Two-Dimensional ^{1}H and ^{13}C Nuclear Magnetic Resonance Studies of Poly(acrylamide)

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ABSTRACT: The ^{1}H and ^{13}C nuclear magnetic resonance spectra of poly(acrylamide) (PAA) in D_2O at a temperature of 343 K were analyzed by two-dimensional NMR (2D NMR) methods including ^{1}H J-resolved spectroscopy, F_1-axis (^{1}H) broad-band decoupled correlation spectroscopy, and ^{1}H broad-band decoupled ^{13}C–^{1}H chemical shift correlation spectroscopy. Combined use of these 2D NMR methods provided absolute assignments of ^{1}H and ^{13}C spectra at the triad–tetrad level. At the pentad–hexad level, the ^{13}C spectra were assigned by the aid of spectral simulation. The polymerization of PAA proceeds in a Bernoulli-trial process with $P_m = 0.45$.
        KEY WORDS   Poly(acrylamide) / ^{1}H NMR / ^{13}C NMR / Tacticity / Two-
            Dimensional NMR /

In a previous paper,[1] we demonstrated that the combined use of various two-dimensional (2D) NMR spectroscopies[2,3] is quite helpful for assigning ^{1}H and ^{13}C spectra of poly(vinyl alcohol) to specific stereo-configuration. In this paper, we extend this method of assignment to poly(acrylamide) (PAA).

EXPERIMENTAL

A PAA sample was prepared by polymerization of acrylamide monomer in aqueous solution using ammonium persulfate as an initiator at room temperature.

^{1}H NMR experiments were performed on a JEOL JNM-GX400 spectrometer operating at a frequency of 400 MHz and ^{13}C NMR experiments were made on a JEOL JNM-GX500 spectrometer at a frequency of 125 MHz. All experiments were conducted at a temperature of 343 K.

In order to suppress a large residual water signal in ^{1}H spectra, exchangeable amino protons were replaced with deuterium by repeated lyophilization from D_2O solution.

The ^{1}H J-resolved spectrum was observed in a 5 mm tube containing about 0.6 ml solution at a concentration of 5% (w/v) in D_2O in the F_1 frequency range of 50 Hz and the F_2 frequency range of 600 Hz. The time domain data matrix of 64×1024 points was obtained using the pulse sequence: $90°\text{-}t_1/2\text{-}180°\text{-}t_1/2\text{-acq}(t_2)$. For each t_1 value, 256 transients were accumulated. The total data acquisition time was 16 h. The data matrix was expanded to 128×2048 by zero-filling and multiplied by a Lorentzian–Gaussian window function in the F_2 dimension and the sine-bell function in the F_1 dimension prior to the Fourier transformation. After the Fourier transformation the spectrum was symmetrized.

The F_1-axis broad-band decoupled corre-

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lation spectroscopy (BDCOSY) was performed in a frequency range of 600 Hz in both dimensions for the same sample as used in the J-resolved experiment. The time domain data were collected in a data matrix of 128×2048 points using the pulse sequence $90°-t_1/2-180°-(t_d-t_1/2)-45°$-acq (t_2) proposed by Brown.[4] For each t_1 value, 160 transients were accumulated. The total data collection time was 18 h. The data matrix was zero-filled to 512×2048 and multiplied by Lorentzian–Gaussian window functions in both dimensions before the Fourier transformation.

The F_1-axis (^{1}H) broad-band decoupled ^{13}C–^{1}H chemical shift correlation spectroscopy (CHCOSY) was made at a concentration of 40% (w/v) in D_2O in the F_1 (^{1}H) frequency range of 600 Hz and the F_2 (^{13}C) frequency range of 1500 Hz. The time domain data matrix of 64×1024 points was obtained using the pulse sequence: $90°(^1H)-t_1/2-90°(^1H)-1/2J-180°(^1H)$, $180°(^{13}C)-1/2J-90°(^1H)-t_1/2-1/2J-90°(^1H)$, $90°(^{13}C)-0.3/J$-acq (^{13}C with ^{1}H decoupled, t_2) proposed by Bax.[5] For each t_1 value, 1024 transients were accumulated in 15.8 h. The data matrix was zero-filled to 256×2048. Lorentzian–Gaussian window functions were multiplied in both dimensions prior to the Fourier transformation.

