Compositional and Stereochemical Analysis of Acrylamide/Vinyl Acetate Copolymers by One and Two-Dimensional NMR Spectroscopy

4 AUTHORS, INCLUDING:

Kaushik Dutta

New York Structural Biology Center

64 PUBLICATIONS **817** CITATIONS

Compositional and Stereochemical Analysis of Acrylamide/Vinyl Acetate Copolymers by One- and Two-Dimensional NMR Spectroscopy

Munia Mukherjee and S. K. Chatterjee

Department of Chemistry, Delhi University, Delhi 110 007, India

A. S. Brar* and Kaushik Dutta

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110 016, India

Received June 15, 1998; Revised Manuscript Received September 1, 1998

ABSTRACT: Acrylamide/vinyl acetate copolymers were prepared by solution polymerization using benzoyl peroxide as the initiator. The copolymer composition was determined from the percent nitrogen in the copolymers. The comonomer reactivity ratios determined using Kelen−Tudos and nonlinear error-in-variable methods are $r_A = 9.28 \pm 0.6$ and $r_V = 0.09 \pm 0.006$. The triad sequence distributions in terms of A- and V-centered triads have been obtained from $^{13}C\{^1H\}$ NMR spectra of the copolymers. The methine and the methylene carbon signals were assigned to compositional (triad, tetrads, and pentads) and configurational (triads) sequences. The broad and overlapping ^1H NMR spectra were assigned with the help of 2D inverse-HETCOR and TOCSY experiments.

Introduction

The macroscopic properties of bulk polymers are influenced fundamentally by their chain level microstructure which can be investigated by NMR spectroscopy.[1−3] Complicated split resonance signals arising from higher order configurational or compositional sequences are usually observed in high-resolution NMR spectra. Two-dimensional NMR, especially the homonuclear (COSY) and heteronuclear (HETCOR) correlation spectroscopies, can be used as reliable techniques for assigning high-resolution spectra.[4−6]

Poly(vinyl acetate) and copolymers of vinyl acetate are widely used in water-based paints, adhesives, paper coating, and nonwoven binders. Many workers have reported the sequence distribution in copolymers of vinyl acetate with ethylene,[7] vinyl alcohol,[8] alkyl acrylates,[9,10] etc. To the best of our knowledge, the microstructure of the acrylamide/vinyl acetate copolymer (A/V) system has not been reported. In this paper, we report the polymerization mechanism of A/V copolymers. The reactivity ratios of the comonomers were calculated using the nonlinear error-in-variable (EVM) method.[11] The microstructure in terms of triads sequence distribution was obtained from the $^{13}C\{^1H\}$ NMR spectra of the copolymers. The methine carbon of the A unit was assigned to both compositional (triad) and configurational (triad) sequences whereas the methine carbon of the V unit showed compositional sequences. The ^1H NMR spectra which consisted of highly overlapping configurational and compositional sequences were completely resolved with the help of 2D NMR spectroscopy.

Experimental Section

Acrylamide (SRL, India) was recrystallized twice from chloroform. *N,N*-Dimethylformamide (DMF; Merck, Germany) was distilled and dried. Vinyl acetate (CDH, India) was distilled under reduced pressure and stored below 5 °C. A series of acrylamide/vinyl acetate (A/V) copolymers containing different mole percents of acrylamide in the feed were prepared

by solution polymerization using benzoyl peroxide as the initiator at 65 °C. The percent conversion was kept below 6% by precipitating the copolymers in acetone. The copolymers were further dissolved in dimethyl sulfoxide (DMSO), reprecipitated in acetone, and vacuum-dried.

The copolymer composition was calculated from the percent nitrogen of the copolymers. The C, H, and N analyses were done on a Perkin-Elmer 240C elemental analyzer instrument.

The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in DMSO-d_6 at 100 °C on a Bruker DPX 300-MHz spectrometer operating at 300.13 and 75.5 MHz, respectively. All of the two-dimensional experiments were carried out on a Bruker DPX 300-MHz spectrometer in DMSO-d_6 at 100 °C. Distortionless enhancement by polarization transfer measurements were carried out using the standard pulse sequence with a *J* modulation time of 3.7 ms (J_{CH} = 135 Hz) with a 2-s delay time. A two-dimensional proton-detected $^1H-^{13}C$ heteronuclear chemical shift correlation spectrum (inverse-HETCOR) was recorded using the standard pulse sequence. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the $512 t_1$ experiments. The 2D homonuclear total correlation spectroscopy (clean-TOCSY) experiment was carried out at two mixing times i.e., 4 and 80 ms. A total of 16 scans were accumulated with a relaxation delay of 2 s for each of the $512 t_1$ experiments. All of the 2D spectra were zero filled to have a 2K × 1K data matrix while processing. All of the curve fittings were done using a nonlinear least-squares deconvoluting program. In all cases regression converged to $\chi^2 < 1$.

