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DETERMINATION BY ^{13}C-NMR SPECTROSCOPY OF THE MICROSTRUCTURE OF COPOLYMERS OF ACRYLIC ACID WITH VINYL ACETATE

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Abstract—Acrylic acid–vinyl acetate copolymers were prepared in bulk using benzoyl peroxide as initiator. Copolymer compositions were determined by volumetric titration; monomer reactivity ratios were determined by the method of Kelen–Tüdős. Terminal and penultimate reactivity ratios have been calculated using the observed monomer triad sequence distribution determined from ^{13}C-NMR spectroscopy. Triad sequence distribution was used to calculate dyad concentrations, probability parameters, number-average sequence lengths and comonomer mol fractions in the copolymers. The observed triad sequence concentrations as determined from ^{13}C-NMR agreed well with those calculated from reactivity ratios.

INTRODUCTION

Acrylic acid(A)–vinyl acetate (V) (A/V) copolymer is an industrially important material. A copolymers are used in fields an varied as mining, textile manufacture, cosmetics, paper manufacture, oil-well drilling, secondary oil recovery, agricultural soil modification and water clarification [1]. A/V copolymers are also used in the manufacture of thickeners, binders and adhesives.

Although many workers have elucidated the tacticity of polyV (PV) using ^{1}H-NMR and ^{13}C-NMR and the monomer sequence distributions in copolymers of ethylene–V [2, 3], vinylidene cyanide–V [4], V–butyl acrylate [5] and A–methyl methacrylate [6], nothing has been reported on the microstructure of A/V copolymer. In our earlier publications, the sequence determinations for copolymers of methyl methacrylate with ethyl methacrylate [7, 8], methyl methacrylate with styrene [9], n-butyl methacrylate with methyl methacrylate [10] and acrylonitrile with V [11] by ^{13}C-NMR spectroscopy have been reported. We now report the ^{13}C-NMR spectra of a series of A/V copolymers. The terminal and penultimate reactivity ratios have been calculated for a sample from the ^{13}C [^{1}H]-NMR spectrum. Structural information such as monomer proportion and monomer sequence distribution in A/V copolymers have been determined on the basis of ^{13}C[^{1}H]-NMR spectral analysis and compared with those calculated from reactivity ratios using Harwood's program [12].

EXPERIMENTAL PROCEDURES

Monomers were distilled under reduced pressure and stored below 5°. Benzoyl peroxide (0.5% by weight) was added to a mixture of monomers. Purified N_2 was flushed in and polymerization was carried out at 60°. The conversion was kept low (3–6%) and copolymers were precipitated in excess hexane after 20 min. Several copolymers having various compositions were prepared similarily ^{13}C[^{1}H]-NMR spectra were recorded on Jeol-FX-100 NMR spectrometer operating at 25 MHz in pulse F. T. mode with noise-modulated proton, at 120° in DMSO-d_6 as solvent. The details of recording the spectra and Lorentzian shape curve fitting have been described [7–10]. The molecular weights of the copolymers were determined at 30 ± 0.1° by viscometry in acetone.

RESULTS AND DISCUSSION

The compositions of A/V copolymers prepared by bulk polymerization were found by volumetric titration. Table 1 shows the comonomer mole fractions in the feeds and in the copolymers. Copolymer composition data were used to calculate the terminal model reactivity ratios by the method of Kelen and Tüdős [13]. The reactivity ratios so obtained are $r_A = 6.32$ and $r_v = 0.020$. The published [14] values of reactivity ratios are $r_A = 10.0$, $r_V = 0.01$. The product $r_A \cdot r_V$ is 0.126 and it is evident that incorporation of A is favoured.

Molecular weights and intrinsic viscosities of A/V copolymers are given in Table 2. The ^{13}C[^{1}H]-NMR spectrum of A/V copolymer (A = 51 mol%) is shown in Fig. 1. The various resonance peaks have been assigned by comparing the copolymer spectrum with those of homopolymers as shown in Table 3. The carbonyl group of polyA (PA) and PV appeared as a sharp singlet but, for the copolymer, the carbonyl

Table 1. Copolymer composition data for A/V copolymers

Sample No.	f_A	f_V	F_A	F_V	% Conversion
1	0.05	0.95	0.51	0.49	3.0
2	0.10	0.90	0.56	0.44	3.2
3	0.15	0.85	0.66	0.34	3.5
4	0.20	0.80	0.71	0.29	5.4
5	0.25	0.75	0.75	0.25	6.1

f, mol fraction of monomers in feed.
F, mol fraction of monomers in copolymer.