All 2D spectra are presented in absolute values. ^{1}H chemical shifts were measured relative to methylene peak b (*mmr*) as 1.75 ppm, and ^{13}C chemical shifts to the largest methine peak 2′ (*mr*) as 42.84 ppm.
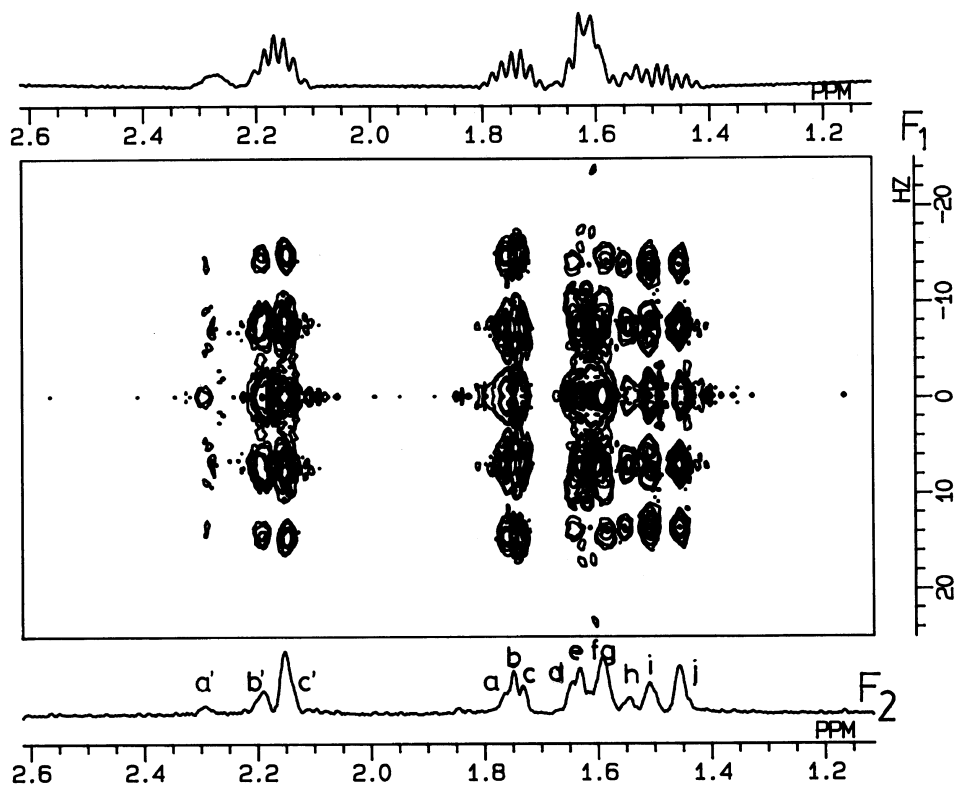

Figure 1. ^{1}H 400 MHz J-resolved 2D spectrum of PAA at a concentration of 5% (w/v) in D_2O at a temperature of 343 K. At the top, the resolution-enhanced normal one-dimensional (1D) spectrum is shown, and at the bottom, the projection of the J-resolved 2D spectrum onto the F_2-axis, the so-called broad-band decoupled spectrum.

RESULTS AND DISCUSSION

Figure 1 shows the ^{1}H 400 MHz J-resolved 2D spectrum of PAA at a concentration of 5% (w/v) in D_2O at 343 K. At the top, the resolution-enhanced normal one-dimensional (1D) spectrum is shown, and at the bottom, projection of the J-resolved 2D spectrum onto the F_2-axis, the so-called broad-band decoupled spectrum. The figure indicates that methines and methylenes exhibit three and ten peaks different in chemical shift, respectively, suggesting that methines and methylenes are resolved at the triad–tetrad level.

