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^{13}C NMR Chemical Shift Assignments of Poly(vinyl chloride) Based on the 2D-INADEQUATE Spectrum

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ABSTRACT: Two-dimensional (2D) heteronuclear ^{1}H–^{13}C, homonuclear ^{1}H, and spin-lock relay NMR experiments have been used to provide ^{13}C NMR chemical shift assignments of stereosequences in poly(vinyl chloride). However, relative areas of methylene tetrad peaks based on the assignments given by these 2D NMR experiments do not agree with the relative areas predicted by Bernoullian propagation statistics. Since the methods of the 2D experiments are correct, this is a puzzle. In this study, tetrad and pentad assignments are proposed on the basis of the carbon–carbon connectivities revealed by the 2D-INADEQUATE (two-dimensional incredible natural abundance double quantum transfer experiment) spectrum. The tetrad assignments given by 2D-INADEQUATE experiments show that there are two mmr peaks and that one of them overlaps the mrm peak. These assignments differ from the previous assignments and resolve the contradication in relative peak areas. The relative areas of methylene peaks based on the assignments from the 2D-INADEQUATE spectrum agree with those predicted by Bernoullian propagation statistics.

Introduction

^{13}C NMR is the most powerful method to analyze the sequence structures in vinyl polymers. Complicated split peaks arising from pentad or hexad sequences are usually observed in the high-resolution NMR spectra. Recently, two-dimensional (2D) NMR experiments have been developed and used as a reliable method of making assignments in high-resolution spectra.

In the field of ^{13}C NMR spectral analysis of poly(vinyl chloride) (PVC), 2D heteronuclear ^{1}H–^{13}C, homonuclear ^{1}H, and spin-lock relay NMR experiments have been used to provide ^{13}C NMR chemical shift assignments of stereosequences in PVC.[1,2] Crowther et al.[2] have demonstrated (from the spin-lock relay experiment) that the mrm and mmr tetrads are reversed from previous assignment in a similar solvent.[3,4]

However, the authors found that the relative areas of methylene tetrad peaks based on the assignments given by these 2D experiments[1,2] do not agree with the relative areas predicted by a Bernoullian propagation model (selection between m and r). The sample used for this investigation was a typical poly(vinyl chloride). It is well-known that vinyl chloride polymerization proceeds under the control of Bernoullian statistics.[4,5] Since the method of the 2D experiment is correct, this contradication is a serious problem.

^{13}C 2D-INADEQUATE (incredible natural abundance double quantum transfer experiment) has been developed as a reliable method to determine the connectivities of carbon atoms.[6–8] Using this method, Hikichi et al.[9] confirmed the validity of the ^{13}C chemical shift assignments of various types of carbons in a stereoirregular ethylene–propylene copolymer proposed by Randall.[10] The pentad and hexad comonomer sequence assignments of stereoregular ethylene–propylene and 1-butene–propylene copolymers were provided from the carbon–carbon connectivities on 2D-INADEQUATE spectra with the aid of chemical shift calculation via the γ-effect method.[11,12] Broad methine peaks with shoulders in the 1D spectrum of ethylene–propylene copolymer are observed separately in the high-resolution 2D-INADEQUATE spectrum.[9] Further, the detailed sequence assignments of regioirregular polypropylene and poly(1-butene) were successfully accomplished in a similar manner.[13,14] Thus, the 2D-INADEQUATE experiment, a powerful method for sequence assignments, is suitable for resolving the contradiction in observed and calculated peak areas of tetrad sequences in PVC.