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Table 2. Intrinsic viscosities and molecular weight of A/V copolymers

Sample No.	A mol fraction (in feed)	Intrinsic viscosity $[\eta]$ dl/g	Molecular weight $M(\times 10^{-5})$
1	0.05	1.72	5.09
2	0.10	1.76	5.26
3	0.15	1.77	5.31
4	0.20	2.51	8.74
5	0.25	2.90	10.75

Solvent = acetone; temperature = $30 \pm 0.1°$; $K = 17.4 \times 10^{-5}$ dl/g; $a = 0.70$. The values of K and a for poly V are taken from Ref. [15].

groups of both types of unit appeared as a multiplet. In the copolymer, there is downfield shift in the position of the carbonyl carbon of A (by ~ 1.3 ppm) and V (by ~ 2.4 ppm) as compared with the homopolymer. This effect may be due to the increase in the deshielding effect of adjacent comonomer in the copolymer. In the case of the copolymer, the carbonyl group of A appeared more downfield (δ 177.0 ppm) as compared to that of V (δ 171.2 ppm) because of the presence of the electron-donating methyl group at the carbonyl carbon of V causing shielding of the carbonyl group.

The carbonyl carbon resonance of A unit (*ca* δ 177.0 ppm) has been found to be comonomer triad sequence sensitive as three resonance signals were observed for all copolymers. The methylene carbon resonance of A and V units and methine carbon resonance of A units (δ 41.66–37.42 ppm) overlap with solvent DMSO-d_6 peaks, therefore they could not be used for sequence analysis. The methine carbon of V unit appears between δ 71.58–70.64 ppm but could not be used for sequence analysis because of poor resolution. The carbonyl carbon of a V unit appears as a multiplet (*ca* δ 171.2 ppm) showing its sensitivity to different monomer placements and configurational changes.

In order to discuss the compositional sequence distribution quantitatively, we denote monomer sequence and mol fractions of the monomers of A/V copolymers by [A] and [V], while those of the three dyads by [A–A], [A–V] and [V–V]. Similar notations are employed for six triads e.g. [A–A–A], [A–A–V], [V–V–V] etc. Firstly, the monomer composition, the copolymerization parameters and the monomer sequence distribution can be determined. The carbonyl $(>C{=}O)_A$ resonance region can give information regarding A-centred triads and the carbonyl $(>C{=}O)_V$ resonance region can give information about V-centred triad sequences.

The carbonyl group $(>C{=}O)_V$ and $(>C{=}O)_A$ expansion of A/V copolymers (A = 51 mol%) are shown in Fig. 1. The three sets of lines with intensities changing with copolymer composition can be assigned to carbonyl carbon centred in AVA, AVV(VVA), VVV triad sequences from low to high field. In the V-centred triad (VVV), the addition of A unit causes a downfield shift in the position of AVV/VVA triad (by ~ 0.26 ppm) and AVA triad (by ~ 0.25 ppm) because of the presence of the carbonyl group in A. Concentrations of various V centred triads can be calculated from the relative areas of resonance peaks. Table 4 contains the compositional information concerning the various V-centred triads, with the distributions obtained from Harwood's program [12] using

Table 3. Comparison of $^{13}C[^1H]$-NMR frequencies of A/V copolymer with those of PV and PA

		δ (ppm)						
Sample No.	Polymers	$(-C{=}O)_A$	$-(CH_2)_A$	$-(CH)_A$	$-(CH_2)_V$	$(-C{=}O)_V$	$-(CH)_V$	$-(CH_3)_V$
1	PA	175.7	37.6–33.3	42.1–40.0	—	—	—	—
2	PV	—	—	—	37.8	168.8	65.3–68.0	19.4
3	A/V	177.0		41.66–37.4		171.2	71.6–70.6	20.6