Results and Discussion

Reactivity Ratio Determination. The compositions of acrylamide/vinyl acetate (A/V) copolymers were determined from the percent nitrogen of the copolymers. Table 1 shows the copolymer composition in the feed and in the copolymers along with the percent nitrogen in the copolymers. The copolymer composition data were used to calculate the terminal model reactivity ratios by the Kelen−Tudos[12] (KT) method. The values of the reactivity ratios are $r_A = 9.27 \pm 1.9$ and $r_V = 0.09 \pm 0.02$. These reactivity ratios served as the initial estimate for the calculation of reactivity ratios by the EVM method. The terminal model reactivity ratios determined are $r_A = 9.28 \pm 0.6$ and $r_V = 0.09 \pm 0.006$. Using the van Herk[13] method, the sum of squares of
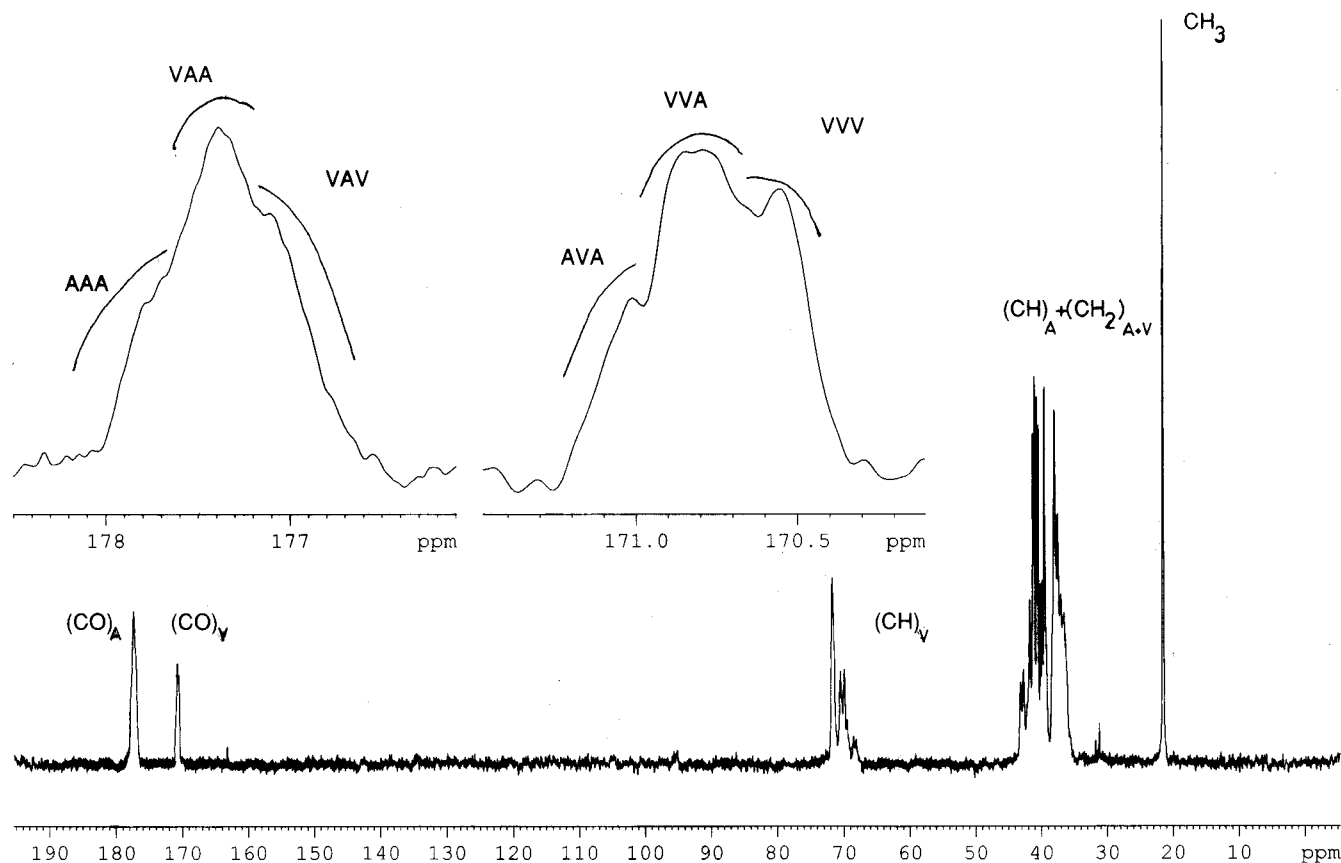
Figure 1. $^{13}C\{^1H\}$ NMR spectrum of the acrylamide/vinyl acetate (A/V) copolymer ($F_A = 0.49$) in DMSO-d_6 at 100 °C.

Table 1. Feed Mole Fractions, Percent Conversion, Copolymer Compositions for Acrylamide/Vinyl Acetate Copolymers (A/V)

| no.	feed mole fraction (f_A)	% conv	F_A from nitrogen anal.
1	0.05	2.5	0.34
2	0.06	3.5	0.39
3	0.08	4.2	0.49
4	0.10	3.8	0.54
5	0.12	5.1	0.56
6	0.15	4.6	0.63
7	0.175	3.9	0.69
8	0.20	3.1	0.71
9	0.25	4.0	0.75
10	0.45	3.9	0.87

the residuals for different reactivity ratios were plotted. From the plot, minima were obtained for $r_A = 9.458$ and $r_V = 0.094$ with a relative sum of squares of 0.0054. The terminal model reactivity ratios obtained from the EVM method ($r_A = 9.28$ and $r_V = 0.09$) are in agreement with the values calculated by the van Herk method. Examination of the residuals showed that there is no systematic variation and that the actual deviation of the data with respect to the fitted (F_A) values is not bigger than the expected error, thus indicating that the reactivity ratios obtained from the compositional data (nitrogen analysis) are reliable.

NMR Studies. Figure 1 shows the $^{13}C\{^1H\}$ NMR spectrum of the A/V copolymer ($F_A = 0.49$) in DMSO-d_6 at 100 °C. The carbonyl carbons (>C=O) of both A and V units resonate around 176.4–178.2 and 170.2–171.3 ppm, respectively. Both of these signals have been assigned to compositional (triad) sequences and can be used to assess the copolymerization mechanism. The aliphatic carbon signals (20.0–75.0 ppm) are differentiated with the help of a DEPT-135 experiment, where

the methine carbon signals are positive and methylene carbon signals are negative (Figure 2).

Figure 3 shows the DEPT subspectra for six different compositions of the A/V copolymers showing the methylene carbon resonances. The methylene carbons, because of their symmetry, are sensitive to diad, tetrad, hexad, etc. The methylene carbon signals can be broadly divided into three regions, 35.2–37.25, 37.25–38.05, and 38.05–40.5 ppm, which can be assigned to AA, AV (VA), and VV diads on the basis of changes in the intensity of the respective signals with copolymer composition. The signals within the AA and VV diads vary with copolymer composition and can be assigned to tetrad compositional sequences. The three signals in the AA diad are assigned to AAAA (35.33–35.87 ppm), AAAV (35.87–36.56 ppm), and VAAV (36.56–37.25 ppm) (Figure 3). These assignments can be confirmed by inverse-HETCOR experiments.

