Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Polymers. Part I. High Resolution Carbon-13 Nuclear Magnetic Resonance Spectroscopy: Tacticity Studies on Poly(vinyl acetate) and Monomer Distribution Analysis in Ethylene–Vinyl Acetate Copolymers

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Noise-decoupled pulsed Fourier transform ^{13}C n.m.r. spectra reveal the tacticity in poly(vinyl acetate) and the monomer sequence distribution (MSD) in ethylene (E)–vinyl acetate (V) copolymers. Assignments of carbon absorptions were made from ^{13}C ' un-decoupled ' spectra and the methylene and methine carbon atoms were found to be especially sensitive to environment. The signal due to the methine carbon atoms in poly(vinyl acetate) is resolved into two peaks, showing a preponderance of heterotactic triads. In E–VA five MSD triad environments are predicted for the five methylene peaks observed and four MSD triad environments predicted for the four methine peaks observed. In addition, multiplicity in the four methine MSD triad peaks reveals a partially resolved MSD pentad and a tactic triad for block vinyl acetate VVV. Evaluation of corrected methine and methylene absorption intensities allows direct comparison of MSD triad intensities and shows the self-consistency in assignments. The compositions of the three samples (67, 38, and 14 mole % vinyl acetate) were determined in terms of the % population of all eight MSD triads and plotted to show triad composition for a whole range of ethylene–vinyl acetate copolymers. In these commercial samples both ethylene and (especially) vinyl acetate units show a tendency to block.

NOISE-DECOUPLED ^{13}C n.m.r. spectra are more useful than the corresponding ^1H spectra in examining the tacticity of homopolymers such as poly(methyl methacrylate),[1-3] poly(vinyl chloride),[4] polystyrene,[1] poly(vinyl methyl ether),[1] polyacrylonitrile,[5] and polypropylene.[1,6] ^{13}C N.m.r. spectra of copolymers are equally informative. For styrene-containing copolymers, the C-1 aromatic carbon absorptions are the most useful in determining monomer distribution in the chain, as shown for styrene–methyl methacrylate[7] and styrene–acrylonitrile[8] copolymers. Ethylene–propylene[9,10] and ethylene–maleic anhydride[11] copolymers have also been examined.

^{13}C N.m.r. spectra have now been used to investigate the tactic triads in poly(vinyl acetate) and the monomer distribution in the chains of a series of ethylene (E)–vinyl acetate (V) copolymers.

Poly(vinyl) acetate.—Peak assignments follow from comparison of coupled spectra with proton noise-decoupled ^{13}C n.m.r. spectra (Figure 1): the multiplicity changes in accord with the number of attached protons. The methine carbon resonance [peaks (a)—(d), Figure 3] is most sensitive to tactic structures [Figure 2(i)]. Figure 3(iv) shows this region expanded: two peaks corresponding to tactic triads are well resolved; this system is also revealed in proton n.m.r. spectra by using shift reagents.[12] We assign the larger peak to the heterotactic absorptions.

Ethylene–Vinyl Acetate Copolymers.—Proton n.m.r. spectroscopy[13] allows the characterisation of monomer

sequence distribution in ethylene–vinyl acetate copolymers by means of acetate methyl chemical shifts. The ^{13}C n.m.r. spectra of copolymers of various compositions now yield more detailed information about the monomer sequence distributions. The methylene
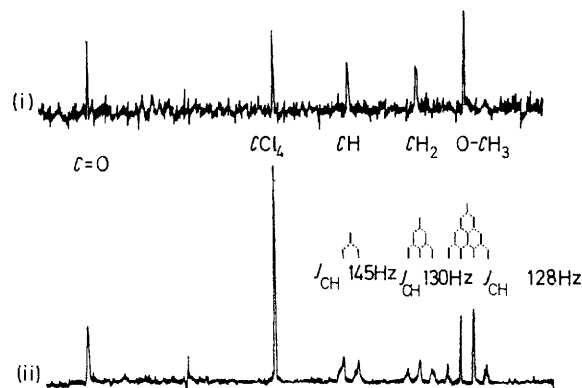

FIGURE 1 ^{13}C N.m.r. spectra of poly(vinyl acetate) at 25·2 MHz in CCl_4 at 35°, (i) with and (ii) without proton decoupling

and methine carbon absorptions are the most sensitive to polymer fine structure (Figure 2).