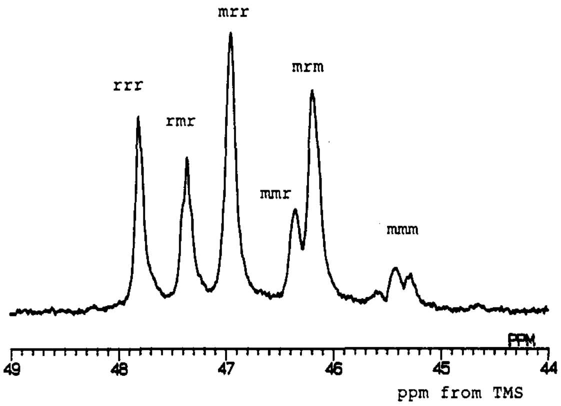

Figure 1. Expanded view of the methylene carbon resonance region of the ^{13}C NMR spectrum of PVCW (whole polymer) with the assignments given by Crowther et al.[2]

Table 1. Comparison of Observed Relative Areas of Methylene Tetrad Peaks with Those Calculated by Bernoullian Statistics

tetrad sequence	obsd	calcd[a]
rrr	0.15	0.16
rmr	0.15	0.14
mrr	0.27	0.27
mmr	0.11	0.23
mrm	0.23	0.11
mmm	0.09	0.10

[a] Calculated by Bernoullian propagation statistics.

In this paper, tetrad assignments of stereosequences in PVC are proposed on the basis of the carbon–carbon connectivities revealed on the 2D-INADEQUATE spectrum. The validity of the proposed assignments is investigated by comparing the relative peak areas observed (based on the assignments by the 2D-INADEQUATE

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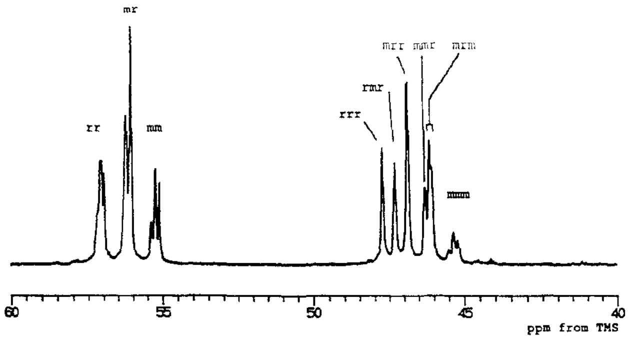


Figure 2. ^{13}C NMR spectrum of PVCS in 1,2,4-trichlorobenzene at 90 °C.

method) with those calculated by the Bernoullian propagation model. Further, pentad assignments are provided from the high-resolution doublet cross peaks in which the connectivities of centered methine carbons in pentads with centered methylene carbons in tetrads appear. Similarly, Bernoullian propagation statistics is used for the confirmation of the pentad assignments.

Experimental Section

Materials. PVC was a commercial product, SA400L, donated by Sun Arrow Chemical Co. Ltd. The samples used in this study were whole polymer (PVCW) and a fraction (PVCS) of PVCW soluble in acetone at 23 °C. The number-average molecular weights were 3.7×10^4 and 3.1×10^4, respectively.

NMR Measurements. ^{13}C NMR spectra were recorded at 90 °C on a JEOL GSX-270 spectrometer operated at 67.8 MHz. The sample solutions at polymer concentrations of 0.1 and 0.25 g cm^{-3} in a 10-mm-o.d. glass tube were prepared by dissolving a polymer in a mixture of 1,2,4,-trichlorobenzene (90 vol %) and benzene-d_6 (10 vol %) for 1D and 2D NMR measurements, respectively. Benzene-d_6 was used for a ^2H NMR internal lock. In the measurement of the 1D ^{13}C NMR spectrum, broad-band noise decoupling was used to remove ^{13}C–^1H couplings. The pulse angle was 90 °C, the pulse repetition time was 15 s, and free induction decays (FIDs) were stored in 64K data points using a spectral window of 20 000 Hz. Hexamethyldisiloxane was used as the internal reference. The 2D-INADEQUATE spectrum was obtained using the pulse sequence developed by Braunschweiler et al.[15] The flip angle of the read pulse was set to be 135° to improve the signal-to-noise ratio.[16] The pulse sequence used is 90°–$1/4J$–180°–$1/4J$–90°–t_1–135°–acquisition (t_2), where J is the coupling constant of ^{13}C signals. The delay time $1/4J$ was set to be 6.80 ms, corresponding to the ^{13}C–^{13}C coupling constant of 34.6 Hz. The repetition time of each pulse sequence was 3 s. FIDs accumulated 256 times at each mixing time (t_1) were stored in a matrix of 4096×128. The data matrix was expanded to 8196×256 by zero-filling for t_1 and t_2 and was multiplied by the exponential window function prior to the double Fourier transform. The row and column frequencies were 1100 and 2200 Hz with data points of 128 and 4096, respectively.