Parts a and b of Figure 4 show the expanded inverse-HETCOR spectra for two different compositions. The central methylene carbons in the AA diad show meso and racemic configurational sensitivity. In the meso configuration (AmA), the central methylene protons become nonequivalent and thus will show two cross-peaks in the F2 domain (^1H axis) of the 2D spectrum, whereas in the racemic configuration (ArA), the central methylene protons are equivalent and will show only one correlation cross-peak. In the AAAA tetrad region (Figure 4b), the cross-peaks at 35.63/1.75 and 35.63/1.47 ppm are assigned to AAmAA, whereas the cross-peak at 35.63/1.61 ppm is assigned to AArAA tetrad sequences. For the AAmAV and AArAV tetrad sequences, the cross-peaks are at 36.37/1.74 (36.37/1.42) and 36.37/1.56 ppm, respectively. Similarly, the cross-peaks at
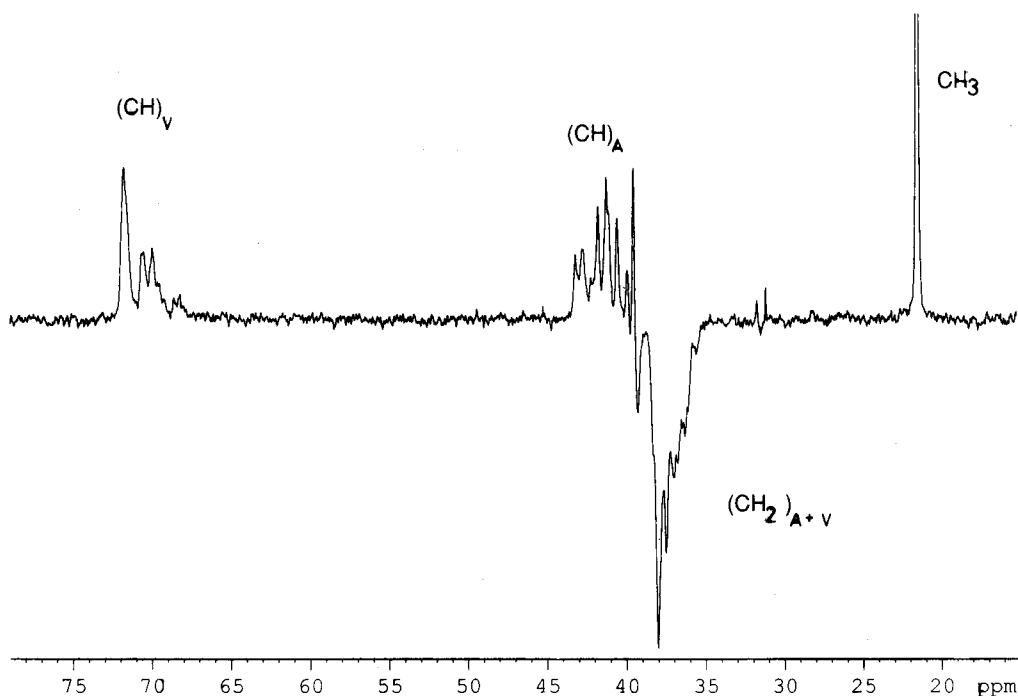
Figure 2. DEPT-135 spectra of the A/V copolymer ($F_A = 0.49$) in DMSO-d_6 at 100 °C.
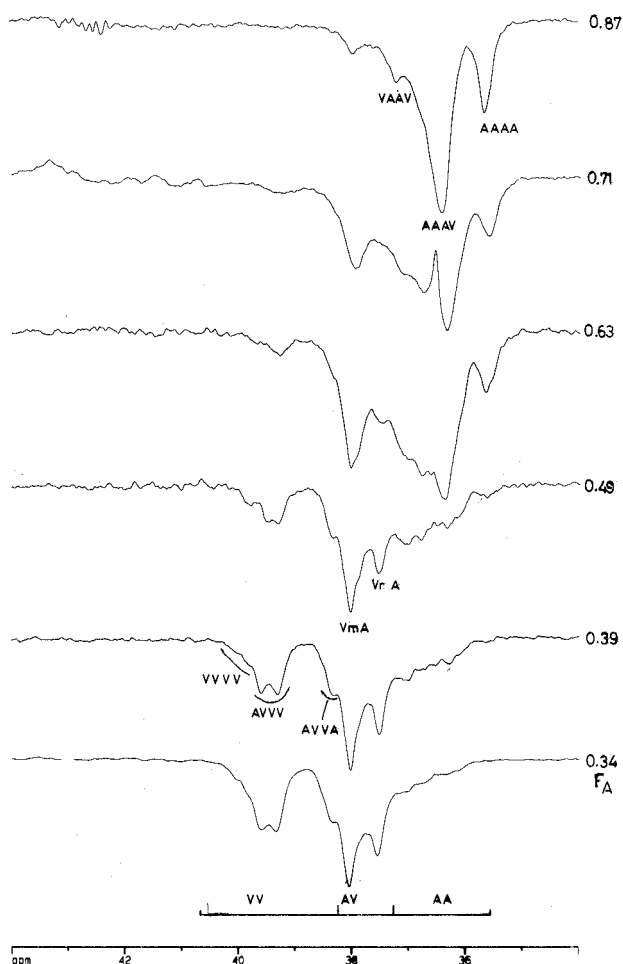
Figure 3. DEPT subspectra showing the methylene carbon signals of different copolymer compositions (F_A): (a) 0.34, (b) 0.39, (c) 0.49, (d) 0.63, (e) 0.71, (f) 0.87.

37.08/1.73 and 37.08/1.37 ppm are assigned to VAmAV tetrad sequences, and the cross-peak at 37.08/1.56 ppm is assigned to VArAV tetrad sequences. All of the

geminal couplings in the meso configurations are seen in the TOCSY (4-ms) spectrum (Figure 9) as discussed later.

Similarly, for the VV diad the three signals at 38.32, 39.0−39.6, and 39.8 ppm are assigned to AVVA, AVVV, and VVVV tetrad sequences (Figure 3). These assignments are confirmed by a 2D HSQC−TOCSY experiment where the central CH$_2$ protons of the AVVA tetrad were found to show a relay peak with the CH proton of the VVA triad. However, in the VA diad, the two signals at 37.53 and 38.02 ppm which do not change with the copolymer composition are assigned to configurational sequences, i.e., VrA (37.53 ppm) and VmA (38.02 ppm), respectively. The methylene protons in the VmA diad are nonequivalent and therefore show two cross-peaks (1.79 and 1.53 ppm) in the F2 domain of the inverse-HETCOR spectrum (Figure 4a).