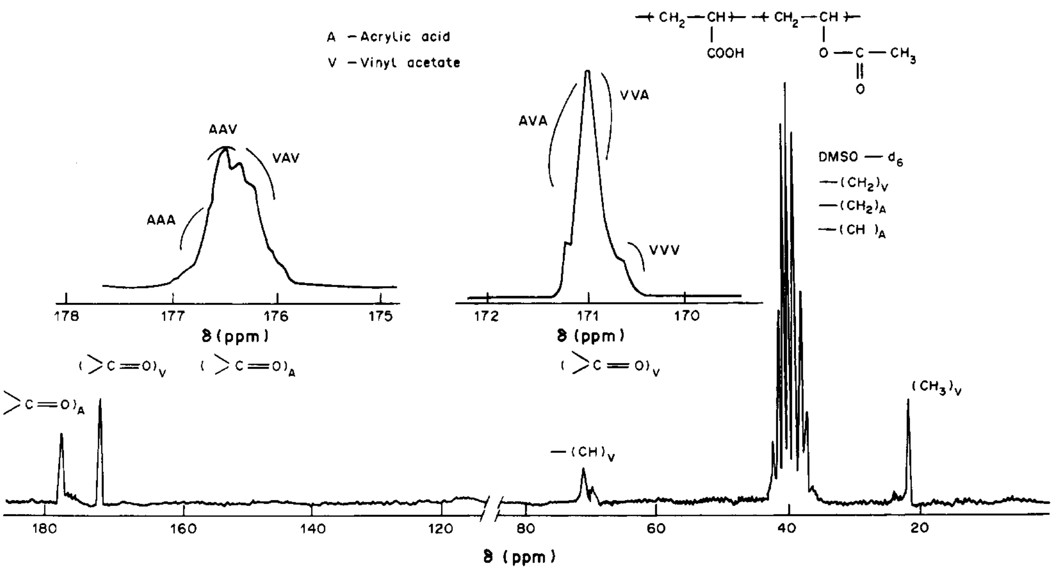

Fig. 1. $^{13}C[^1H]$-NMR spectrum of A/V copolymer (A = 51 mol %).

Table 4. Calculated and observed fraction of A- and V-centred triads in A/V copolymers

Sample No.	A mol fraction (in feed)	Triads	Obs.	Calculated from Harwood method		Penultimate reactivity ratios
				Ter.	Pen.	
1	0.05	AAA	0.053	0.062	0.056	$r_{AA} = 5.17$
		AAV	0.390	0.376	0.369	$r_{VA} = 6.65$
		VAV	0.557	0.562	0.575	$r_{VV} = 0.019$
		VVV	0.071	0.076	0.092	$r_{AV} = 0.019$
		VVA	0.386	0.399	0.387	
		AVA	0.543	0.525	0.521	
2	0.15	AAA	0.259	0.279	0.258	$r_{AA} = 5.85$
		AAV	0.502	0.498	0.507	$r_{VA} = 5.95$
		VAV	0.239	0.223	0.235	$r_{VV} = 0.034$
		VVV	0.017	0.011	0.013	$r_{AV} = 0.019$
		VVA	0.176	0.189	0.179	
		AVA	0.807	0.800	0.808	
3	0.20	AAA	0.362	0.376	0.352	$r_{AA} = 5.46$
		AAV	0.477	0.475	0.488	$r_{VA} = 5.78$
		VAV	0.161	0.149	0.160	$r_{VV} = 0.029$
		VVV	0.007	0.006	0.006	$r_{AV} = 0.017$
		VVA	0.136	0.137	0.135	
		AVA	0.857	0.857	0.859	

Obs, by ^{13}C-NMR spectroscopy using carbonyl carbon resonance of V and A units for V- and A-centred triad fractions.
Ter, by terminal model by Harwood's program.
Pen, by penultimate model by Harwood's program.

terminal model reactivity ratios $r_A = 6.32$, $r_V = 0.02$. Penultimate reactivity ratios (r_{VV} and r_{AV}) were evaluated (Table 4) from experimentally obtained triad distributions and average monomer feed ratios (V_f/A_f) by using the following equations

$$r_{VV} = \frac{2(VVV)}{[VVA + AVV]} \cdot [A_f]/[V_f] \qquad (1a)$$

$$r_{AV} = \frac{[AVV + VVA]}{2[AVA]} \cdot [A_f]/[V_f]. \qquad (1b)$$

The values of r_{VV} and r_{AV} are listed in Table 4.

Similar compositional information regarding A-centred triads can be made using the carbonyl ($>$C=O)$_A$ carbon resonance region. The three sets of lines with intensities changing with copolymer composition can be assigned to VAV, AAV(VAA), AAA triad sequence from high field to low field. In the A-centred triad (AAA), the addition of V unit causes an upfield shift in the position of AAV/VAA triad (by ~0.22 ppm) and VAV triad (by ~0.22 ppm) because of the presence of the electron-donating methyl group at the carbonyl carbon of V. Concentrations of various A-centred triads can be calculated from the relative areas of resonance peaks. The expanded ^{13}C[^{1}H]-NMR spectra of carbonyl resonance of A unit and carbonyl resonance of V unit in the copolymer (A = 51 mol%), overlaid with plots of the individual Lorentzian peaks used to deconvolute the spectrum, are shown in Fig. 2. Concentrations of various A-centred triads, with those calculated using the terminal model in Harwood's program, are given in Table 4.