Figure 2 shows the ^{1}H 400 MHz DBCOSY spectrum of PAA at a concentration of 5% (w/v) in D_2O at 343 K. At the bottom the resolution-enhanced normal 1D spectrum is shown, and at the left-hand side is shown the projection of the J-resolved 2D spectrum. Along a line with a slope of $-1/2$ appear ghost diagonal peaks accompanyed by ghost cross peaks due to fast relaxation recovery for a constant period of t_d.
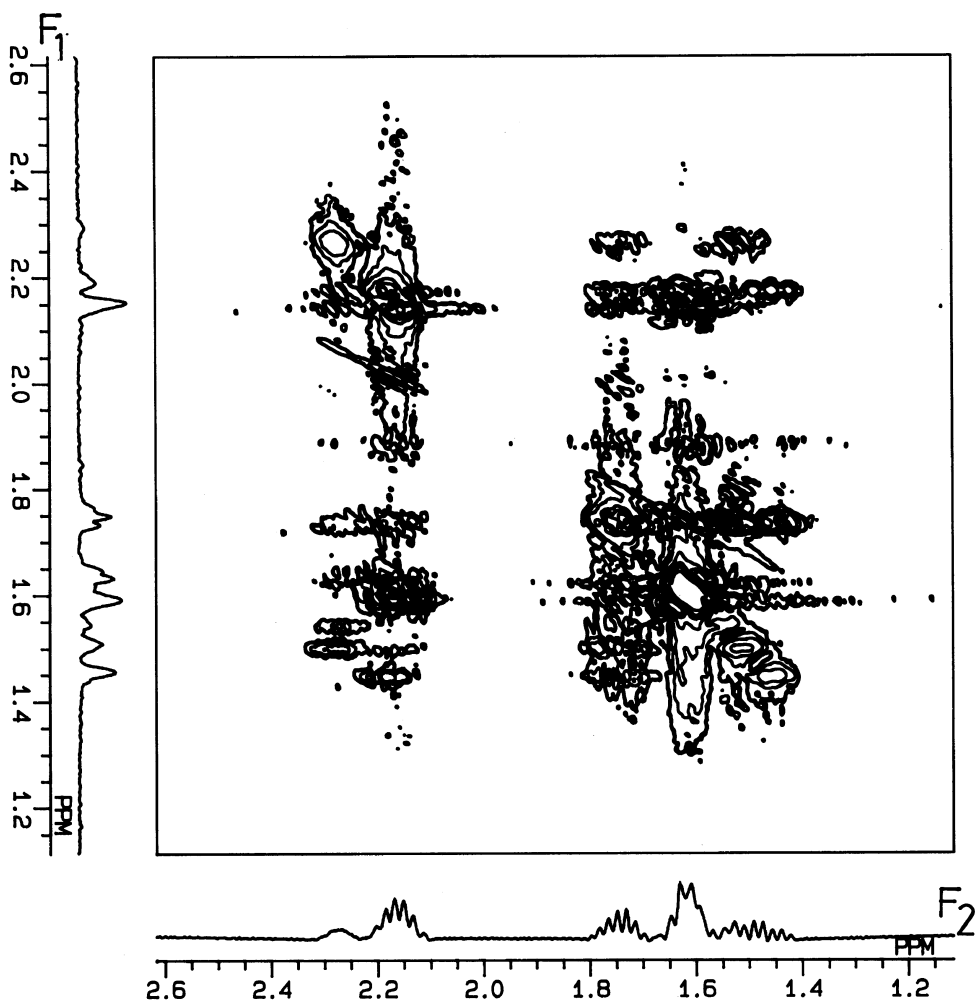