Figure 5 shows the expanded $^{13}C\{^1H\}$ NMR spectra of the methine carbon region of the V unit for A/V copolymers of five different compositions. The methine carbon signals of the V unit show compositional sensitivity and can be divided into three broad envelopes. The resonance signals in the region 67.5−70.5 ppm decrease while those around 71.6−72.5 ppm increase with an increase in the acrylamide content in the copolymer (F_A) and were assigned to VVV and AVA triads, respectively. The resonance signals around 69.5−71.6 ppm first increase and then decrease as F_A increases and were assigned to VVA triad fractions. Further splitting within the VVV and VVA triad fractions could not be assigned to higher compositional sequences because of considerable overlap of signals. However, in the AVA triad region, further signals are assigned to VAVAV + AAVAV (VAVAA) (71.8 ppm) and AAVAA (72.2 ppm) pentad sequences, respectively. The areas under the various V-centered triad fractions are shown in Table 2.

The corresponding methine protons of the V unit can be assigned with the help of the inverse-HETCOR spectra. Parts a and b of Figure 6 show the inverse-

Figure 4. Inverse-HETCOR spectrum showing the methine and methylene regions of the acrylamide/vinyl acetate (A/V) copolymer: (a) $F_A = 0.39$ and (b) $F_A = 0.87$ in DMSO-d_6 at 100 °C.

HETCOR spectra of the methine region of the V unit of two different compositions. From the one-to-one correlation between the various carbons and their corresponding protons, the broad and overlapping ^{1}H NMR spectra can be assigned. The signals around 4.81–4.84, 4.73–4.80, and 4.67–4.76 ppm are assigned to VVV, VVA (AVV), and AVA triad fractions, respectively. The various CH/CH$_2$ couplings in the triad fractions can be assigned with the help of a double quantum filter correlation spectroscopy (DQFCOSY) spectrum. In the DQFCOSY spectrum, all of the cross-peaks are not seen clearly because of the overlap and cancellation of negative and positive signals. These cross-peaks can be clearly seen in the low-mixing-time TOCSY spectrum. At shorter mixing time one can see the direct coupling (AM spin type) between the bonded protons, whereas at higher mixing time one can see the relay coupling (AMX spin type) through magnetization transfer. Figure 7 shows the expanded TOCSY (4-ms) spectrum of the A/V copolymer ($F_A = 0.39$). The methine/methylene cross-peaks at 4.81/1.77, 4.74/1.79 (4.74/1.53), and 4.68/1.54 ppm are assigned to VVV, VVA (AVV), and AVA triad sequences. In the VVA (AVV) triad fraction, two cross-peaks (4.74/1.79 and 4.74/1.53 ppm) are seen, as the methine proton is coupled to two different types of methylene protons, i.e., (CH$_2$)$_A$ and (CH$_2$)$_V$ types. Further, three cross-peaks seen in this region are assigned to VVVAV (4.80/1.57), AVVAV (4.74/1.53 ppm), and AVVAA (4.73/1.76 ppm) pentad sequences.

The methine carbon (36.0–44.0 ppm) of the A unit shows considerable overlap with the methylene carbons, which can be resolved by employing DEPT-90 NMR experiments as shown in Figure 8. The methine carbon of the A unit shows both stereochemical and compositional sensitivity. On comparison with the ^{13}C{^{1}H} NMR spectrum of the homopolymer, poly(acrylamide)[14] (PAM), the methine signals in the region 42.1–43.6 ppm, which increase in intensity as the acrylamide

Figure 5. ^{13}C{^{1}H} NMR spectra showing the methine carbon (CH)$_V$ signals of different copolymer compositions (F_A): (a) 0.34, (b) 0.39, (c) 0.49, (d) 0.71, (e) 0.87.

Table 2. Triad Compositions Calculated from NMR Spectra and the Alfrey–Mayo Model in Acrylamide/Vinyl Acetate (A/V) Copolymers

| no.	feed mole fraction of A	triads	triad concentration[a]		
			$^{13}C\{^1H\}$ NMR[b]		
			>CO	(CH)$_V$	Alfrey–Mayo
1	0.05	AAA	0.11		0.11
		AAV	0.43		0.44
		VAV	0.46		0.45
		VVV	0.43	0.42	0.40
		VVA	0.45	0.46	0.46
		AVA	0.12	0.12	0.14
2	0.06	AAA	0.17		0.14
		AAV	0.43		0.47
		VAV	0.40		0.39
		VVV	0.35	0.34	0.34
		VVA	0.46	0.50	0.49
		AVA	0.19	0.16	0.17
3	0.08	AAA	0.19		0.20
		AAV	0.48		0.49
		VAV	0.33		0.31
		VVV	0.25	0.27	0.26
		VVA	0.51	0.49	0.50
		AVA	0.24	0.24	0.24
4	0.10	AAA	0.27		0.26
		AAV	0.50		0.50
		VAV	0.23		0.24
		VVV	0.22		0.20
		VVA	0.47		0.49
		AVA	0.31		0.31
5	0.12	AAA	0.29		0.31
		AAV	0.51		0.49
		VAV	0.20		0.19
		VVV	0.17	0.15	0.16
		VVA	0.49	0.50	0.48
		AVA	0.34	0.35	0.36
6	0.15	AAA	0.37		0.39
		AAV	0.49		0.47
		VAV	0.14		0.14
		VVV	0.12	0.11	0.11
		VVA	0.46	0.47	0.45
		AVA	0.42	0.42	0.44
7	0.175	AAA	0.44		0.44
		AAV	0.44		0.45
		VAV	0.12		0.11
		VVV	0.10		0.09
		VVA	0.43		0.42
		AVA	0.47		0.49
8	0.20	AAA	0.48		0.49
		AAV	0.42		0.42
		VAV	0.10		0.09
		VVV	0.08	0.09	0.07
		VVA	0.36	0.38	0.39
		AVA	0.56	0.53	0.54
9	0.25	AAA	0.58		0.57
		AAV	0.36		0.37
		VAV	0.06		0.06
		VVV	0.05		0.05
		VVA	0.34		0.33
		AVA	0.61		0.62
10	0.45	AAA	0.78		0.78
		AAV	0.22		0.21
		VAV	0.00		0.01
		VVV	0.00	0.00	0.01
		VVA	0.17	0.17	0.18
		AVA	0.83	0.17	0.81