Figure 4 defines the possible different environments for the methylene carbon atoms in copolymers of ethylene (E) and vinyl acetate (V). Five peaks are predicted, corresponding to five different methylene environments. In Figure 5 the methylene carbon

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[3] I. R. Peat and W. F. Reynolds, *Tetrahedron Letters,* 1972, 1359.

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[6] Y. Inoue, A. Nishioka, and R. Chûjò, *Makromol. Chem.,* 1972, **152,** 15.

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[8] J. Schaefer, *Macromolecules,* 1971, **4,** 107.

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[11] J. Schaefer, *Macromolecules,* 1971, **4,** 98.

[12] A. R. Katritzky and A. Smith, *Brit. Polymer J.,* 1972 **4,** 199.

[13] T. K. Wu, *J. Polymer Sci., Part A-2, Polymer Phys.,* 1970, **8,** 167.

resonances are expanded: four methylene peaks are well resolved; these are designated (e)—(h) (low to high field). We believe that the fifth peak (i) is hidden under the acetate methyl peaks. The 100% vinyl acetate polymer contains only VVV sequences; thus peak (e) (40·3 p.p.m.) must be assigned to the CÇČÇC environment. Copolymers with a high proportion of vinyl acetate contain mainly VVV, VVE, and EVV sequences and Figure 4 shows that the two carbon environments CÇČÇC and CÇČCC should predominate. Hence from Figure 5(iii) the peak (f) (at 35·6 p.p.m.) is due to carbons in CCČÇC environment. For co-polymers with high ethylene content the main sequences, EEE, EEV, and VEE will produce three different environments, CCČÇC, ÇCČCC, and CCČCC, and the EEE sequences should give the largest peak due to CCČCC. Thus in Figure 5(i) the peak (g) (at 30·9 p.p.m.) must be due to CCČCC environments leaving the peak (h) (at 26·5 p.p.m.) to the carbons in ÇCČCC positions.

One β-OAc causes a shift of —4·4 p.p.m. The signal corresponding to the remaining type of environment ÇCČCÇ, arising from VEV sequences, is therefore

FIGURE 3 Noise-decoupled ¹³C n.m.r. spectra of the methine carbon atoms in copolymers of ethylene and vinyl acetate at 25·2 MHz in CCl₄; vinyl acetate (i) 14; (ii) 38; (iii) 67; (iv) 100 mole %. The positions of peaks designated (a)—(d) in Figure 6 are shown on the ordinate