Figure 2. ^{1}H 400 MHz F_1-axis broad-band decoupled COSY spectrum (DBCOSY) of PAA at a concentration of 5% (w/v) in D_2O at a temperature of 343 K. At the bottom, the resolution-enhanced normal 1D spectrum is shown, and at the left-hand side, projection of the J-resolved 2D spectrum.
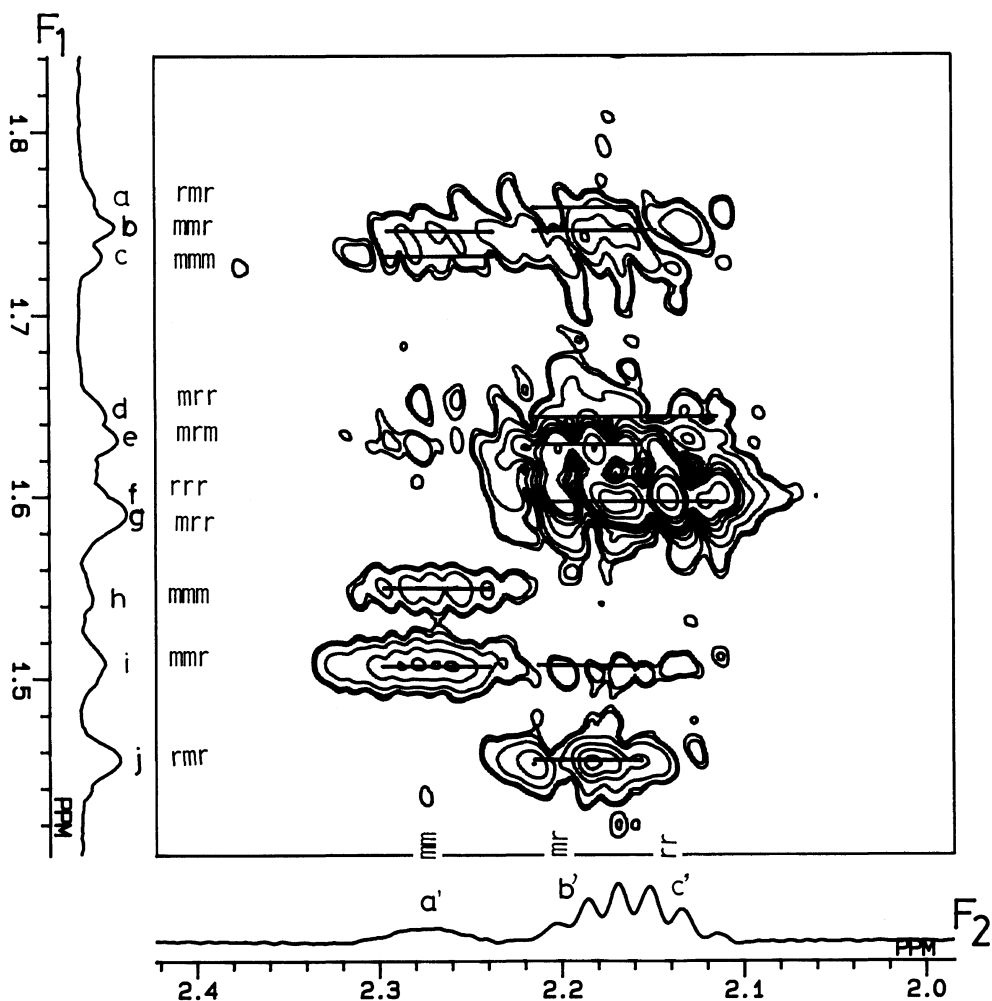
Figure 3. Expanded view of a cross peak region of methine–methylene protons of Figure 2. Bars indicate predicted cross peaks.

Expanded views of a cross peak region of methine–methylene and a diagonal/cross peak region of methylenes are shown in Figures 3 and 4, respectively.

Consideration of the connectivity of methylene and methine at the triad–tetrad level leads to the following rules[1,6]: (1) methylenes that have only one cross peak with methine must be one of *mmm*, *rmr*, *mrm*, or *rrr* methylenes (*e.g.*, *mmm*—*mm*, *rmr*—*rm*, *mrm*—*mr*, *rrr*—*rr*), (2) among these four methylenes, *mmm* and *rmr* methylenes may show cross

peaks between methylene protons, because *mmm* and *rmr* methylenes have non-equivalent geminal protons, and (3) *mm* methine has cross peaks with only non-equivalent methylenes, *mmm* and *mmr*.