[a] A- and V-centered triad fractions add up to unity. [b] The error in estimating the triad concentration from NMR spectroscopy is ±0.05.

content in the copolymer increases, are assigned to the AAA triads. The intensity of the methine signals in the region 39.0–40.2 ppm decreases as F_A increases and therefore is assigned to the VAV triad fraction. The AAV triad fraction is assigned at 40.2–42.1 ppm. All of these triad fractions further show signals which can

be assigned to configurational sequences as they do not change with copolymer composition (Figure 8). In the AAA region, the signals at 42.28, 42.76, and 43.2 ppm are assigned to AmAmA, AmArA, and ArArA triad sequences, respectively, on the basis of the signals observed in the homopolymer PAM spectrum.[14] In the AAV triad region, further splittings are assigned to AmAmV (40.59 ppm), ArAmV + AmArV (41.27 ppm), and ArArV (41.78 ppm) whereas the signals at 39.53 and 39.92 ppm are assigned to VmAmV + VmArV and VrArV triad sequences. The corresponding methine protons can be assigned with the help of inverse-HETCOR experiments.

The methine proton of the A unit can be assigned to various configurational sequences with the help of inverse-HETCOR spectra (Figure 4a,b). In the VAV region the cross-peaks at 39.53/2.24 and 39.92/2.17 ppm are assigned to VmAmV and VrArV triad sequences. The cross-peaks at 40.59/2.22, 41.27/2.18, and 41.78/2.17 ppm are assigned to AmAmV, AmArV + ArAmV, and ArArV triad sequences. Similarly in the AAA region (Figure 4b), the cross-peaks at 42.28/2.21, 42.76/2.19, and 43.08/2.17 ppm are assigned to AmAmA, AmArA, and ArArA triad sequences, respectively. Thus, it is clear that the methine proton of the A unit shows both compositional and configurational sensitivity. The various methine/methylene proton couplings present within these triad fractions can be seen in the TOCSY (4-ms) spectrum (Figure 9a,b).

In Figure 9a, the methine proton (2.24 ppm) of the VAV triad fraction shows three-bond couplings with the two nonequivalent methylene protons at 1.77 and 1.53 ppm and is assigned to the VmAmV triad sequence. The cross-peak at 1.77/1.53 ppm is due to the geminal coupling of the nonequivalent methylene protons. Similarly, the cross-peaks at 2.17/1.52 and 2.17/1.77 ppm are assigned to the three-bond coupling of the methine proton of the VAA triad fraction with the two different types of methylene protons, i.e., (CH$_2$)$_A$ and (CH$_2$)$_V$. The cross-peak at 2.20/1.38 ppm is due to the AmAmA triad fraction. The methine proton (2.20 ppm) in the AmAmA triad fraction shows two three-bond couplings with nonequivalent methylene protons at 1.70 and 1.38 ppm. These two nonequivalent methylene protons show geminal coupling at 1.70/1.38 ppm. In Figure 9b, the cross-peaks at 2.20/1.75 and 2.22/1.45 (2.18/1.39) ppm are assigned to the three-bond coupling between the methine proton with the two nonequivalent methylene protons in the mm and mr configurations in the AAA triads whereas the cross-peak at 2.17/1.56 ppm is assigned to the rr configuration. The geminal couplings in the AA-centered tetrads are assigned at 1.75/1.47 (AAmAA), 1.74/1.42 (AAmAV), and 1.73/1.37 (VAmAV) ppm. Parts a–c of Figure 10 show the 2D TOCSY spectra of the A/V copolymer (F_A = 0.39) recorded at 80-ms mixing time. The cross-peak at 4.74/2.24 ppm is the relayed coupling between the methine protons of the VVA and VAV triads, thus accounting for the VVAV tetrad. The methine proton of the VVA triad fraction (4.78 ppm) shows a relayed coupling with the methine proton of the AmAmA triad fraction (2.21 ppm). This cross-peak can be assigned to the VVAmAmA pentad sequence (Figure 10b). Similarly, the methine proton of VVA shows a relay coupling with the methine proton of the AVA triad fraction, thus accounting for the VVAVA pentad sequence (4.79/4.68 ppm). The cross-peak at 4.81/4.74 ppm is a four-bond relay coupling
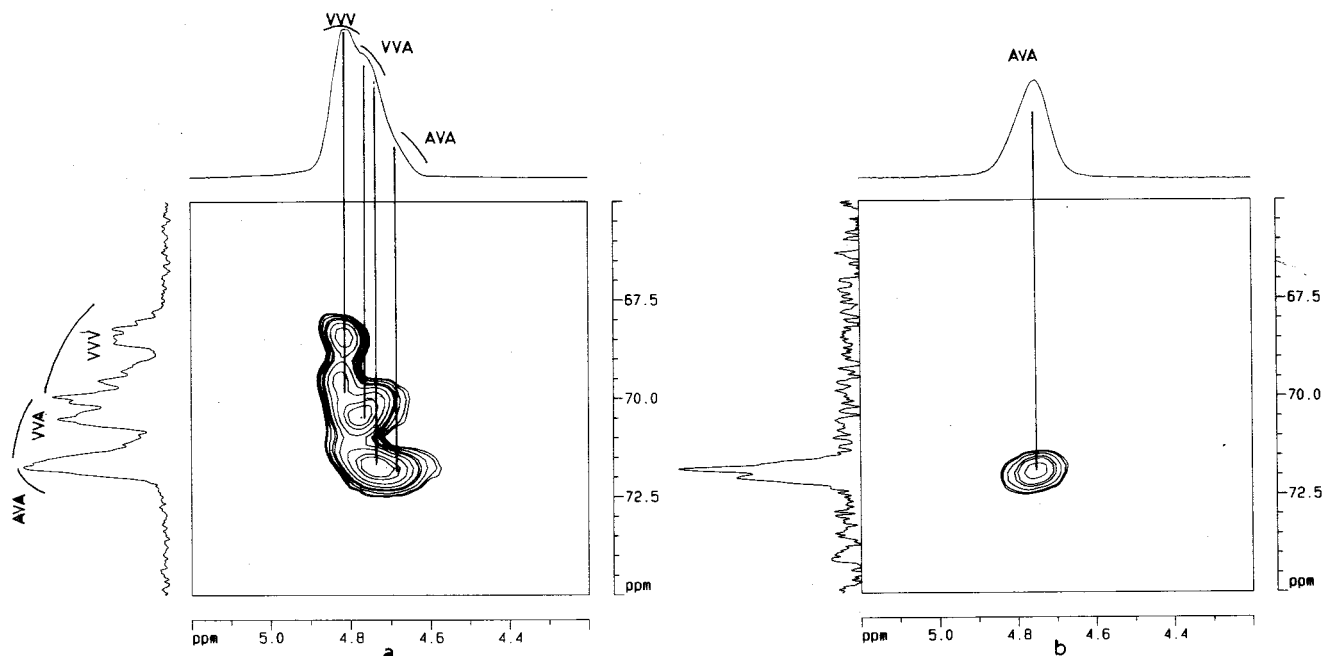
Figure 6. Methine $(CH)_V$ region of the inverse-HETCOR spectrum of A/V copolymers: (a) $F_A = 0.39$ and (b) $F_A = 0.87$.
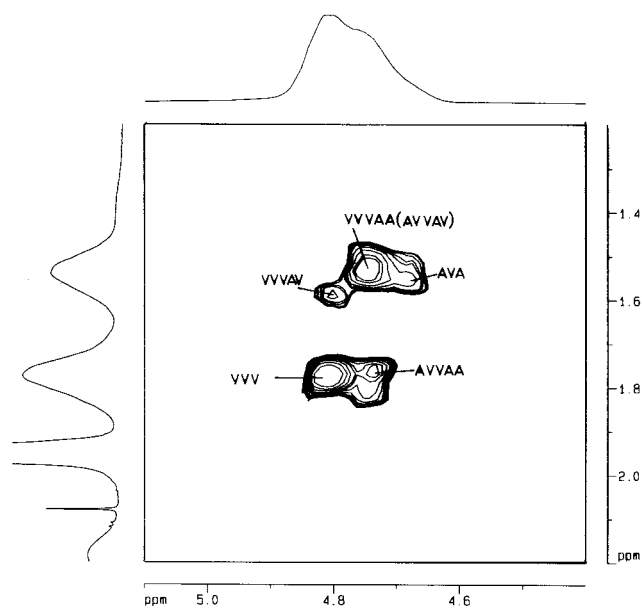
Figure 7. Expanded 2D TOCSY spectrum (4 ms) showing the methine region of the V unit of the A/V copolymer ($F_A = 0.39$) in DMSO-d_6.