Results and Discussion

1D Spectrum. In Figure 1 is shown the expanded view of methylene carbon resonance region of the ^{13}C NMR spectrum of PVCW (whole polymer) with the assignments given by Crowther et al.[2] The observed relative areas of methylene tetrad peaks were obtained from this spectrum. On the other hand, the relative peak areas were calculated by Bernoullian propagation statistics (selection between m and r). The probabilities of selecting meso dyad (Pm) and of racemic dyad (Pr = 1 − Pm) were determined from the triad sequence distribution, since the relative areas of observed triad peaks are well reproduced by the calculation of Bernoullian model. In Table 1 is shown the comparison of the observed relative areas of tetrad methylene peaks with those calculated. There exists an apparent disagreement of the observed areas with those calculated in mmr and mrm peaks.

In Figure 2 is shown the ^{13}C NMR spectrum of PVCS (fraction of PVCW soluble in acetone) with the assignments by 2D spin-lock relay experiment. In the resonance regions of methylene and methine carbons, tetrad (partly hexad) and pentad splittings are observed, respectively.

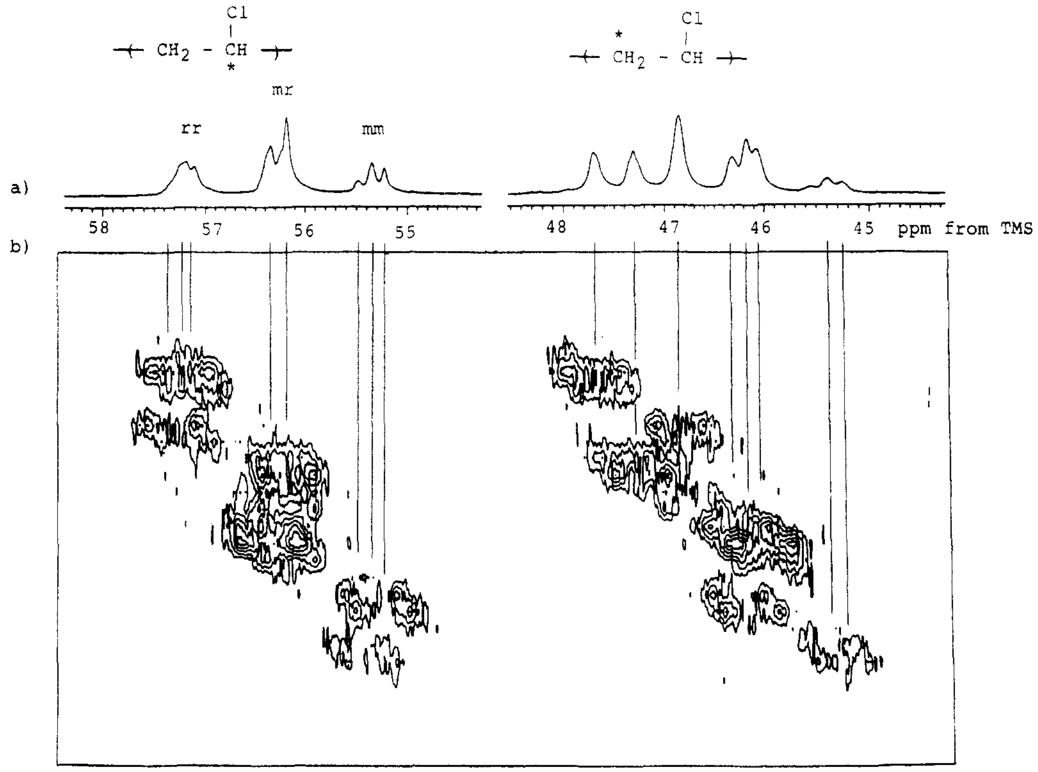


Figure 3. 1D (a) and 2D-INADEQUATE (b) ^{13}C NMR spectra of PVCS at 90 °C. Vertial lines represent the correspondence of split peaks on the 1D spectrum and doublets on the 2D spectrum.