Inspection of the cross peak region of methine–methylene indicates that methylene peak j has a cross peak with only one methine peak b′, and that methylene peak h has a cross peak with only one methine peak a′. Rule 1 indicates that possible candidates for j and h are *mmm*, *rmr*, *mrm*, and *rrr* methylene pro-
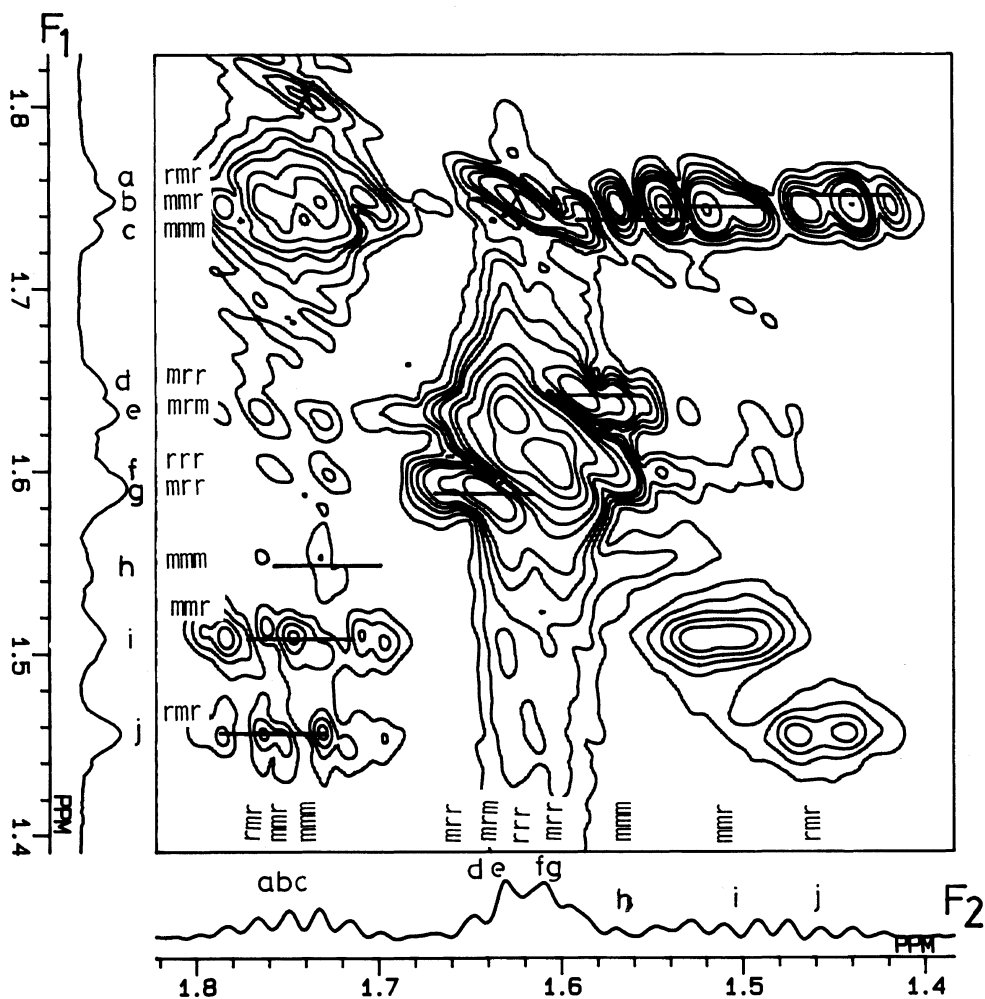
Figure 4. The expanded view of a diagonal/cross peak region of methylenes in Figure 2. Bars indicate predicted peaks. × indicates ghost peaks.

tons. Figure 4 shows that methylene peaks h, i, and j have cross peaks with other methylene peaks c, b, and a, respectively, indicating that pairs of peaks, a—j, b—i, and c—h, are due to non-equivalent methylene protons. Thus, methylene peaks h and c are assignable to geminal protons of *mmm* methylene and methylene peaks j and a to geminal protons of *rmr* methylene, or *vice versa*. Correspondingly, methine peaks a′ and b′ are assignable, respectively, to *mm* and *mr*, or *vice versa*.

It can be seen in Figure 3 that methine a′ has

cross peaks with only non-equivalent methylenes (peaks b, c, h, and i). Therefore, we can assign methines a′, b′, and c′ to *mm*, *mr*, and *rr* methines, respectively. Consequently, methylene peaks j and a can be assigned to *rmr* methylene and methylene peaks h and c to *mmm* methylene. Methylene peak i has two cross peaks with methines a′ and b′, indicating that methylene peak i as well as its partner b is assignable to *mmr*.

Figure 4 shows that peaks e and f have no cross peak between methylene peaks, indicat-

ing that these two peaks are assignable to equivalent methylene protons of *mrm* and *rrr*. Figure 3 shows that peak e has a cross peak with *mr* methine and that peak f seems to have a cross peak with *rr*, indicating that peaks e and f are assignable to *mrm* and *rrr* methylenes, respectively. Figure 4 shows that peaks d and g are due to two non-equivalent geminal protons of a methylene. These two peaks d and g have cross peaks with *mr* and *rr* methines as seen in Figure 3. Thus, we can assign peaks d and g to geminal protons of *mrr* methylene. Predicted cross peaks are shown by bars in Figures 3 and 4.

Table I lists the assignments of the ^{1}H spectrum of PAA in D$_2$O at 343 K. To author's knowledge, this is the first report on assignments of ^{1}H spectrum of PAA. The present assignment indicates that peaks a and

Table I. Resonance assignments and chemical shift values of the ^{1}H spectrum of PAA in D$_2$O at 343 K