between the methine protons of the VVV and VVA triad fractions and is thus assigned to VVVA tetrad sequences (Figure 10c).

The expanded $^{13}C\{^1H\}$ NMR spectra of carbonyl ($>C=O$) carbons of both acrylamide and vinyl acetate units are shown in Figure 1. The carbonyl carbon of the V unit can be divided into three distinct regions. The resonance signals around 170.2–170.65 ppm decrease while those around 170.90–171.25 ppm increase as F_A increases and thus are assigned to VVV and AVA triad sequences, respectively (Figure 11). The resonance signals around 170.65–170.90 ppm first increase, go through a maximum, and then decrease as F_A increases. These signals have been assigned to the VVA (AVV) triad fraction. The resonance signals around 176.4–177.25, 177.25–177.6, and 177.6–178.1 ppm have been assigned as VAV, VAA (AAV), and AAA triad sequences,
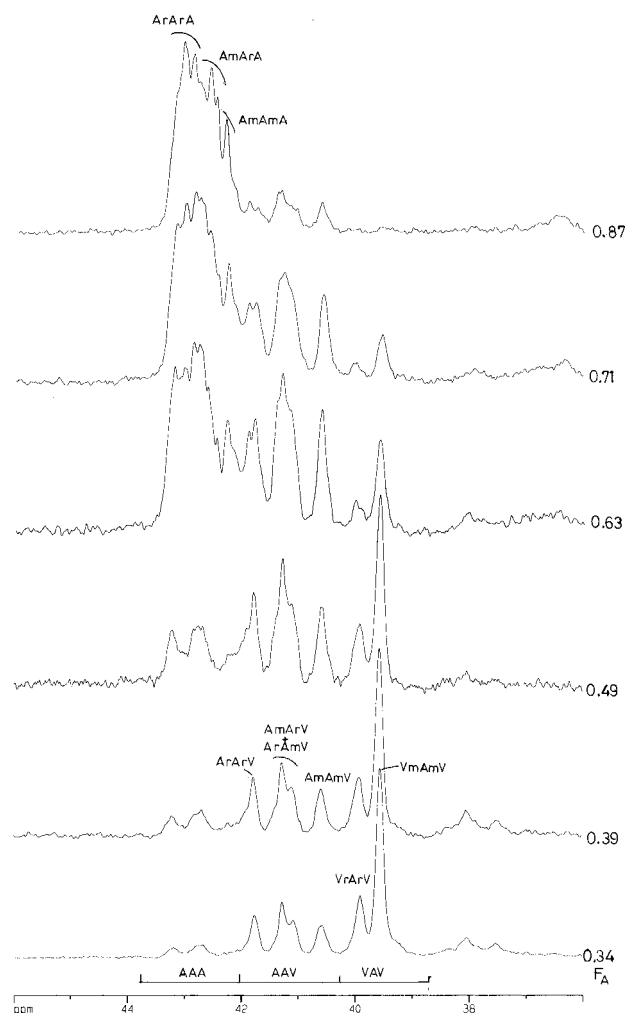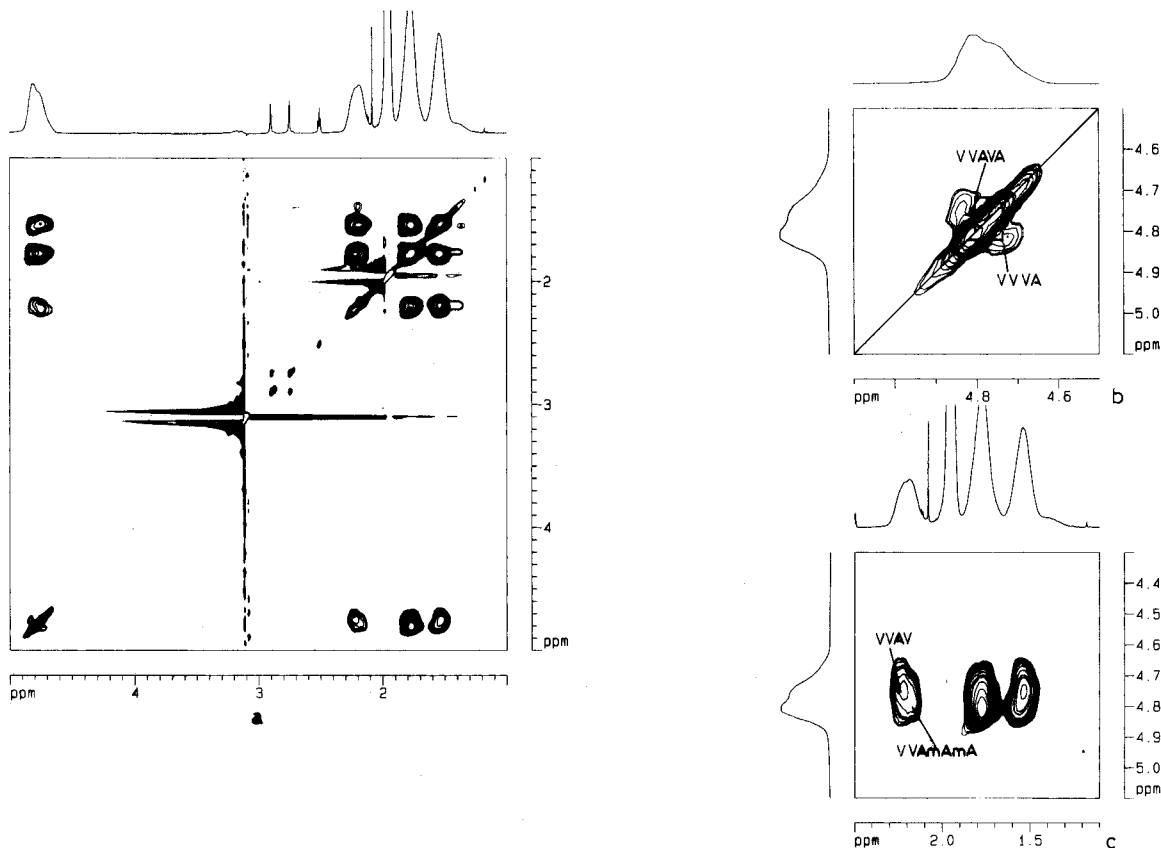