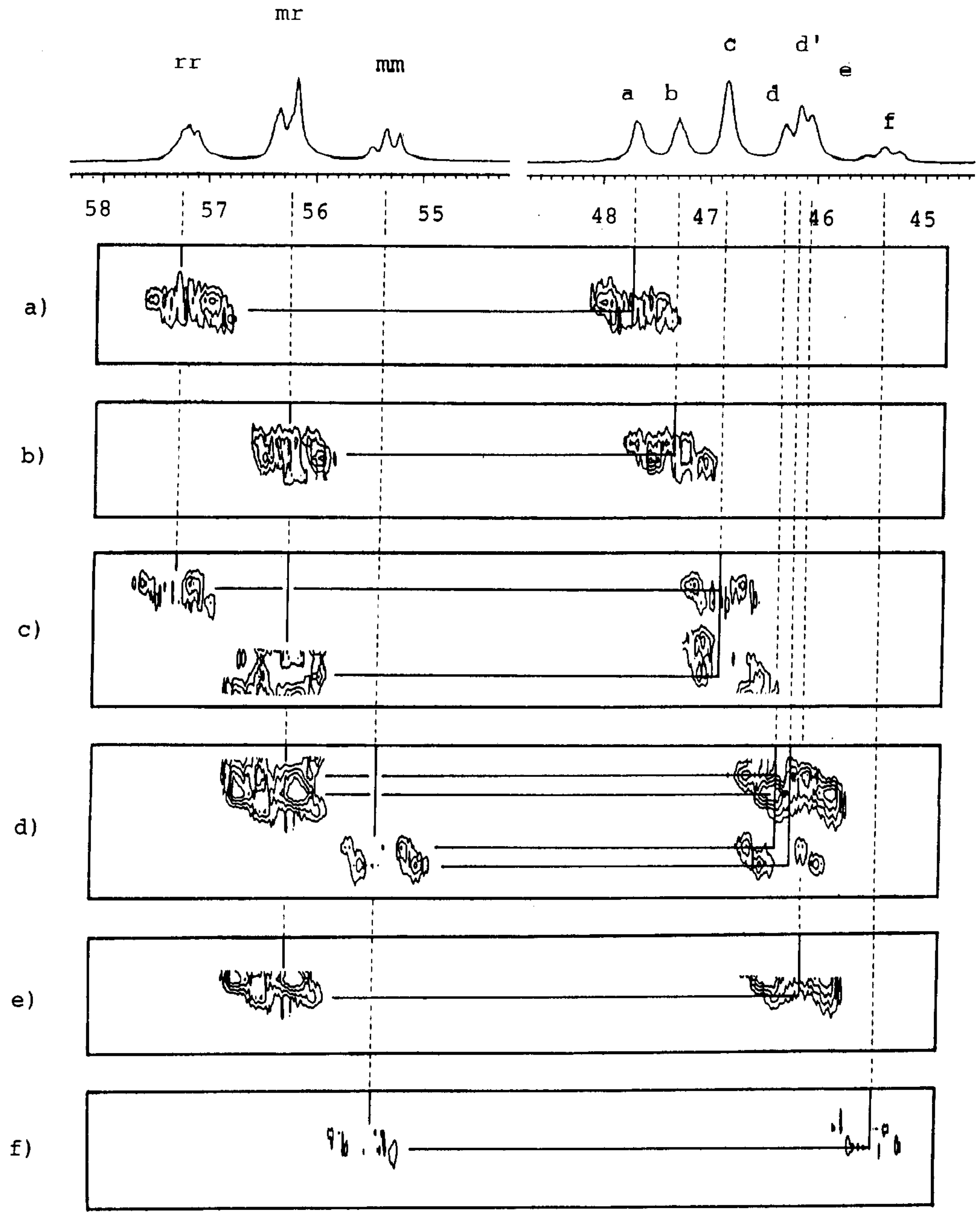


Figure 4. Connectivities between methine and methylene carbons are indicated by solid lines. Resultant assignments of split peaks of methylene carbon resonance regions are (a) rrr, (b) mrm or rmr, (c) mrr, (d) mmr, (e) mrm or rmr, and (f) mmm.

In the region of mrm sequence (based on the previous assignments[2]), apparently observed are split peaks arising from different hexad sequences. 2D ^1H–^{13}C shift correlated (COSY) and spin-lock relay spectra[2] indicate that there are two mmr peaks and the mmr peak at the higher field is very close to mrm peak. It is assumed that the peak at the lower field of the split peaks (in the region of mrm sequence) is mmr and the peak at the higher field is mrm.

