

Microstructure of Vinylidene Chloride–Ethyl Acrylate Copolymers by One- and Two-Dimensional NMR Spectroscopy

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ABSTRACT: Vinylidene chloride/ethyl acrylate (V/E) copolymers were prepared by photopolymerization using uranyl ion as a photosensitizer at room temperature. Copolymers were characterized by chlorine estimation, gel permeation chromatography, ^1H - and ^{13}C -NMR, 2D heteronuclear single quantum correlation (HSQC), and homonuclear 1H–2D double quantum filter correlation spectroscopy (DQF-COSY). Reactivity ratios for the copolymerization of V with E were calculated using the Kelen–Tudos (KT) and the nonlinear error in variables (EVM) methods. The reactivity ratios obtained from the EVM methods are $r_V = 0.80 \pm 0.15$ and $r_E = 0.87 \pm 0.04$. The microstructure was calculated in terms of the distribution of V- and E-centered triad sequences from $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the copolymers. 2D HSQC was used to analyze the complex ^1H -NMR spectrum and 2D COSY shows the various bond interactions, thus inferring the possible structure of the copolymers. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 417–426, 1998

INTRODUCTION

^{13}C -NMR spectroscopy in solution has been used as a powerful experimental technique to determine the intramolecular and intermolecular chain structures of vinyl copolymers^{1,2–10} can give information about the polymerization process as the chemical shift is sensitive to structural and stereochemical variations.^{2,3} The microstructure of vinylidene chloride/ethyl acrylate (V/E), a commercially important copolymer⁴ whose knowledge is essential to understand the macroscopic properties of the polymers, has not been reported as yet. Two-dimensional NMR spectroscopy⁵ has now successfully entered into the characterization of the copolymers.^{6,7} Earlier, we reported the compositional assignments for

vinylidene chloride–methyl acrylate⁸ copolymers.

In the continuation of our earlier work, we report the copolymerization mechanism of V/E using 2D-NMR spectroscopy. A series of copolymers of different compositions were prepared. The reactivity ratios of the comonomers were calculated using the Kelen–Tudos (KT) and the nonlinear error in variables (EVM)⁹ methods. The composition of the copolymers is determined from chlorine estimation using the Schoneger technique.^{10,11} The triad sequence distribution in terms of V- and E-centered triads were obtained from the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the copolymers and are compared with those calculated from statistical model and Monte Carlo (MC) simulation methods.¹²

The highly complex ^1H -NMR of the copolymer has been assigned to different compositional sequences with the help of 2D HSQC and 2D COSY experiments. 2D COSY also confirms the various structures proposed for the copolymer chain.

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Table I Copolymer Composition Data and Molecular Weights of V/E Copolymers

No.	Monomer Content in Feed (Mol Fraction)		Copolymer Composition (Mol Fraction)		% Cl	% Conversion	$\bar{M}_n \times 10^{-4}$ g/mol	$\bar{M}_w \times 10^{-4}$ g/mol
	f_V	f_E	F_V	F_E				
1.	0.2	0.8	0.21	0.79	15.12	7	16	28
2.	0.3	0.7	0.31	0.69	22.31	2	13	26
3.	0.4	0.6	0.40	0.60	28.61	6	5	13
4.	0.5	0.5	0.49	0.51	35.25	5	5	13
5.	0.6	0.4	0.58	0.42	41.75	5	4	10

\bar{M}_n = number average; \bar{M}_w = weight average.

EXPERIMENTAL

Ethyl acrylate (E) and vinylidene chloride (V) (Fluka) were distilled and stored below 5°C. A series of V/E copolymers containing different mol percents of E in the feed were prepared by photopolymerization using uranyl ion as a photoinitiator. Gel permeation chromatography was used to determine the molecular weight averages. The experimental details for the preparation of copolymers, the composition determination, and the NMR spectra recording were discussed in our earlier publication.⁸ The percent conversion of the copolymers prepared was kept below 10%. The exact degrees of conversion are reported in Table I.

