

¹H-NMR Spectra of Ethylene—Vinyl Acetate Copolymers in the Presence of Shift Reagent

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ABSTRACT: The high-resolution ¹H-NMR spectra of poly(ethylene—vinyl acetate) with low vinyl acetate content were measured by the use of tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-1,4,6-octanedionato)europium(III) as a shift reagent. As a result, the peak assigned to the acetate methyl protons was split into a triplet, and the peak assigned to the methine proton was split into a quintet and a broad peak. These split peaks were tentatively assigned to the acetate methyl and the methine protons of the central vinyl acetate unit in the triad sequences, respectively. Since the samples were determined to be random copolymers from their ¹H-NMR measurements in benzene-d₆, the triad concentrations were calculated by means of the random copolymerization theory. These calculated concentrations were compared with the observed concentrations for the above split peaks in the acetate methyl and methine proton signal, and the former were in close agreement with the latter.

KEY WORDS Poly(ethylene—vinyl acetate) / ¹H-NMR / Shift
Reagent / Eu(fod)₃ / Run Number / *R*_{obs} / *R*_{rand} /

The copolymerization of ethylene and vinyl acetate has been deduced as a random process from the investigation of the monomer reactivity ratios.^{1,2} On the other hand, the high-resolution NMR spectroscopy has been used very usefully for the structural investigation of ethylene—vinyl acetate (E—VA) copolymers.^{3,4} In the spectral analysis of E—VA copolymers, Schaefer has employed the double-resonance technique.⁵ Wu has determined the diad sequence distribution from the acetate methyl proton resonance spectra of E—VA copolymers in benzene solution.⁶

Recently, paramagnetic salts containing lanthanides such as europium or praseodymium have been effectively used for the investigation of polymers.^{7–10} Such salts have also been used as copolymers: for example, the analysis of the NMR spectra of copoly(ethylene terephthalate—*isophthalate*)¹¹ and poly(chloroprene—methyl methacrylate).¹²

In this paper, the signal of the acetate methyl and the methine protons split by the addition

of tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium (III) (Eu(fod)₃) in the solution of E—VA copolymer was tentatively assigned to the triad sequences with a VA unit as a center, and the observed concentrations were compared with the calculated concentrations by means of the random copolymerization theory,

EXPERIMENTAL

Material

All E—VA copolymers and poly(vinyl acetate) (PVAc) were obtained from commercial sources; the former were purified by precipitation from *o*-dichlorobenzene solution with methanol, and the latter from benzene solution with cyclohexane, followed by freeze-drying.

Methods

The NMR sample solutions were prepared in benzene-d₆ or chloroform-d₁ with a small amount of tetramethylsilane as an internal reference. The ¹H-NMR spectra were obtained by using a

Varian HA-100D spectrometer with variable-temperature probes. In the case of the addition of $\text{Eu}(\text{fod})_3$, a fixed quantity of this reagent was introduced into the sample solution. Subsequently, the $^1\text{H-NMR}$ spectra were measured at 60°C at 2 hr after the addition of $\text{Eu}(\text{fod})_3$.

RESULTS AND DISCUSSION

In Table I, the mole fractions of VA, diad sequence distributions, and the run numbers are shown. The mole fractions of VA were determined by the method of Chen and Lewis.¹³

Table I. Composition determinations, diad sequence distributions, and run numbers of E-VA copolymers

Sample No.	Mole fraction of VA	Diads		R_{obs}	R_{rand}
		$F(\text{E-VA})$	$F(\text{VA-VA})$		
1	0.202	0.79	0.21	31.9	32.8
2	0.187	0.83	0.17	30.7	30.4
3	0.177	0.84	0.16	28.7	29.2
4	0.162	0.86	0.14	27.9	27.2