Tetrad Assignments Based on the 2D-INADEQUATE Spectrum. In Figure 3 is shown the 2D-INADEQUATE spectrum of PVC. Many doublet signals corresponding to the 1D peaks are observed. Tetrad assignments are provided by tracing the carbon–carbon connectivities on the 2D-INADEQUATE spectrum. Triad peaks of methine carbons are used as the references for the tetrad assignments, since these assignments are absolutely correct on the basis of the ^1H–^1H and ^1H–^{13}C COSY experiments.[1,2] In Figure 4 are shown the expanded doublet peaks of methylene and methine carbons. The connectivities between tetrad methylene and triad methine peaks are represented by solid lines.

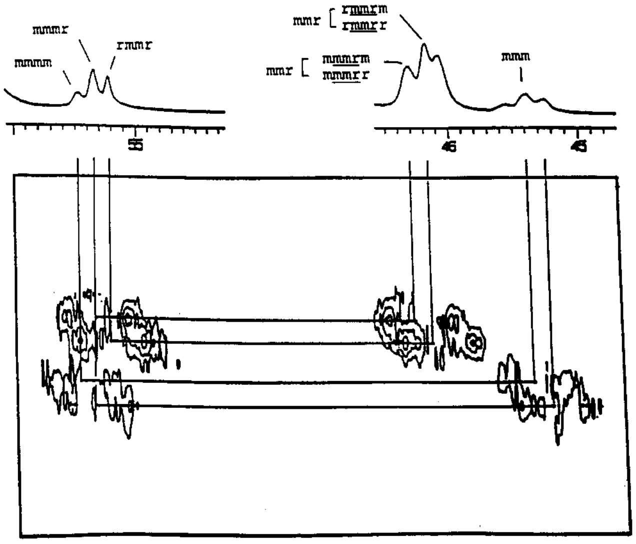


Figure 5. Expanded ^{13}C doublets of the mm centered pentad region and mmr and mmm tetrad regions in the 2D-INADEQUATE spectrum of PVCS.