On the basis of the triad resonance assignments made as described above, penultimate reactivity

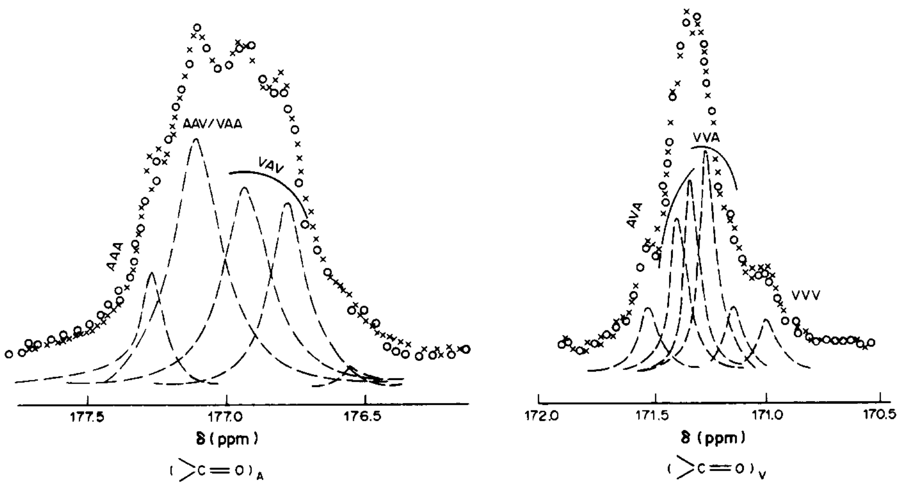

Fig. 2. The expanded ^{13}C[^{1}H]-NMR spectra of ($>$C=O)$_A$ and ($>$C=O)$_V$ in the copolymer (A = 51 mol %) with plots of individual Lorentzian peaks. ×, Computer fitted points; ○, experimental points; ---, individual Lorentzian peaks.

ratios were evaluated for the A/V system from triad fraction measured by NMR and average monomer feed ratios by using the following equations:

$$r_{AA} = \frac{2[AAA]}{[AAV + VAA]} \cdot [V_f]/[A_f] \qquad (2a)$$

$$r_{VA} = \frac{[AAV + VAA]}{2[VAV]} \cdot [V_f]/[A_f]. \qquad (2b)$$

The values of r_{AA} and r_{VA} are listed for individual samples in Table 4.

From the results of composition with respect to various A- and V-centred triads, the conditional probabilities P_{AV} and P_{VA} have been calculated using the equations:

$$P_{AV} = \frac{[VAV] + [VAA]/2}{[VAV] + [VAA] + [AAA]} \qquad (3a)$$

$$P_{VA} = \frac{[AVA] + [VVA]/2}{[AVA] + [VVA] + [VVV]} \qquad (3b)$$

where P_{AV} is the probability that A–V unit arises as a result of A growing chain-end adding V and P_{VA} is the probability that V–A unit arises as a result of V-growing chain-end adding A. Parameters in square brackets are the fractions of various triads, determined by ^{13}C-NMR spectroscopy. Using these equations, the terminal model reactivity ratios (r_A and r_V) have been calculated by using the equations:

$$r_A = \frac{[M_v]}{[M_A]} = \left[\frac{1}{P_{AV} - 1}\right] \qquad (4a)$$

$$r_V = \frac{[M_A]}{[M_V]}\left[\frac{1}{P_{VA} - 1}\right] \qquad (4b)$$

where $[M_A]$ and $[M_V]$ are the mol fractions of A and V respectively in the feed. The number-average sequence lengths ($\bar{N}_A$ and $\bar{N}_V$), being reciprocals of the conditional probabilities, can be calculated. Table 5 contains the copolymerization parameters of A/V copolymers for various monomer feeds. The value of $\bar{N}_A$ increases from 1.33 to 2.50 as the concentration of A in the copolymer increases while the value of $\bar{N}_V$ decreases from 1.36 to 1.12 with increase in concentration of A in the copolymer. The reactivity ratios obtained for individual samples using the observed triad fractions are in good agreement with published [14] values showing our triad sequence assignments to be correct. The reactivity ratios calculated by the Kelen–Tüdős method are $r_A = 6.32$, $r_V = 0.02$ and from triad compositions they are $r_A = 5.96$, $r_V = 0.02$; the two pairs are in good agreement.