RESULTS AND DISCUSSION

Reactivity Ratios and Composition Determination

The composition of the V/E copolymers was determined through the estimation of the chlorine con-

tent of the copolymers. The comonomer mol fractions in the feed and in the copolymer along with their chlorine contents are tabulated in Table I. The copolymer composition data thus obtained were used to calculate the terminal model reactivity ratios by the methods of Kelen-Tudos (KT) and the error in variables (EVM) method using the RREVM program. In the RREVM program, the percentage error in measuring the comonomer composition in the feed and in the copolymer were taken as 1 and 3%, respectively. The values of the reactivity ratios obtained from the KT method are $r_V = 0.79 \pm 0.05$ and $r_E = 0.86 \pm 0.03$. These values were used as the initial estimates in the RREVM program and obtained as $r_V = 0.80$ and $r_E = 0.87$. Figure 1 shows a 95% joint confidence interval plot for this comonomer pair. The theoretical composition¹³ curve obtained from the copolymer composition equation using terminal model reactivity ratios ($r_V = 0.80$ and $r_E = 0.87$) along

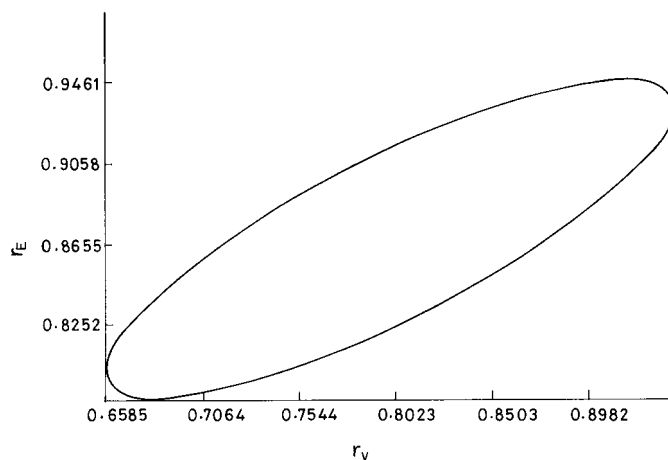


Figure 1 95% posterior probability contour for V/E comonomer pair.

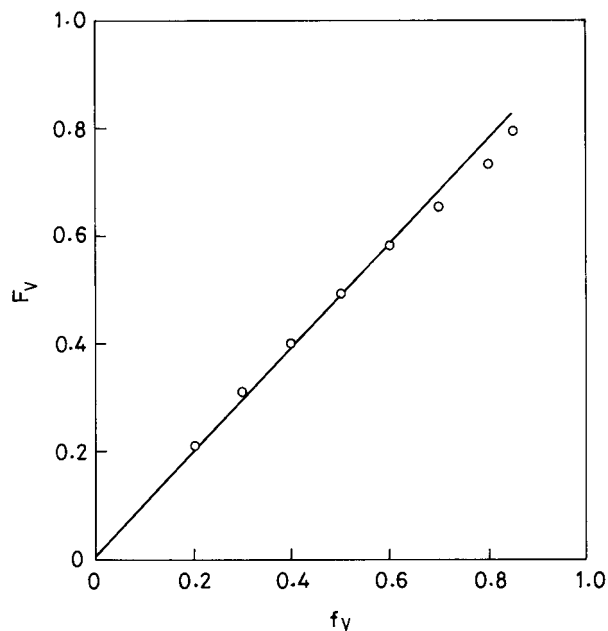


Figure 2 Theoretical composition curve obtained using reactivity ratios $r_V = 0.80$ and $r_E = 0.87$ along with experimentally determined copolymer composition (\circ).

with experimentally determined copolymer compositions is shown in Figure 2. The molecular weight averages of the copolymer are given in Table I. With the constant increase in the composi-

tion of V, there is a regular decrease in molecular weight.