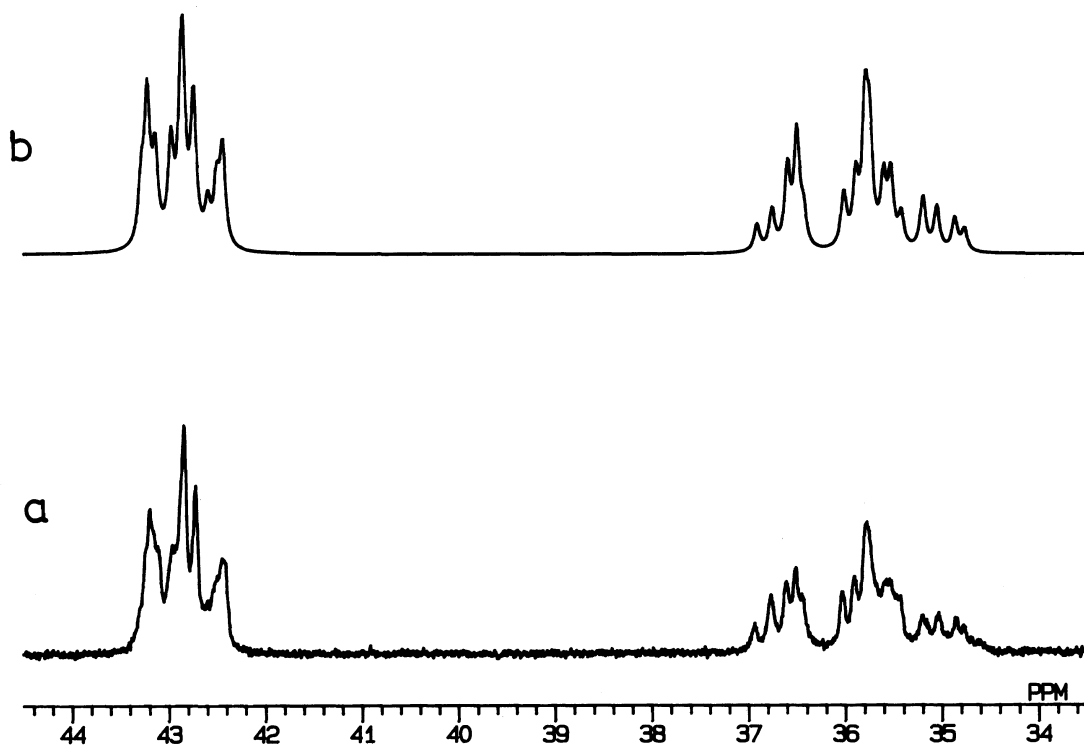| Peak	Configuration	Chemical shift/ppm
CH$_2$		
a	*rmr*	1.77
b	*mmr*	1.75
c	*mmm*	1.73
d	*mrr*	1.65
e	*mrm*	1.63
f	*rrr*	1.61
g	*mrr*	1.59
h	*mmm*	1.55
i	*mmr*	1.51
j	*rmr*	1.46
CH		
a′	*mm*	2.29
b′	*mr*	2.19
c′	*rr*	2.15

Figure 5. (a) 125 MHz ^{1}H noise-decoupled ^{13}C NMR spectrum of PAA at a concentration of 40% (w/v) in D$_2$O at temperature of 343 K. (b) The simulated spectrum calculated using the chemical shift values in Table II, $P_m = 0.45$, and a line width of 7 Hz.

j, peaks b and i, peaks c and h, and peaks d and g are pairs of geminal protons of non-equivalent methylenes *rmr*, *mmr*, *mmm*, and *mrr*, and that these pairs should be doublets of equal intensity. It should be noticed that the so-called broad-band decoupled spectrum which is shown in Figures 2, 3, and 4 does not necessarily have a correct intensity relationship. This is because of the use of resolution-enhanced window function, the failure of weak-coupling assumption, and the dispersion of chemical shifts due to higher order tacticity.

Figure 5(a) shows the 125 MHz ^{1}H noise-decoupled ^{13}C spectrum of PAA at a concentration of 40% (w/v) in D_2O. The spectrum displays two groups of resonances from methine and methylene as does also the ^{1}H spectrum. Methine and methylene resonances consist, respectively, of at least 10 and 16

resolved peaks due to different configurations, suggesting that resonances are distinguishable at the pentad–hexad or higher level.

Figure 6 shows the F_1 (^{1}H)-axis broad-band decoupled CHCOSY spectrum of PAA at a concentration of 40% (w/v) in D_2O at a temperature of 343 K; (a) is the expanded view of methine region and (b) is that of the methylene region. F_1-axis corresponds to the ^{1}H resonance and F_2-axis to the ^{13}C resonance. Since methine proton resonances a′, b′, and c′ have already been assigned to *mm*, *mr*, and *rr* triad, the C–H correlation of methines shown in Figure 6(a) indicates that methine carbon resonances 1′, 2′, and 3′ are assignable to *rr*-centered pentads, 4′, 5′, 6′, and 7′ to *mr*-centered pentads, and 8′, 9′, and 10′ to *mm*-centered pentads.