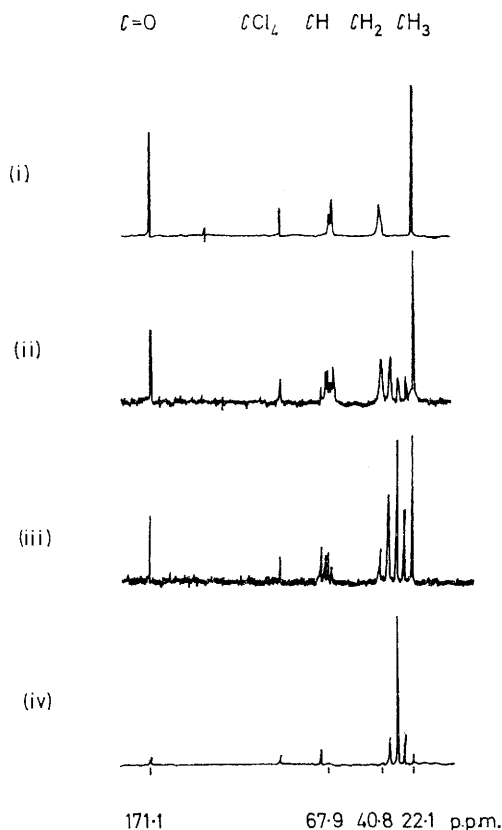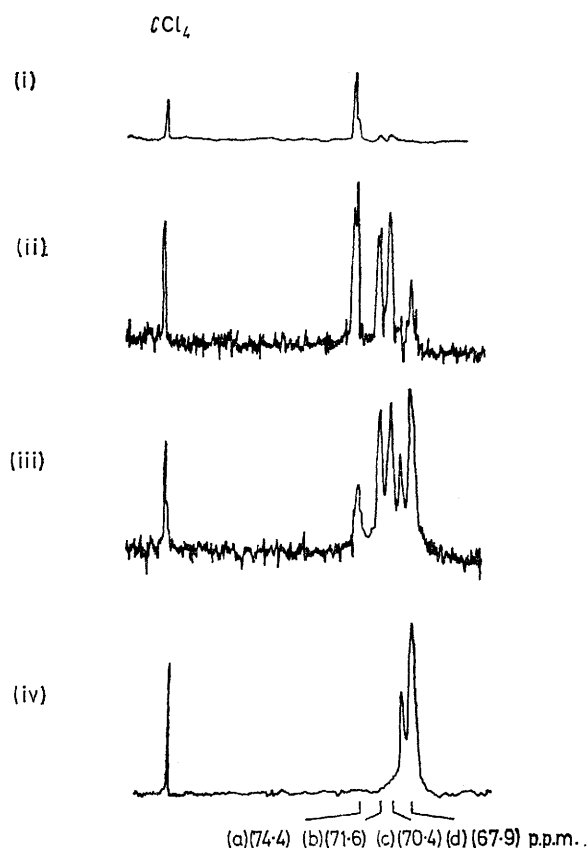expected to occur near 22·1 p.p.m., and will clearly be obscured by the methyl carbon signals at 22·0 p.p.m.

FIGURE 2 Noise-decoupled ¹³C n.m.r. spectra of ethylene–vinyl acetate copolymers obtained at 25·2 MHz in CCl₄ at 35°; vinyl acetate: (i), 100; (ii), 67; (iii), 38; (iv), 14 mole %

In comparison with the CH₂ peak with neither an α- nor a β-acetoxy-group, one α-OAc causes a shift of +4·7 p.p.m. and two α-OAc a shift of +9·2 p.p.m.

TABLE 1

Intensity [a] of peak (i) representing half the methylene absorption for E in VEV triads as deduced from the peak (i′)

		Mole % vinyl acetate			
Peak	Absorption	100	67	38	14
(i′)	[CH₃ + ÇCČCÇ	32	22	18	4
(a) + (b) + (c) + (d)	All methine	35	20	16	6
(i)	ÇCČCÇ	0	3·8	3·5	0

[a] Expressed as % total CH, CH₂, and CH₃ ¹³C absorption.