^{13}C -NMR Studies

A representative $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of a V/E copolymer ($V = 50.0$ mol % in the feed) in CDCl_3 at room temperature is shown in Figure 3. The various resonance peaks were assigned by comparing the copolymer spectrum with those of homopolymers. The resonance signals due to the methyl group ($-\text{CH}_3$) of E is insensitive to tacticity. The methine and quaternary carbon resonances showed multiplets, indicating that they are sensitive toward the compositional sequences and can be used for the assessment of the copolymerization mechanism. The resonance signals like the carbonyl carbon signal ($\text{C}=\text{O}$) appearing in the region $\delta 173.0$ – 175.0 ppm and the oxymethylene carbon of the side-chain ($-\text{OCH}_2$) signal appearing in the region $\delta 60.0$ – 62.0 ppm due to E units, though, show a multiplet, but as these resonances are complex because of overlapping with one another, they cannot be used for predicting the copolymerization behavior. The β -methylene ($-\text{CH}_2$) resonance signal which is due to both V and E monomeric units is extended over a wide range from $\delta 34.7$ – 63.5 ppm which appears

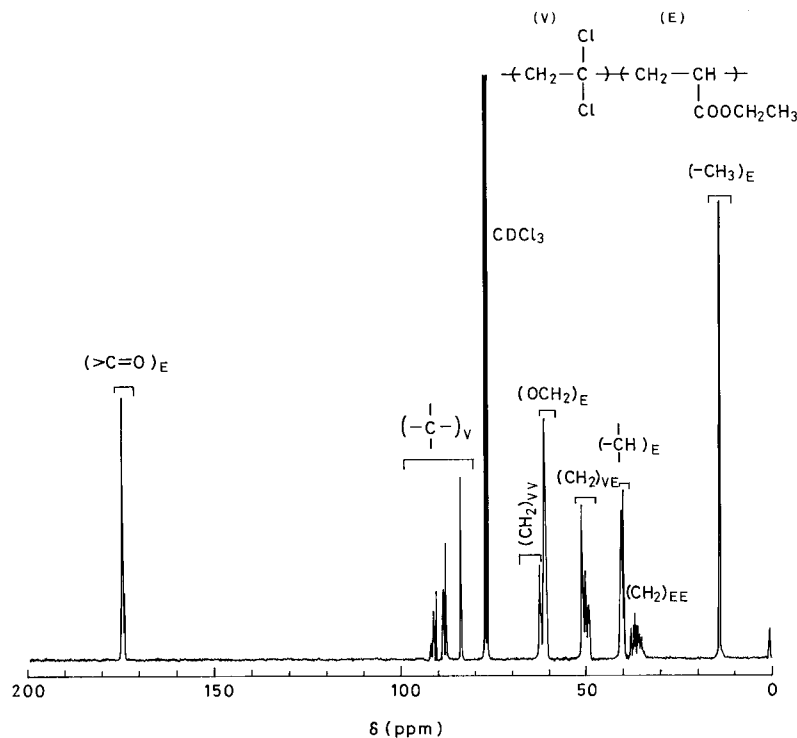


Figure 3 75 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the V/E copolymer ($F_V = 0.5$).

Table II Triad Compositions Calculated from NMR Spectra, Monte Carlo Simulations, and the Alfrey–Mayo Model in V/E Copolymers

Sample No.	Feed Mole Fraction of V	Triads	Triad Compositions ^a		
			NMR ^b ¹³ C{ ¹ H}	Alfrey Mayo	Monte Carlo ^c
1	0.3	VVV	0.13	0.07	0.05
		VVE	0.38	0.38	0.33
		EVE	0.49	0.55	0.62
		EEE	0.39	0.45	0.45
		EEV	0.50	0.44	0.44
		VEV	0.11	0.11	0.11
2	0.4	VVV	0.17	0.12	0.10
		VVE	0.45	0.45	0.44
		EVE	0.38	0.43	0.46
		EEE	0.37	0.32	0.35
		EEV	0.50	0.49	0.48
		VEV	0.13	0.19	0.17
3	0.5	VVV	0.25	0.20	0.18
		VVE	0.48	0.49	0.49
		EVE	0.27	0.31	0.33
		EEE	0.22	0.22	0.19
		EVE	0.48	0.50	0.49
		VEV	0.30	0.28	0.32
4	0.6	VVV	0.35	0.30	0.31
		VVE	0.47	0.49	0.49
		EVE	0.17	0.21	0.20
		EEE	0.18	0.14	0.09
		EVE	0.42	0.46	0.43
		VEV	0.40	0.40	0.48
5	0.7	VVV	0.47	0.42	0.45
		VVE	0.46	0.46	0.44
		EVE	0.07	0.12	0.11
		EEE	0.06	0.07	0.04
		EVE	0.37	0.40	0.33
		VEV	0.57	0.53	0.63
6	0.8	VVV	0.63	0.58	0.62
		VVE	0.32	0.36	0.34
		EVE	0.05	0.06	0.04
		EEE	0.01	0.03	0.02
		EVE	0.27	0.29	0.21
		VEV	0.72	0.68	0.77