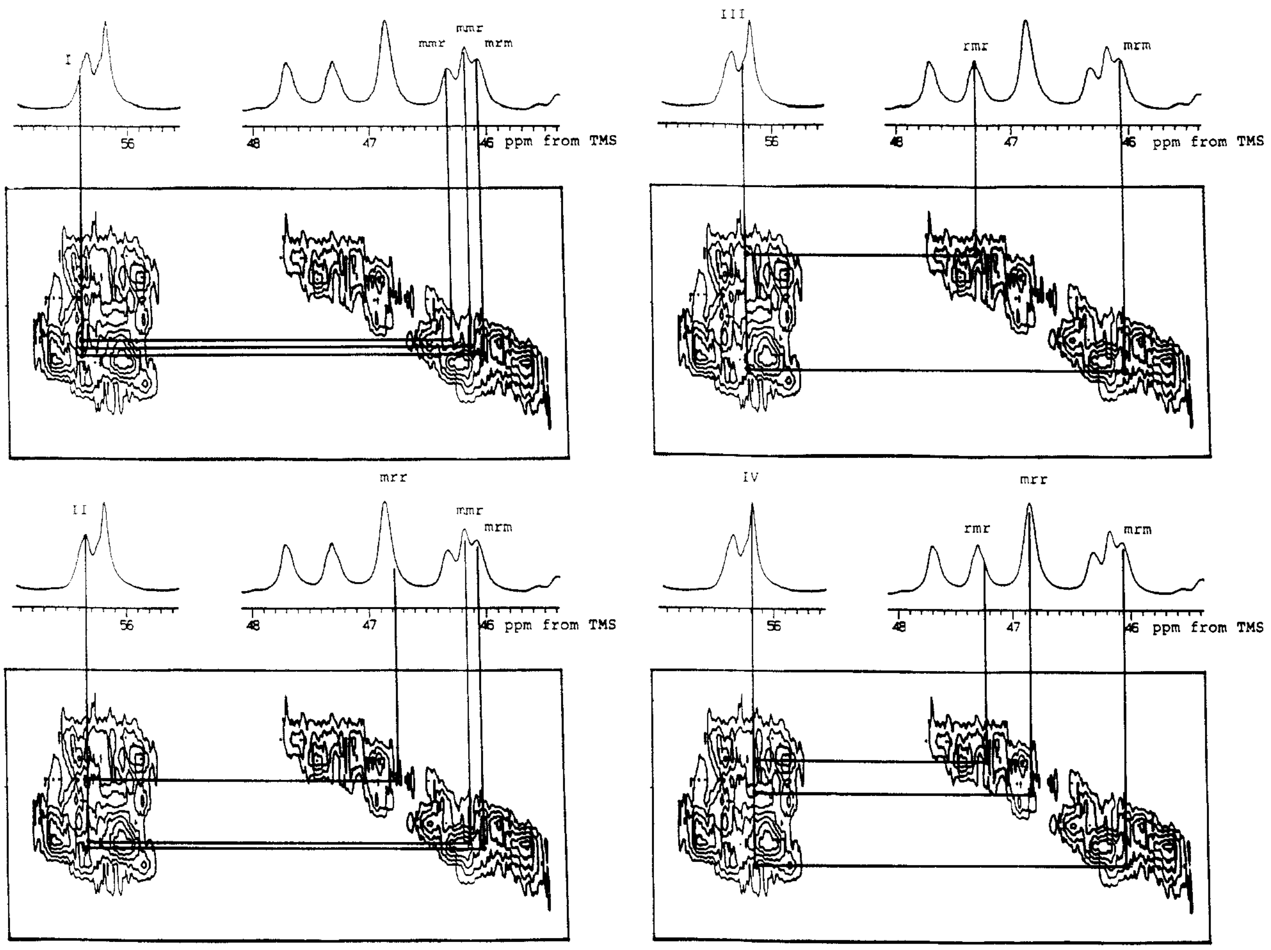


Figure 6. Expanded ^{13}C doublet peaks of methine carbons in mr centered pentads and those of methylene carbons in the 2D-INADEQUATE spectrum of PVCS: (a, top left) connectivities between I and tetrad methylene carbons; (b, bottom left) connectivities between II and tetrad methylene carbons; (c, top right) connectivities between III and tetrad methylene carbons; (d, bottom right) connectivities between IV and tetrad methylene carbons.