(cf. Figure 2). The portion of the signal at 22·0 p.p.m. which is due to peak (i) for the ÇCČCÇ environment methylene may be obtained by subtraction of the
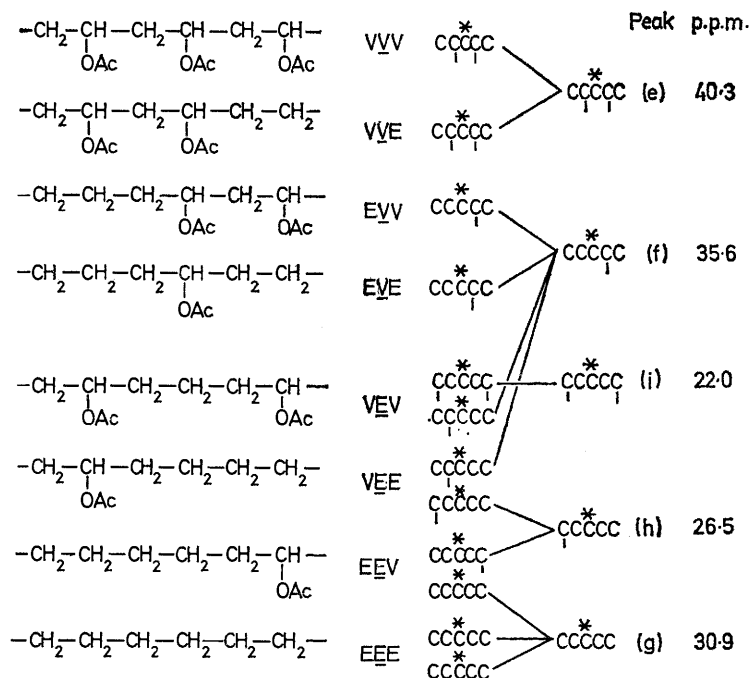
FIGURE 4   Various environments possible for the methylene carbon atoms in a copolymer of ethylene (E) and vinyl acetate (V); C̊ represents the methylene carbon atom under consideration, C other methylene carbons, and Ç methine carbon atoms
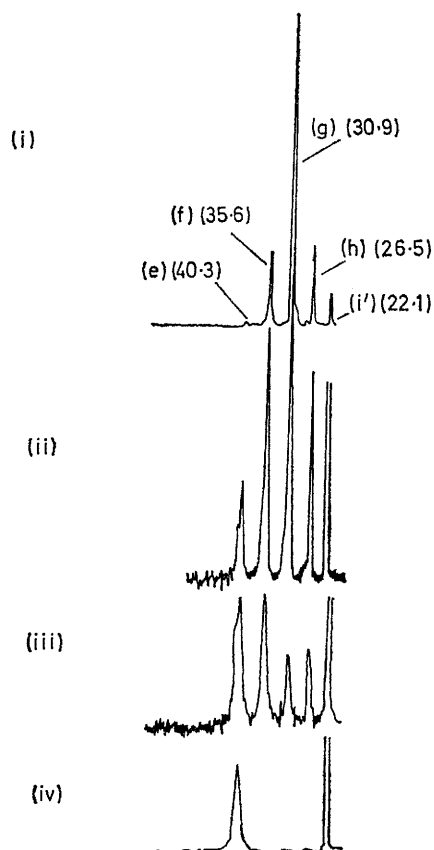

FIGURE 5   Noise-decoupled ^{13}C n.m.r. spectra of the methylene carbon atoms of ethylene–vinyl acetate copolymers obtained at 25·2 MHz in CCl$_4$; vinyl acetate: (i) 14; (ii) 38; (iii) 67; (iv) 100 mole %. The designation of the peaks is shown (see text) together with the chemical shifts in p.p.m. from Me$_4$Si

absorption attributed to the methyl carbon. The ratio of intensities for the methine and CH$_3$ absorptions in 100% vinyl acetate (Table 1) is 0·91; if we assume that this ratio is constant for varying compositions of ethylene and vinyl acetate, the intensity of absorption (i) due to ÇCČCÇ in each of the copolymers is given by equation (1).