^a V- and E-centered triad fractions add up to unity.

^b Triad fractions obtained using quaternary carbon and methine carbon resonance signals for V- and E-centered triads, respectively, of the ¹³C-NMR.

^c Triad fractions calculated using average reactivity ratios of $r_V = 0.80$ and $r_E = 0.87$.

resonance signal intensities, the assignment was done up to the pentad level as shown in Figure 5. The relative fractions of EEE, EEV, and VEV triads were calculated from area measurements of these various resonance signals. Within experimental error, values of E-centered triads are in

agreement with theoretical values obtained using $r_V = 0.80$ and $r_E = 0.87$ in Harwood's statistical model and Monte Carlo simulation¹⁴ methods (Table II).

The signals, because of the dichloro-substituted carbons of V in the copolymers, are sharp and

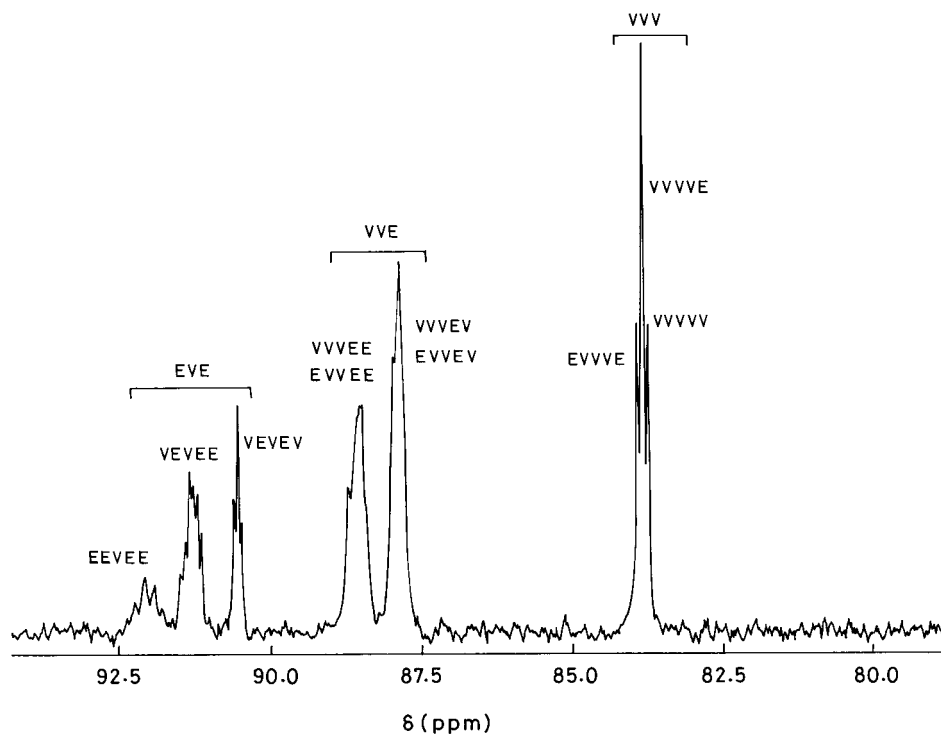


Figure 6 Expanded quaternary carbon resonance region of V monomeric unit of the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum in the V/E copolymer.

well separated. By following trends in the series of spectra, the various groups of signals are assigned up to the pentad level as represented in

Figure 6, which is in accordance with that predicted by Henrichs.¹⁵ The relative fractions of the VVV, VVE, and EVE triads were obtained by mea-