Since the centered methylene carbons in mmm and rrr tetrads should connect only centered methine carbons in mm and rr triads, respectively, the assignments of mmm (peak f) and rrr (peak a) tetrads are easily provided from the connectivities (f) and (a). Hexad splittings are observed in the area of peak d. Since the mmr peak should correlate to mm and mr peaks, the assignments of peaks d and d′ are mmr centered hexads from the connectivity (d). Similarly, the assignment of peak c is mrr (from connectivity (c)). The peaks of mrm and rmr are not distinguishable, because centered methylene carbons in mrm and rmr tetrads connect only centered methine carbons in mr triad.

Pentad and Hexad Assignments. In Figure 5 are shown the connectivities between mm centered pentads and tetrad (mmr and mmm) peaks. The assignments of mmmm, mmmr, and rmmr pentads (in Figure 5) are provided by tracing the represented connectivities, because methine carbons in mmmm and rmmr pentads should connect only centered methylene carbons in mmm and mmr tetrad, respectively, and because methine carbon in mmmr pentad should connect centered methylene carbons in mmm and mmr tetrads. The assignments of rr centered pentad peaks are similarly provided.

Since methylene centered hexad sequences should include neighboring methine centered pentad sequences, the upfield peak of mmr centered hexads is r*mmr*x (x = m or r) and the lower field one is m*mmr*x.

In Figure 6a–d are shown the connectivities between *mr* centered pentad and tetrad peaks. Two m*mr* centered hexad peaks correlate to peaks I (shoulder) and II. This result indicates that methine carbons appearing as peaks I and II are included in the tetrad structure of m*mr*. Methine carbons as peaks III (shoulder) and IV should be included in the structure of r*mr*, which is the other tetrad of x*mr* (x = m or r). On the basis of this consideration, mrm and rmr peaks are distinguishable. The peak of rmr cannot correlate to peaks I and II. Since the peak at 47.3 ppm correlates to peaks III and IV (Figure 6c,d), this peak is rmr. The peak at 46.1 ppm, correlating to peaks I, II, III, and IV, is mrm. Thus, triad assignments are complete. Further, mr centered pentad assignments are provided from the following correlations revealed in the high-resolution 2D spectra. The pentad sequences satisfying

correlation	methine carbon peak	methylene carbon peak
I	I	mmr, mrm
II	II	mrr, mmr, mrm
III	III	rmr, mrm
IV	IV	rmr, mrr, mrm

correlations I and III are mmrm and rmrm, respectively. Possible pentad sequences corresponding to correlations II and IV are mmrm and mmrr, and rmrm and rmrr, respectively. Proposed assignments of mr centered pentads from 2D spectrum are as follows. This indicates that

peak	assignments
I	mmrm
II	mmrm and mmrr
III	rmrm
IV	rmrm and rmrr

Table 2. Comparison of Observed Relative Areas of Methine and Methylene Peaks with Those Calculated by Bernoullian Propagation Statistics

methine (CH)				
no.	obsd pentad		assignment	calcd pentad
1	0.07		mrrm	0.06
2	0.15		mrrr	0.15
3	0.08		rrrr	0.09
4	0.07	0.24	mmrm	0.23
5	0.18		mmrm	
			mmrr	
6	0.07	0.26	rmrm	0.27
			rmrm	
7	0.19		rmrr	
8	0.05		mmmm	0.04
9	0.09		mmmr	0.10
10	0.07		rmmr	0.06

methylene (CH_2)			calcd	
no.	obsd tetrad	assignment	hexad	tetrad
1′	0.15	rrr		0.16
2′	0.15	rmr		0.14
3′	0.27	mrr		0.27
4′	0.11	mmmrm	0.05	0.11
		mmmrr	0.06	
5′	0.14	rmmrm	0.06	0.13
		rmmrr	0.07	
		mmrmm	0.02	
6′	0.09	mmrmr	0.06	0.11
		rmrmr	0.03	
			0.02	
7′	0.09	mmm	0.05	0.10
			0.03	