$$(i) = (i') - 0·91[(a) + (b) + (c) + (d)] \qquad (1)$$

Figure 6 defines the possible environments for the methine carbon atoms in the vinyl acetate units. The signal in the 100% vinyl acetate polymer, peak (d), due to carbons in the ÇCČCÇ environment of VVV sequences, is itself a multiplet owing to the variable tacticity of the chain as described above. In the low-content vinyl acetate copolymer, Figure 3(i), EVE sequences predominate and the peak (a) (at 74·4 p.p.m.) may be assigned to CCČCC carbon environments. The peaks (b) (at 71·6) and (c) (at 70·4 p.p.m.) are considered both to be due to the ÇCČCC environment which arises from VVE and EVV sequences, and splitting is due to monomer sequence distribution (cf. Figure 7). Thus, peak (b) is assigned to the VVEE tetrad, which is observed in the 38% vinyl acetate sample to be further split, indicating pentad placement (i.e. EVVEE and VVVEE). Peak (c) is accordingly assigned to the VVEV tetrad, also split owing to pentad placement. Peak (a) is split into two peaks and one shoulder representing three members of the pentad. These splittings in peaks (a)—(c) are probably not due to tacticity [contrast those of peak (d)] since the V observed in

every case has only one V neighbour, with other V too distant for stereochemistry to be important.†

It is now possible from the above assignments to determine the populations of both the V-centred and

should show self-consistency. The data in Table 2 are normalised by a factor N (Table 3). This factor is calculated from equation (2) where x is mole % vinyl acetate. Each ethylene unit gives rise to two
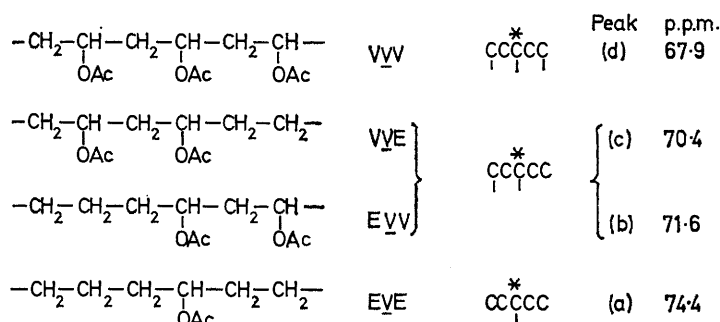

FIGURE 6 Various environments possible for the methine carbon atoms in a copolymer of ethylene (E) and vinyl acetate (V); $\overset{*}{\underset{|}{C}}$ represents the methine carbon atom under consideration, C the methylene carbons, and $\underset{|}{C}$ the methine carbon atoms

TABLE 2

Measured intensities of methylene and methine absorptions

Peak:	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i) [a]
Peak posn.:	74·4	71·6	70·4	67·9	40·3	35·6	30·9	26·5	22·0
Environment:	$CC\overset{*}{C}CC$	$CC\overset{*}{C}CC$	$CC\overset{*}{C}CC$	$CC\overset{*}{C}CC$	$CC\overset{*}{C}CC$	$CC\overset{*}{C}CC$	$CC\overset{*}{C}CC$	$CC\overset{*}{C}CC$	$CC\overset{*}{C}CC$
Carbon:		Methine				Methylene			
		% Total methine carbon absorption				% Total methylene carbon absorption			
Sample [b]									
100	0	0	0	100	100	0	0	0	0
67	12	28	22	38	34	29	13	13	11
38	28	19	23	30	13	28	33	17	9
14	80	10	10	0	0	14	75	11	0

[a] (i) represents intensity of peak (i′) corrected by subtraction of acetate methyl absorption (see Table 1).   [b] Mole % vinyl acetate.

the E-centred triads (expressed as percent of the total composition) for the ethylene–vinyl acetate copolymers. In Table 2 the measured intensities of peaks (a)—(i) representing both CH_2 and CH absorption are shown.
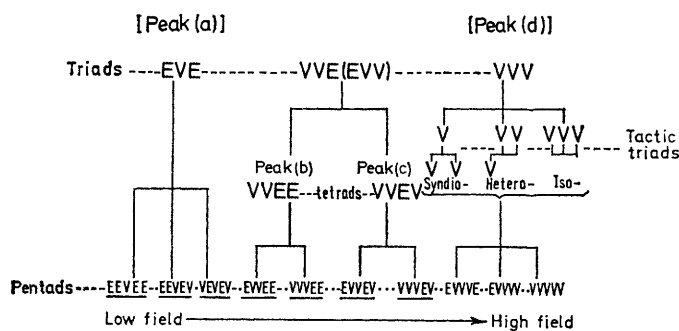