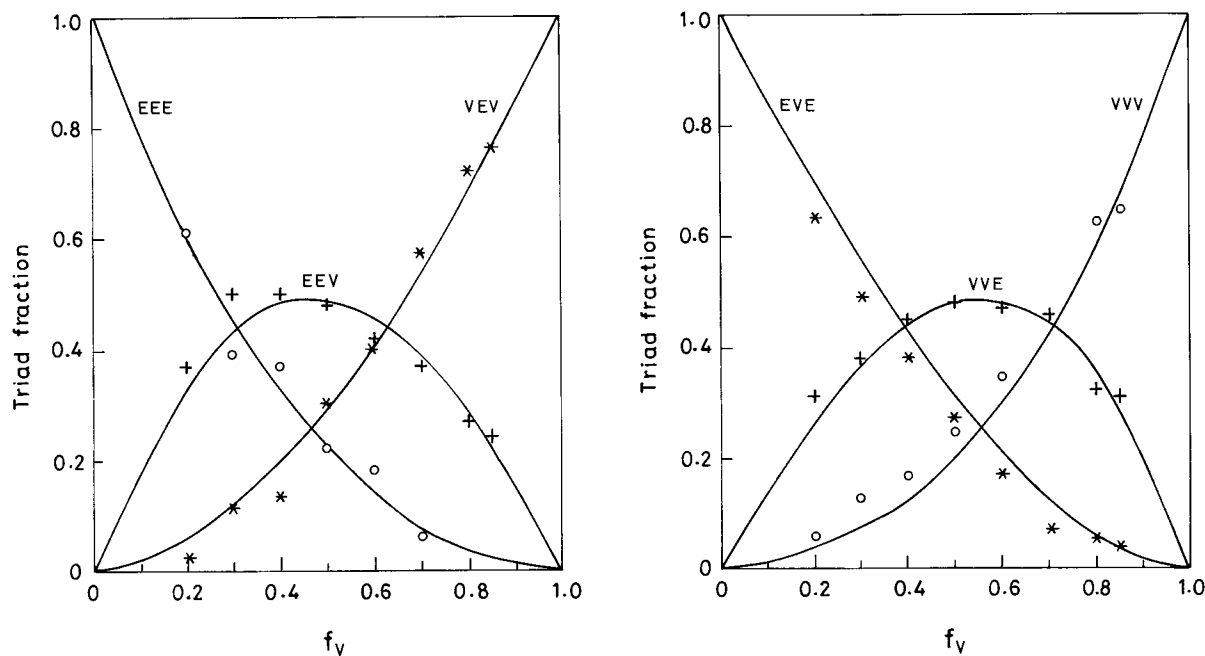


Figure 7 Variation of V- and E-centered triad fractions obtained from theoretical calculation (solid lines) and NMR spectroscopy (symbols) for the V/E copolymer plotted against feed mol fraction (F_V) of V.