Figure 8. DEPT-90 spectra showing the methine $(CH)_A$ carbon signals of different copolymer compositions (F_A): (a) 0.34, (b) 0.39, (c) 0.49, (d) 0.63, (e) 0.71, (f) 0.87.

respectively, on the basis of variation of the intensity of these signals with changes in copolymer composition.
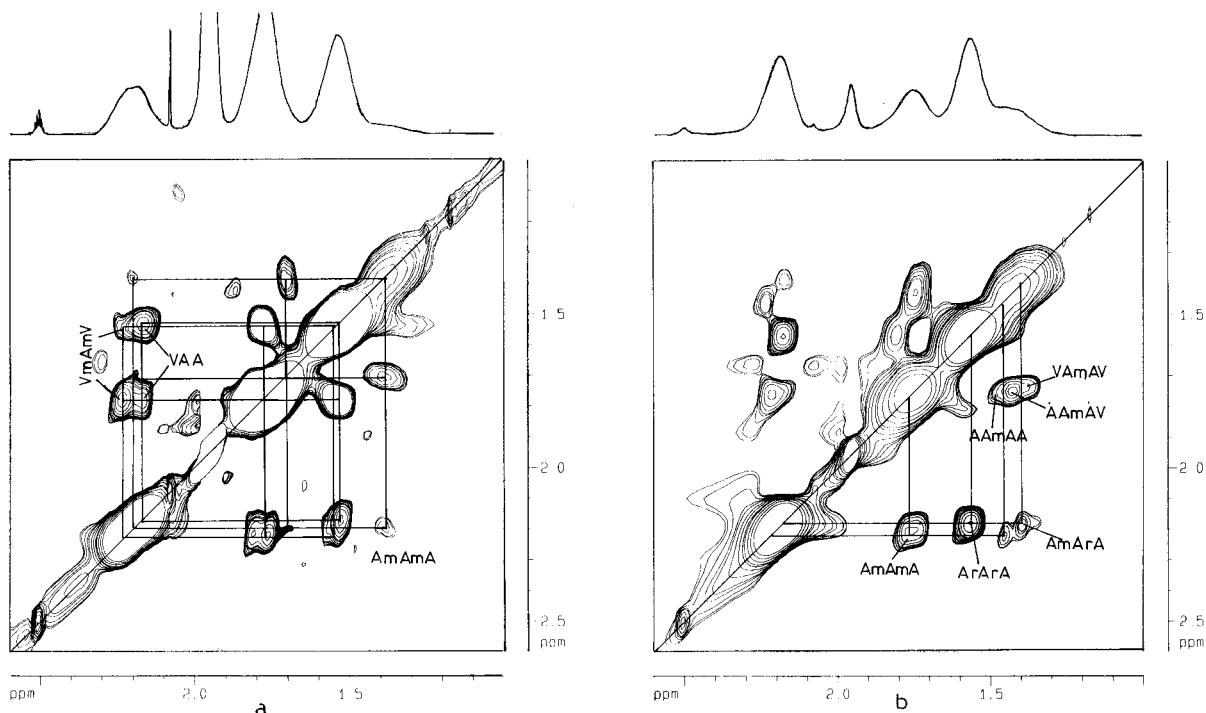
Figure 9. 2D TOCSY (4-ms) spectrum of the acrylamide/vinyl acetate (A/V) copolymer: (a) $F_A = 0.39$ and (b) $F_A = 0.87$ in DMSO-d_6 at 100 °C.