FIGURE 7 Assignment of the monomer sequence distribution pentads in the methine absorption of the 65% vinyl acetate sample (Figure 3); only the underlined pentads were resolved

If the assignments are correct, normalisation of peaks (e)—(i) will allow correlation with peaks (a)—(d) and

† A publication (M. Delfini, A. L. Segre, and F. Conti, Macro-molecules, 1973, 6, 456) which appeared since the preparation of this manuscript reports a ^{13}C n.m.r. spectra analysis on ethylene-vinyl acetate copolymers of 20 mole % or less vinyl acetate and notes this partial pentad resolution for the CH absorption.

methylene carbons and each vinyl acetate unit to one methylene and one methine carbon; hence the methylene absorption as listed in Table 2 must be normalised by multiplication by factor N [equation (2)] to give the expected distribution of intensity. The results of this normalisation are listed in Table 3. The measured

TABLE 3

Normalised intensities for methylene and methine absorptions

Mole % vinyl acetate:		67	38	14
Factor N (see text): [a]		2·0	4·3	13
Measured dist. (CH_2/CH):		1·9	4·0	13
Corrected intensities for	(e)	21	11	0
methylene peaks:	(f)	20	23	13
	(g)	10	26	70
	(h)	9	14	10
	(i)	7	7	0
	Total	67	81	93
Corrected intensities for	(a)	4	6	5
methine peaks:	(b)	9	3	1
	(c)	8	4	1
	(d)	12	6	0
	Total	33	19	7

[a] Normalisation factor.

distribution of intensity (ratio $CH_2 : CH$) agrees closely with that predicted by N (Table 3).

The relationships (derived from Figures 4 and 6) among peaks (a)—(i) and the 10 triads are shown in

$$N = \text{expected} \left\{\frac{CH_2 \text{ intensity}}{CH \text{ intensity}}\right\} = \frac{x + 2(100 - x)}{x} = \frac{200 - x}{x} \quad (2)$$

equations (3)—(10). The % absorption for each of the 10 triads evaluated from the simplest combination of peaks is shown in Table 4.

$$(a) = EVE \quad (3)$$

$$(b) + (c) = EVV + VVE \quad (4)$$

$$(d) = VVV \quad (5)$$

$$(e) = VVE + VVV \quad (6)$$

$$(f) = EVV + EVE + VEV + VEE \quad (7)$$

$$(g) = 2(EEE) + EEV \quad (8)$$

$$(h) = EEV + VEE \quad (9)$$

$$(i) = VEV \quad (10)$$

$$EVE + VVE = VEE + VEV \quad (11)$$

$$VEE = EEV \quad (12)$$

$$EEV + VEV = EVE + EVV \quad (13)$$

$$EVV = VVE \quad (14)$$

$$2(a) + (b) + (c) = (f) \quad (15)$$

$$(i) + (a) + (e) + \tfrac{1}{2}(h) = (f) + (d) \quad (16)$$

$$(h) + 2(i) = (f) \quad (17)$$

$$(b) + (c) + 2(d) = 2(e) \quad (18)$$

TABLE 4

Triad intensities (% population) as determined from the simplest combination of peaks. Values for triad populations were determined from corrected intensities for peaks (a)—(i) (Table 3) and rounded (1 or 2%) to total 100%

Mole % vinyl acetate:		67	38	14
Triad	Peak comb.		% Population	
VVV	2(d)	24	12	0
VVE	(b) + (c)	17	7	2
EVV	(b) + (c)	17	7	2
EVE	2(a)	8	12	10
EEE	(g) − ½(h)	6	20	66
VEE	(h)	8	14	10
EEV	(h)	8	14	10
VEV	2(i)	12	14	0
		100	100	100

