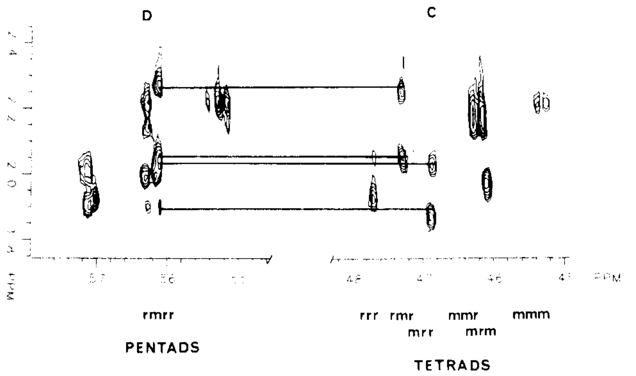

Figure 7. Expansion of regions C and D from Figure 5. The horizontal lines connect a single carbon pentad resonance to tetrad resonances *mrr* and *rmr*, which combine to give only one possible pentad sequence—*rmrr*.

table below region B which simulates the observed pattern of correlated sequences. Four of the six tetrad sequences are comprised of the *mr* triad. Two of these also correlate with the *mm* and *rr* triads and hence are the *mmr* and *rrm* tetrads, respectively. The other two, *mrm* and *rmr*, are distinguishable by their homo- and heterosteric property observed in the shift-correlated spectrum. The *mrm* and *mmr* tetrads are reversed from previous assignments in a similar solvent.[21,25]

The tetrad assignments for the methylene carbon from region B can be easily projected vertically to region C and then correlated to the proton axis, giving the tetrad assignments for the methylene protons. Pentad assignments for the methine carbon in region D can be made by their unique communication to the tetrad assignments of region C (Figure 7). Notice that pentads of the methine carbon are more resolved in region D than in region A since the methine carbon is correlated to the methylene protons vs. the methine proton. The horizontal lines in Figure 7 indicate correlation of a single pentad shift correlated to the *rmr* and *mrr* tetrads, which can only combine to give the *rmrr* assignment. This assignment agrees with Tonelli's calculated shifts for methine pentads.[24]

Conclusions

Configurational assignments have been demonstrated at the tetrad and pentad level for the carbon-13 spectrum of poly(vinyl chloride). The RELAY experiment is used to recognize adjacent carbon-13 nuclei analogous to the INADEQUATE experiment but with greatly increased sensitivity since it uses all carbon-13 sites rather than only 1% of these sites. The RELAY experiment also preserves proton chemical shift information used to discriminate configurational sequences and allow simultaneous assignment of the proton spectra. The newly published RELAY experiment with spin-locking is significant in the application to polymers where short T_2's often limit the obtainable signal to noise in two-dimensional experiments. The new RELAY experiment also provides pure-absorption-mode spectra, adding improved sensitivity and resolution. The stereosequence assignments for the carbon-13 spectrum of PVC differ slightly from previous assignments but have been determined by direct experimental evidence. The effectiveness of this method is not compromised by ambiguities due to shifts from solvent or very atactic nature of the sample. In addition to carbon and proton spectral assignments, proton coupling constants corresponding to each unique stereosequence have been observed with adequate resolution in the F_1 dimension. This information is important in conformational analysis. This method could be extended to other homo vinyl polymers as well as to the determination of monomer sequence distributions in copolymers.

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Registry No. PVC, 9002-86-2.

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