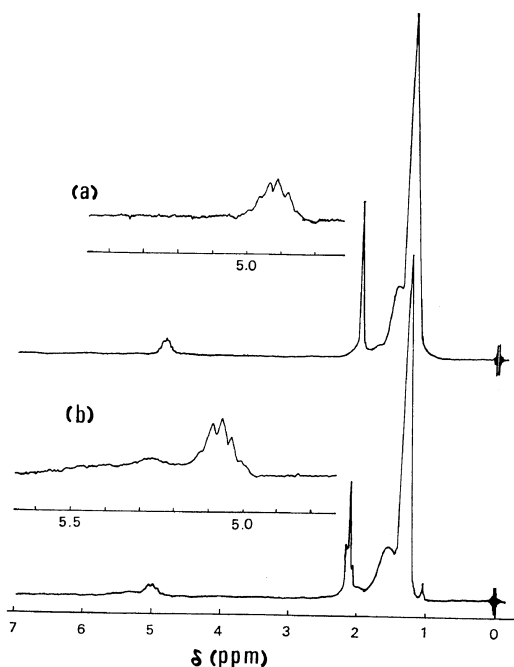


Figure 1. $^1\text{H-NMR}$ spectra of sample No. 1 (25 mg) in chloroform- d_1 with the addition of $\text{Eu}(\text{fod})_3$: (a) 0.0 mg; (b) 1.5 mg.

Table II. Assignment of proton resonances in E-VA copolymers

Peak No.	(ppm)	Proton ^a
1	4.67—5.10	$-\text{CH}\bar{\text{R}}-$
2	1.90—2.10	$-\text{OCOCH}_3$
3	1.60—1.90	$-\text{CHR}-\text{CH}_2-\text{CHR}-$
4	1.40—1.60	$-\text{CHR}-\text{CH}_2-\text{CH}_2-$
5	1.10—1.40	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-$

^a R, $-\text{OCOCH}_3$

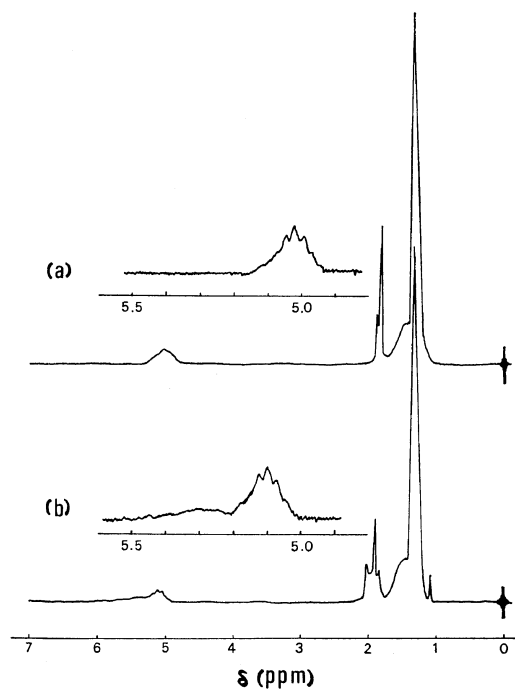


Figure 2. $^1\text{H-NMR}$ spectra of sample No. 1 (25 mg) in benzene- d_6 with the addition of $\text{Eu}(\text{fod})_3$: (a) 0.0 mg; (b) 3.7 mg.

The diad sequence distributions were obtained from the acetate methyl proton resonance spectra measured in benzene- d_6 ,⁶ and the run number (R_{obs}) can be readily calculated by using the following equation.¹⁴

$$R_{\text{obs}} = 200 \times F(\text{VA-E}) \quad (1)$$

where $F(\text{VA-E})$ denotes the mole fraction of the linkages between VA and E units. In an ideal random copolymerization, the run number (R_{rand}) can be expressed by the relationship¹⁴

$$R_{\text{rand}} = 200 \times F(\text{VA}) \times F(\text{E}) \quad (2)$$

where $F(VA)$ and $F(E)$ denote the mole fraction of vinyl acetate and ethylene in the E-VA copolymer, respectively. Consequently, it is thought that E-VA copolymers in Table I are ideally random.