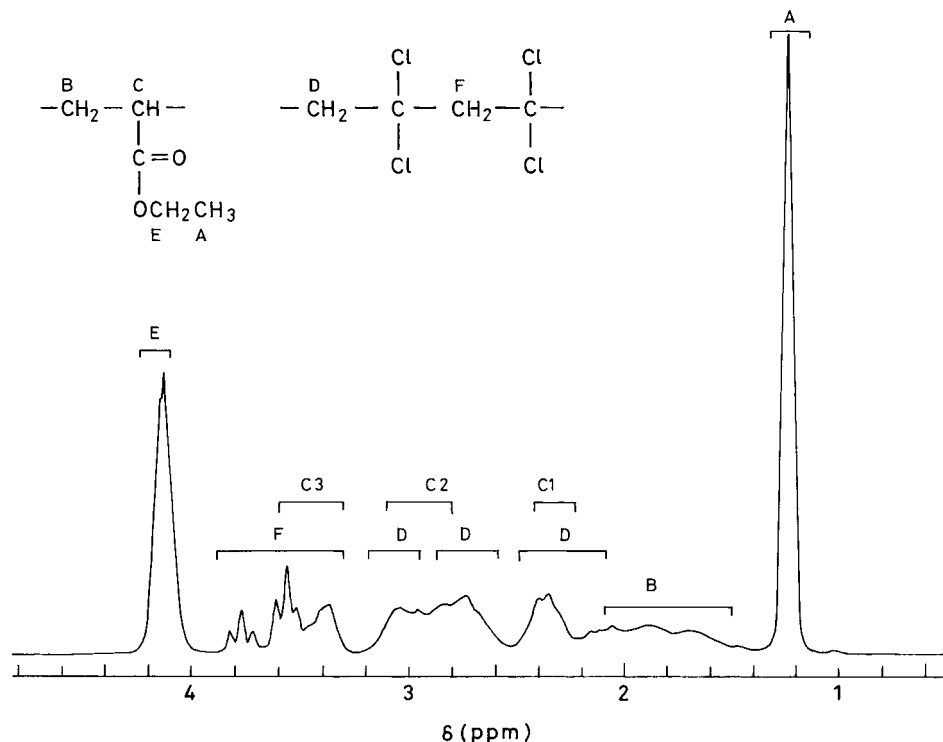


Figure 8 300 MHz ^1H -NMR spectrum of V/E copolymer ($F_V = 0.5$).

asuring areas under the respective triad sequences. These triad fractions, when compared with triad fractions obtained using reactivity ratios $r_V = 0.80$ and $r_E = 0.87$ in Harwood's statistical model, were found to be in excellent agreement (Table II).

Figure 7 shows the plots of normalized V- and E-centered triad concentrations against the mol fraction of V. The variation of V- and E-centered triads are as expected with a maximum fraction of EEV and VVE triads reaching a 0.45 and 0.55 mol fraction of V, respectively. In the figure, the solid lines represent the theoretically calculated (Alfrey Mayo) triad fractions, whereas symbols represent the experimentally determined (NMR) triad fractions.

The Monte Carlo (MC) simulation method was also used to monitor the changes in copolymer sequence behavior during the course of polymerization and the V- and E-centered triads obtained from this method are also in good agreement with the experimentally calculated values from NMR which is predicted from the correlation coefficient. The correlation coefficient for both NMR–Alfrey Mayo and NMR–MC is $R = 0.975$.

^1H -NMR and 2D-NMR Studies

The ^1H -NMR spectrum of the V/E copolymer ($F_V = 0.5$) in CDCl_3 recorded at 27.6°C is shown in

Figure 8. The side-chain methyl protons are assigned to $\delta 1.24$ ppm (labeled A). The oxymethylene protons ($-\text{OCH}_2$) of the side chain appear the most downfield at $\delta 4.1$ ppm (labeled E). The methine and the β -methylene proton signals of the main chain overlap, covering the region $\delta 1.5$ – 3.9 ppm. These signals are distinguished using the 2D ^{13}C – ^1H -HSQC NMR spectrum [Fig. 9(a)], which gives the direct correlation of proton and carbon atoms. Since in the ^{13}C -NMR spectrum the methine region ($\delta 39.7$ – 41.2 ppm) is completely separable from the methylene resonance signals and is correlated to protons at $\delta 2.25$ – 2.45 , $\delta 2.8$ – 3.1 , and $\delta 3.3$ – 3.6 ppm, the regions $\delta 2.25$ – 2.45 , $\delta 2.8$ – 3.1 , and $\delta 3.3$ – 3.6 ppm thus correspond to the methine protons of EEE, EEV, and VEV triads (labeled C1, C2, and C3) in the ^1H -NMR spectrum. 2D HSQC shows the cross peaks which help to label the ^1H -NMR up to pentad sequences, viz., $\delta 39.74/3.39$ ppm for VVEVV, $\delta 39.96/3.47$ ppm for EVEVV, and $\delta 40.15/3.53$ ppm for EVEVE sequences, and similarly, $\delta 40.37/2.85$ ppm for VEEVV, $\delta 40.48/2.90$ ppm for EEEVV, and $\delta 40.61/2.98$ ppm for EEEVE pentad sequences. The pentads of the EEE triads overlap in the ^1H -NMR at $\delta 2.38$ ppm. All these assignments are shown in Table III. The 2D HSQC spectrum [Fig. 9(b)] also gives clear information re-