Figure 10. 2D TOCSY (80-ms) spectrum of the acrylamide/vinyl acetate (A/V) copolymer ($F_A = 0.39$) in DMSO-d_6 at 100 °C: (a) complete spectrum; (b) expanded CH/CH coupling of the V unit; (c) expanded (CH)$_A$/(CH)$_V$.

The concentrations of the respective A- and V-centered triads were calculated by measuring the area under the carbonyl carbon resonance signals from the ^{13}C{^{1}H} NMR spectra of the A/V copolymers. The overlapping regions were resolved using a nonlinear least-squares curve-fitting deconvolution program. The triad fractions obtained from NMR spectroscopy were compared with the triad fractions calculated using the terminal model reactivity ratios, $r_A = 9.28$ and $r_V = 0.09$, from Harwood's program[15] assuming that the Alfrey–Mayo model is valid at any moment of polymerization at low conversion. There is a good agreement between
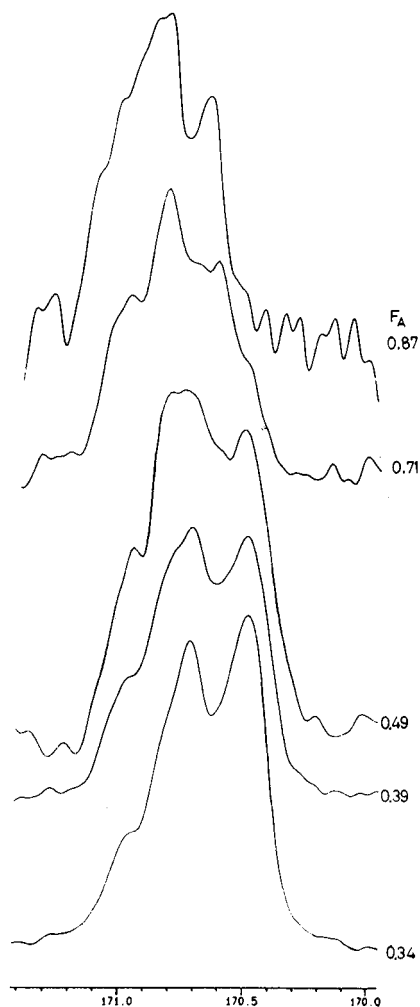
Figure 11. 11. $^{13}C\{^1H\}$ NMR spectra showing the carbonyl carbon $(>CO)_V$ signals of different copolymer compositions (F_A): (a) 0.34, (b) 0.39, (c) 0.49, (d) 0.71, (e) 0.87.

the theoretically calculated and experimentally (NMR) determined triad fractions (correlation coefficient for NMR and the Alfrey–Mayo model is 0.99; Table 2).

The conditional probabilities[16] $P_{V/A}$ and $P_{A/V}$ were calculated from the various A- and V-centered triad concentrations. The values of $P_{V/A}$ decrease linearly from 0.68 to 0.26 and those of $P_{A/V}$ increase from 0.37 to 0.91 with an increase in the acrylamide content of the copolymer. From the slopes of the respective plots of $1/[P_{V/A} - 1]$ verses f_A/f_V and $1/[P_{A/V} - 1]$ verses f_V/f_A,

the values of r_A and r_V were calculated as 9.23 and 0.09, respectively, which are within the experimental error of those found from nitrogen analysis.

Conclusions

The reactivity ratios of the A/V copolymer system are $r_A = 9.28$ and $r_V = 0.09$. The overlapping and broad signals in the carbon and proton spectra were assigned completely to various compositional and configurational sequences with the help of inverse-HETCOR and TOC-SY experiments. The methine carbon resonances of both A and V units were assigned to compositional and configurational sequences. The methylene carbon resonances were assigned to tetrad sequences with the help of inverse-HETCOR experiments. The copolymerization mechanism of the A/V copolymers was found to follow the first-order Markov model.

References and Notes

(1) Bovey, F. A. *Chain Structure and Conformation of Macro-molecules*; Academic Press: New York, 1982.
(2) Aerdts, A. M.; de Haan, J. W.; German, A. L.; van der Velden, G. P. M. *Macromolecules* **1991**, *24*, 1473.
(3) Dhal, P. K.; Vogt, B.; Steigal, A.; Wulff, G. *Macromolecules* **1992**, *25*, 5601.
(4) Suchoparek, M.; Spacevek, J. *Macromolecules* **1993**, *26*, 102.
(5) Dale, L. L.; Ray, G.; Rinaldi, P. L.; Wang, H.; Harwood, H. J. *Macromolecules* **1996**, *29*, 4706.
(6) Brar, A. S.; Dutta, K. *J. Appl. Polym. Sci.* **1998**, in press.
(7) Tart, E.; Wood, G.; Wernsman, D.; Sangwatanaroj, U.; Howe, C.; Zhou, Q.; Zhang, S.; Tonelli, A. E. *Macromolecules* **1993**, *26*, 4283.
(8) Isasi, J. R.; Cesteros, L. C.; Katime, I. *Macromolecules* **1994**, *27*, 2200.
(9) Brar, A. S.; Charan, S. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 109.
(10) Brar, A. S.; Charan, S. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 333.
(11) Dubey, M.; Sanyel, R. A.; Penlidis, A.; O'Driscoll, K. F.; Reilly, P. M. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 703.
(12) Kelen, T.; Tudos, F. J. *J. Macromol. Sci. Chem.* **1975**, *A9*, 1.
(13) van Herk, A. M. *J. Chem. Educ.* **1995**, *72*, 138.
(14) Hikichi, K.; Ikura, M.; Yasuda, M. *Polym. J.* **1988**, *20*, 851.
(15) Harwood, H. J. *J. Polym. Sci. C* **1968**, *25*, 37.
(16) Koenig, J. L. *Chemical Microstructure of Polymer Chains*; Wiley-Interscience: New York, 1980.

MA980940S