In Figure 1 are shown the spectra of the E-VA copolymer (sample No. 1 in Table I) dissolved in chloroform-*d*₁ with (b) and without (a) Eu(fod)₃. The assignments of each proton resonance in Figure 1a are shown in Table II. The peak at $\delta=4.67-5.10$ ppm assigned to the methine proton in Figure 1a was split into a quintet at $\delta=4.97-5.12$ ppm and a broad peak at $\delta=5.12-5.80$ ppm, as shown in Figure 1b, by the addition of Eu(fod)₃. The peak at $\delta=2.02$ ppm assigned to the acetate methyl protons in Figure 1a was split into a triplet at $\delta=2.10, 2.13,$ and 2.16 ppm in Figure 1b.

The spectra in Figure 2 were obtained by using benzene-*d*₆ as solvent. The peaks at $\delta=4.80-5.20$ and $1.78-1.95$ ppm in Figure 2a are also assigned to the methine and the acetate methyl protons, respectively, and the latter was split into a doublet.^{3,6} The splitting phenomenon of the methine and the acetate methyl proton resonance spectra in Figure 2b was similar to that in Figure 1b.

In the present case, Eu(fod)₃ makes a complex with the VA unit in the E-VA copolymers following addition of this reagent, and the magnitude of the shift is different according to the copolymer configuration. If the signal from the acetate methyl protons split into a triplet is tentatively assigned to triads with VA unit as a center, the distinguishable triad placements in the E-VA copolymers are depicted as shown in Figure 3. In order to estimate the difference of the shift due to the distinguishable placements, Eu(fod)₃ was added to the E-VA copolymer and PVAc so that the mole ratio of this reagent to the VA content in these two polymers was equal.

Figure 4a and c show the spectra in the region of the acetate methyl proton resonances of E-VA copolymer (sample No. 1 in Table I) and PVAc dissolved in chloroform-*d*₁, respectively, and Figure 4b and d the spectra of these polymers with Eu(fod)₃, respectively. The peak at $\delta=2.02$ ppm in Figure 4a was split into three at $\delta=2.10, 2.13,$ and 2.16 ppm in Figure 4b.

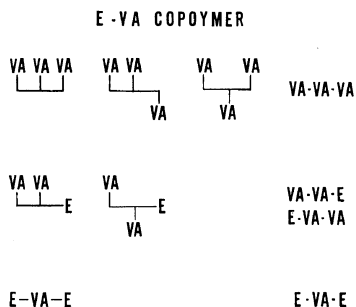


Figure 3. Distinguishable triad placements in E-VA copolymers. The up and down positions represent the *d*- and *l*-form of the monomers, respectively.

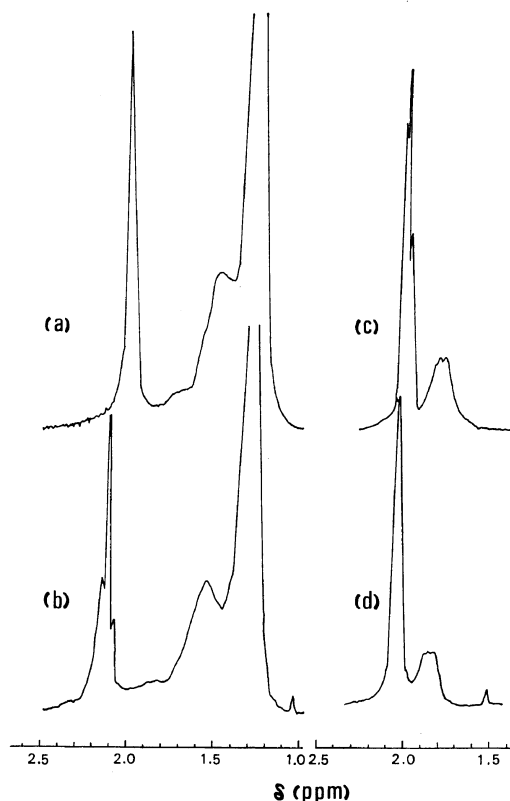


Figure 4. ¹H-NMR spectra in the region of the acetate methyl proton resonances of sample No. 1 and PVAc in chloroform-*d*₁. Eu(fod)₃/(VA) ((VA) expressed in concentration of VA units in E-VA copolymer and PVAc): (a) 0.000; (b) 0.013; (c) 0.000; (d) 0.013. Spectra: (a), (b) sample No. 1; (c), (d) PVAc.