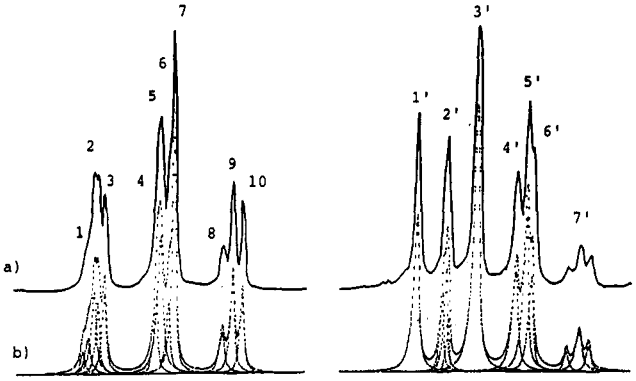
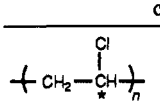
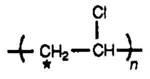


Figure 7. ^{13}C NMR spectrum of PVCS and the results of curve resolution: (a) observed spectrum; (b) results of curve resolution.

methine resonances of mmrm and mmrr overlap as peak II and those of rmrm and rmrr as peak IV and that shoulder peaks I and III are mmrm and rmrm, respectively.

Confirmation of the Assignments by Propagation Statistics. It is well-known that the polymerization of vinyl chloride proceeds under the control of the Bernoullian statistical model[4,5] (selection between meso and racemo). In Table 2 is shown the comparison of the observed relative areas of methine pentad and methylene peaks with those calculated by Bernoullian propagation statistics. Relative areas of observed peaks are determined by the curve resolution method[17] obtained using a PC-9801 microcomputer.[18] The observed spectrum and the results of curve resolution are shown in Figure 7. The relative areas of observed pentad peaks agree well with those calculated, indicating the validity of our pentad assignments. As for the methylene peaks, observed areas (except peak 6′) agree well with those calculated. Assuming that the resonance of m*mrm*m overlaps peak 5′, the agreement of the observed and calculated areas of peak 6′ is improved. From the correlation (Figure 5) between methine peak of rmmr and methylene peak (peak 5′) of r*mmr*x (x = m or r), this overlap is plausible. It is impossible for the resonances of m*mrm*r and r*mrm*r to overlap peak 5′ because this hexad should include the pentad structure, rmmr. Consequently, tactic sequence assignments of PVC are proposed, as shown in Table 3. In the 1D spectrum of PVCW (whole polymer, Figure 1), the peak with the assignment of mmr and mrm by 2D spin-lock relay experiment should be m*mmr*x (x = m or r) and the overlap of r*mmr*x (x = m or r) and mrm, respectively.

Table 3. ^{13}C NMR Chemical Shift Assignments of PVC in 1,2,4-Trichlorobenzene at 90 °C

	chemical shift (ppm)	assignment
	57.11	mrrm
	57.05	mrrr
	56.96	
	56.82	rrrr
	56.47	mmrm
	56.43	mmrm + mmrr
	56.22	rmrm
	56.04	rmrm + rmrr
	55.37	mmmm
	55.23	mmmr
	55.10	rmmr
	47.73	rrr
	47.29	rmr
	46.82	mrr
	46.27	mmmrm + mmmrr
	46.12	rmmrm + rmmrr + mmrmm
	46.04	mmrmm + rmrmr
	45.47	
	46.32	mmm
	45.18	

Conclusions

Tactic pentad assignments of PVC were proposed on the basis of 2D-INADEQUATE spectrum and propagation statistics of vinyl chloride polymerization. Connectivities of carbon atoms revealed in the high-resolution 2D spectrum provide detailed assignments of complicated split peaks, even though they are shoulders. This analysis resolved the contradication in previous assignments of methylene tetrad sequences concerning the disagreement of the observed and calculated peak areas. Thus, it was demonstrated that the 2D-INADEQUATE experiment is very powerful for the assignments of tactic sequences in vinyl polymers.

References and Notes

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