Figure 6(b) shows that methylene carbon
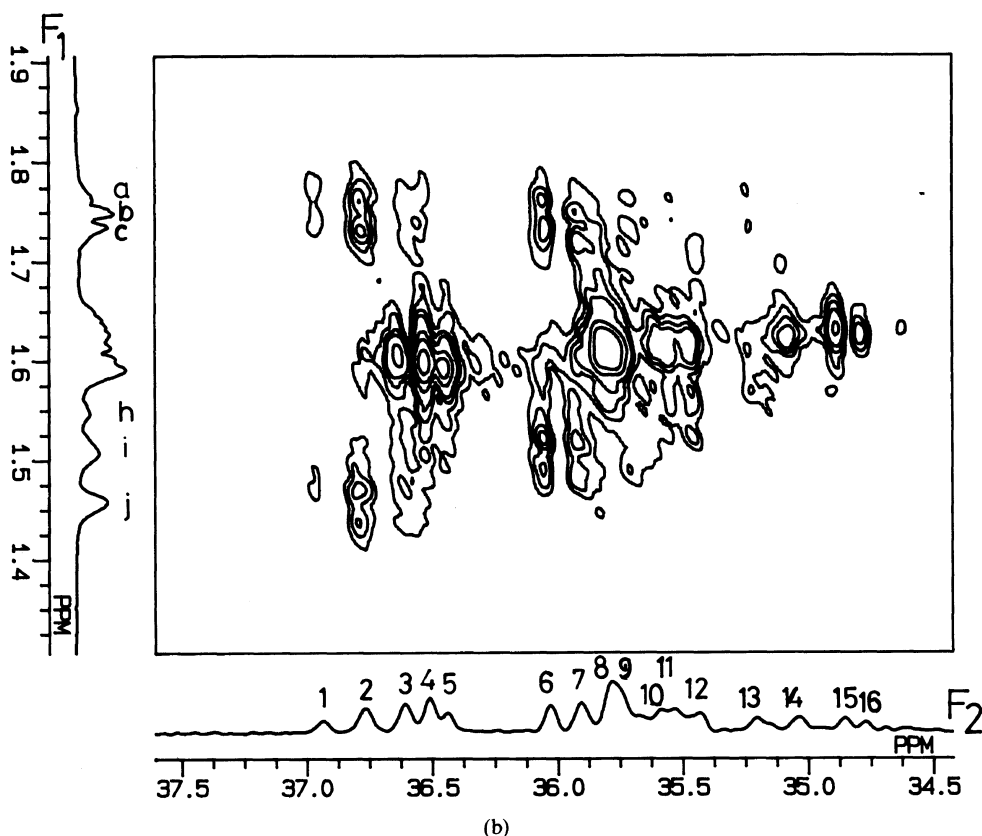

(a)

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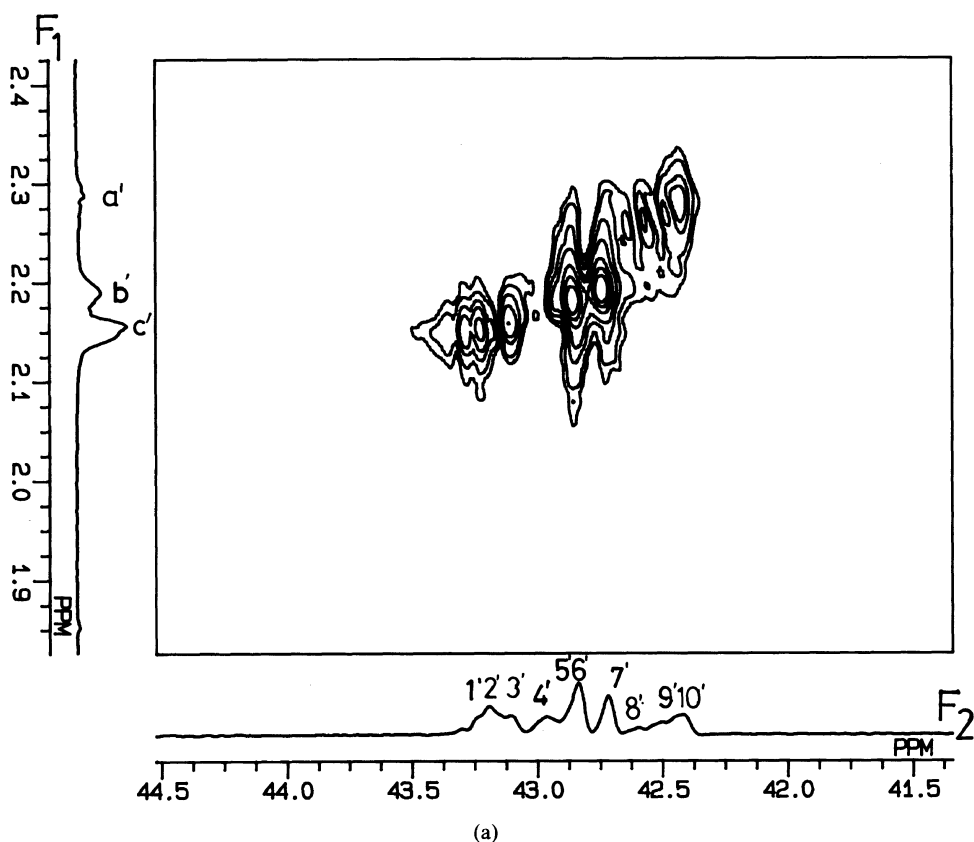
Figure 6. 125 MHz $F_1(^1H)$-axis broad-band decoupled CHCOSY spectrum of PPA at a concentration of 40% (w/v) in D_2O at a temperature of 343 K; (a) expanded view of methine region and (b) expanded view of the methylene region.