Table 5. Copolymerization parameters of A/V copolymer determined by ^{13}C-NMR spectroscopy

Sample No.	A mol fraction (in feed)	P_{AV}	P_{VA}	r_A	r_V	$\bar{N}_A$	$\bar{N}_V$
1	0.05	0.752	0.736	6.26	0.019	1.33	1.36
2	0.15	0.490	0.895	5.60	0.021	2.04	1.19
3	0.20	0.399	0.925	6.01	0.020	2.50	1.12

r_A, Reactivity ratio calculated from equation (4a).
r_V, Reactivity ratio calculated from equation (4b).

Table 6. Copolymer compositions and diad fractions determined by observed triad fractions

Sample No.	A mol fraction (in feed)	Dyad fractions	[A]	[V]
1	0.05	[AA] = 0.248 [VV] = 0.264 [VA] = 0.488	0.49(0.51)	0.51(0.49)
2	0.15	[AA] = 0.510 [VV] = 0.105 [VA] = 0.385	0.70(0.66)	0.30(0.34)
3	0.20	[AA] = 0.600 [VV] = 0.075 [VA] = 0.325	0.76(0.71)	0.24(0.29)

( ) Calculated from volumetric analysis.

The triad compositional distribution can be used to determine the composition of three possible dyads i.e. [AA], [AV] and [VV] by using the equations:

$$[A\text{–}A] = [A\text{–}A\text{–}A] + [V\text{–}A\text{–}A]/2 \qquad (5a)$$

$$[V\text{–}V] = [V\text{–}V\text{–}V] + [V\text{–}V\text{–}A]/2. \qquad (5b)$$

Thus the composition of [A–V] dyads can be readily calculated from

$$[A\text{–}V] = 1 - [A\text{–}A] - [V\text{–}V]. \qquad (5c)$$

Monomer compositions of A/V copolymers are easily calculated from the dyad compositions similarily:

$$[A] = [A\text{–}A] + [A\text{–}V]/2 \qquad (6a)$$

$$[V] = [V\text{–}V] + [A\text{–}V]/2. \qquad (6b)$$

Table 6 gives the dyads and monomer concentrations calculated from the observed triad distribution as determined from ^{13}C-NMR spectra. The monomer compositions are in good agreement with those found by the volumetric analysis. The differences in the compositions calculated from triad distribution and volumetric analysis are in the range ± 0.02 to ± 0.05 mol fraction of each component.

REFERENCES

1. H. F. Mark, N. M. Bikales and C. G. Overberger. *Encyclopedia of Polymer Science and Engineering*, Vol. 10, p. 229. Wiley Interscience, New York (1987).
2. Y. Inoue R. Chujo, A. Nishioka, S. Nozakura and H. Imuro. *Polym. J.* **3,** 244 (1973).
3. T. K., Wu, D. W. Ovenall and G. Reddy. *J. Polym. Sci.; Polym. Phys. Edn* **12,** 901 (1974).
4. Y. S. Jo, Y. Inoue, R. Chujo, K. Saito and S. Miyata. *Macromolecules* **18,** 1850 (1985).
5. C. Pichot, Marie-France L. Lauro and Quang-Thopham. *J. Polym. Sci.; Polym. Chem. Edn* **19,** 2619 (1981).
6. A. S. Brar, E. Arunan and G. S. Kapur. *Polym. J.* **21,** 689 (1989).
7. A. S. Brar and A. K. Saini. *J. appl. Polym. Sci.* **32,** 4607 (1986).
8. A. S. Brar, G. S. Kapur and S. K. Dubey. *Eur. Polym. J.* **24,** 807 (1988).
9. A. S. Brar and G. S. Kapur. *Polym. J.* **20,** 371 (1988).
10. A. S. Brar and G. S. Kapur. *Polym. J.* **20,** 811 (1988).
11. A. S. Brar and Sunita. *Polym. Bull.* (Accepted).
12. H. J. Harwood. *J. Polym. Sci. Part C* **25,** 37 (1968).
13. T. Kelen and F. Tüdős. *J. macromolec. Sci. Chem.* **A9,** 1 (1975).
14. R. Z. Greenley. *J. macromolec. Sci. Chem.* **A14,** 445 (1980).
15. J. Brandrup and E. H. Immergut. *Polymer Handbook*. Interscience, New York (1966).