The validity of these data and the self-consistency of the approach can be tested. Relationships (11)—(14) follow from consideration of possible environments expected for EE, EV, VE, and VV diads in a continuous chain. Each diad unit must be preceded and followed by either ethylene or vinyl acetate; hence the logic of our deduction. These four equations

are expressed in terms of peaks (a)—(i) as equations (15)—(18), respectively. They are evaluated (Table 5) from normalised values obtained for peaks (a)—(i) and clearly show agreement within experimental error (assuming variation of at least ± 1 in peak values).

TABLE 5

Evaluation of relations (15)—(18) by substitution of normalised values for peaks (a)—(i) in Table 3

	Mole % vinyl acetate		
Relation	67	38	14
(15)	25 = 20	19 = 23	12 = 13
(16)	36 = 32	31 = 29	10 = 13
(17)	23 = 20	28 = 23	10 = 13
(18)	41 = 42	19 = 22	2 = 0

The values in Table 4 representing percent $CH_2 + CH$ absorption for each of the 10 triads are normalised (by the factor N) and represent actual percent populations of these triads in the copolymer (*i.e* data adjusted such that the V-centred triads add up to the vinyl acetate composition in the copolymer and similarly for the E-centred triads). In Figure 8 the normalised triads are plotted to show a whole range of triad compositions for varying mole % vinyl acetate.
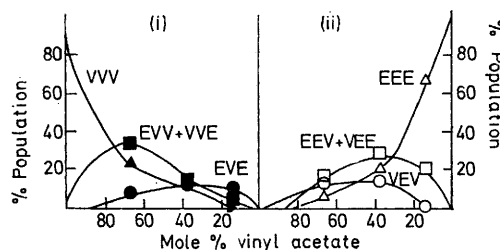

FIGURE 8 Plot of (i) V-centred and (ii) E-centred triad populations over a whole range of copolymer composition; data points plotted appear in Table 4

In contrasting the graphs in Figure 8, a rough similarity is apparent between V-centred and E-centred triad populations. At 50 mole % vinyl acetate composition VVV = EEE, EVV + VVE = EEV + VEE, and EVE is only slightly less than VEV. The curves for EEE and VVV are nearly identical; the others indicate a slightly greater tendency for ethylene to alternate (*e.g.* the population of VEV at 60% ethylene, 40% vinyl acetate is about 50% greater than the population of EVE at 60% vinyl acetate). Overall, the copolymer composition gives the appearance of being 'blocky'; there is proportionately a larger amount of VVV and EEE than would be predicted for a random copolymer and consequently a lower amount of alternating sequences. This conclusion is in conflict with results previously published [13] which indicate a more random distribution. However, the copolymers we have studied are commercial and therefore expected to be produced to high conversion.

This technique has allowed straightforward assignment of peaks to individual environments and accurate measurements of all eight triad populations. The

wide range of frequency over which ^{13}C signals occur has made it possible to observe, without the complications of coupling, seven signals for the CH and five for the CH$_2$ systems. In view of the simplicity of the molecules observed (chains of methylenes with acetate groups appearing in quantity and manner determined by the percent vinyl acetate content), no technique is superior to [13]C n.m.r. for measuring sensitivity due to environmental effects extending over several atoms.

EXPERIMENTAL

The noise-decoupled, natural abundance Fourier transform [13]C n.m.r. spectra were obtained at ambient tem-

perature on a Varian XL100 spectrometer, with 12 mm n.m.r. tubes containing ca. 700 mg of polymer in 2·5 ml of solvent. Poly(vinyl acetate) and the ethylene–vinyl acetate copolymers were dissolved in CCl$_4$ and external locks of D$_2$O were inserted in 5 mm n.m.r. tubes down the centre of the larger tubes. Chemical shifts were measured with reference to Me$_4$Si. All compounds were prepared by free-radical methods.