resonances 1, 2, and 3 or 4 have cross peaks with methylene protons a and j, suggesting that these carbon resonances can be assigned to *rmr*-centered hexads. Peaks 6, 7, 8, and 9 have cross peaks with i and b, indicating that these are assignable to *mmr*-centered hexads. Some of peaks 10, 11, 12, 13, and 14 are correlated with methylene peak h, implying that these are assignable to *mmm*-centered hexads. Peaks 3, 4, 5, and peaks from 8 to 16 seem to be correlated with the central band of methylene resonances including *rrr*, *mrm*, and *mrr*.

We could not make complete assignment of methine and methylene carbon resonances at the pentad–hexad level through the CHCOSY, because ^1H resonances are not resolved at the same level. To perform assignments at the pentad–hexad level, we adopted the statistical method at this stage. Assuming the Bernoulli-trial process for polymerization, we obtained $P_m = 0.45$ as the probability of adding a monomer to the chain in the meso fashion from the integral intensity of methine carbon peaks $1'$—$7'$ at the triad–tetrad level. Using this probability value, we calculated the distribution of pentads and hexads and simulated spectrum by adjusting chemical shifts of pentads and hexads in accordance with assignments at the triad–tetrad level. Figure 5(b) shows one of the simulated spectra, which is in a relatively good agreement with the observed one. This agreement suggests that the polymerization proceeds in the Bernoulli-trial process.

Table II. Resonance assignments and chemical shift values used for simulation of the ^{13}C spectrum of PAA in D_2O at 343 K

Peak	Configuration	Chemical shift/ppm
CH_2		
1	*mrmrm*	36.90
2	*rrmrr*	36.74
3	*mrrrr*	36.58
4	*rrmrm, rrrrr*	36.48
5	*mrrrm*	36.42
6	*rmmrm*	36.00
7	*rmmrr*	35.88
8	*mmmrr, rmrrr*	35.78
9	*mmmrm, rmrrm*	35.73
10	*mmrrr*	35.59
11	*mmmmm, mmrrm*	35.51
12	*rmmmr*	35.41
13	*rmrmm*	35.18
14	*mmmmr*	35.04
15	*rmrmr*	34.85
16	*mmrmm*	34.75
CH		
1'	*mrrm*	43.27
2'	*mrrr*	43.21
3'	*rrrr*	43.13
4'	*mmrm*	42.96
5'	*rmrm*	42.86
6'	*mmrr*	42.84
7'	*rmrr*	42.73
8'	*mmmm*	42.58
9'	*rmmr*	42.49
10'	*mmmr*	42.43

Exact agreement between observed and simulated spectra is difficult to obtain because of line broadening and chemical shift dispersion at higher levels.

Table II lists a compilation of assignments and chemical shift values used in the simulation of the ^{13}C spectrum of PAA in D_2O at 343 K. We believe that assignments of methine carbon resonances are mostly correct, but methylene carbon assignments are left to be revised.

Inoue, et al.,[7] reported the analysis of ^{13}C spectrum of PAA. They assigned the central band of methine resonance to the *mr* triad, but could not assign the other resonances. The present work is the first to report assignments of ^{13}C NMR spectrum of PAA.

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