On the other hand, the peaks at $\delta=1.97$, 2.00, and 2.02 ppm in Figure 4c collapsed into one peak at $\delta=2.07$ ppm in Figure 4d. Thus, the following results were obtained from the above experiment. First, the splitting in Figure 4b does not depend on the *d*- and *l*-form of the monomers in Figure 3. Second, the peak at $\delta=2.10$ ppm in Figure 4b is assigned to the acetate methyl protons in VA—VA—VA sequence from the peak at $\delta=2.07$ ppm in Figure 4d. Now, if the peaks at $\delta=2.13$ and 2.16 ppm in Figure 4b are assigned tentatively to E—VA—E and VA—VA—E (E—VA—VA) sequences, respectively, the relative concentrations of the above triad sequences can be obtained by using a Du Pont Curve Resolver, as shown in Figure 5.

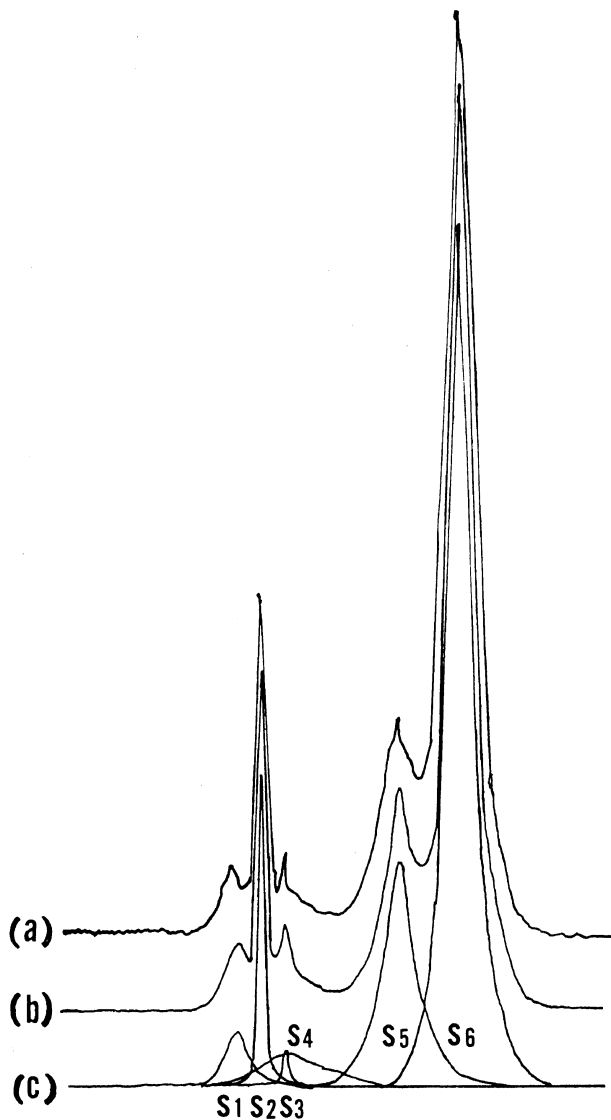


Figure 5. $^1\text{H-NMR}$ spectra in the region of the acetate methyl proton resonances of E—VA copolymer (sample No. 2) split by the use of $\text{Eu}(\text{fod})_3$: (a) the observed spectrum; (b) the synthesized spectrum of each component in (c); (c) six Lorentzian components.

Table III. Monomer sequence distributions of E-VA copolymers

Sample No.		Triads ^a		
		$F(\text{E-VA-E})$	$F(\text{VA-VA-E})$	$F(\text{VA-VA-VA})$
1	Obsd	0.64	0.30	0.06
	Calcd	0.65	0.31	0.04
2	Obsd	0.69	0.27	0.04
	Calcd	0.66	0.30	0.04
3	Obsd	0.70	0.27	0.03
	Calcd	0.68	0.29	0.03
4	Obsd	0.74	0.23	0.03
	Calcd	0.74	0.24	0.02

^a Obsd designates the observed fractions of triads. Calcd represents the triad fractions calculated by using eq 3-5 and the mole fractions of VA and R_{rand} in Table I.

Table IV. Monomer sequence distributions of E-VA copolymers

Sample No.		Triads ^a	
		$F(\text{E-VA-E})$	$F(\text{VA-VA-E}) + F(\text{VA-VA-VA})$
1	Obsd	0.65	0.35
	Calcd	0.65	0.35
2	Obsd	0.68	0.32
	Calcd	0.66	0.34
3	Obsd	0.70	0.30
	Calcd	0.68	0.32
4	Obsd	0.75	0.25
	Calcd	0.74	0.26

^a Obsd designates the observed fractions of triads. Calcd represents the triad fractions calculated by using eq 3-5 and the mole fractions of VA and R_{rand} in Table I.

In Figure 5c, S_1 , S_2 , and S_3 are assigned to the triads of the acetate methyl protons, and S_4 , S_5 , and S_6 to $-\text{CHR}-\text{CH}_2-\text{CHR}-$, $-\text{CHR}-\text{CH}_2-\text{CH}_2-$, and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ protons. Since the samples are random copolymers, triad sequences are obtained by using the R_{rand} and the mole fraction of VA in Table I, and the following equations:¹⁴

$$F(\text{E-VA-E}) = \frac{R_{\text{rand}}^2}{4(100 \times F(\text{VA}))^2} \quad (3)$$

$$F(\text{VA-VA-VA}) = \frac{(100 \times F(\text{VA}) - R_{\text{rand}}/2)^2}{(100 \times F(\text{VA}))^2} \quad (4)$$

$$\begin{aligned} F(\text{VA-VA-E}) + F(\text{E-VA-VA}) \\ = \frac{R_{\text{rand}}(100 \times F(\text{VA}) - R_{\text{rand}}/2)}{(100 \times F(\text{VA}))^2} \quad (5) \end{aligned}$$

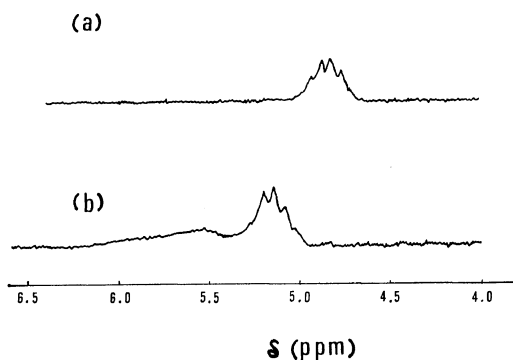


Figure 6. $^1\text{H-NMR}$ spectra of the methine proton of sample No. 1 (25 mg) in chloroform- d_1 with the addition of $\text{Eu}(\text{fod})_3$: (a) 0.0 mg; (b) 1.8 mg.

where $F(E-VA-E)$, $F(VA-VA-E)$, $F(E-VA-VA)$, and $F(VA-VA-VA)$ represent the mole fractions of $E-VA-E$, $VA-VA-E$, $E-VA-VA$, and $VA-VA-VA$ sequences, respectively. In Table III, the observed and the calculated triad sequence concentrations are shown; the former were in close agreement with the latter. Thus it may be thought that the acetate methyl resonance assignments to triads is reasonable.

In Figure 6 are shown the spectra of the methine proton of $E-VA$ copolymer (sample No. 1 in Table I) dissolved in chloroform- d_1 with (b) and without (a) $Eu(fod)_3$. The peak at $\delta=4.67-5.10$ ppm in Figure 6a was split into a quintet at $\delta=4.94-5.34$ ppm and a broad peak at $\delta=5.34-6.10$ ppm, as shown in Figure 6b. If these peaks are assigned tentatively to $E-VA-E$ and the sum of $E-VA-VA$ and $VA-VA-VA$ from a higher field, respectively, the relative concentrations are also obtained by using a Curve Resolver. In Table IV, the observed concentrations are tabulated with the concentrations calculated according to eq 3-5; the former were in close agreement with the latter.

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