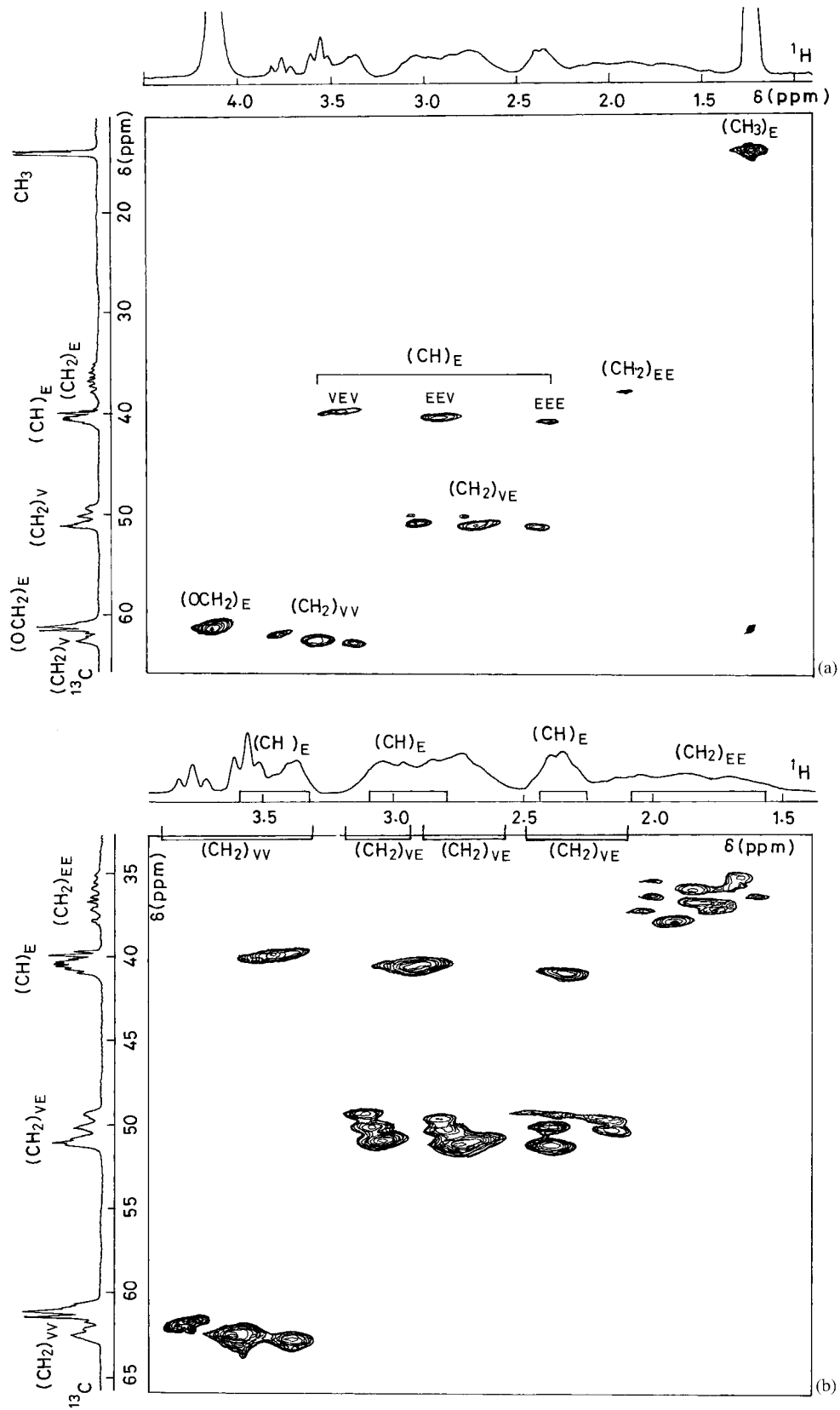


Figure 9 (a) 75 MHz 2D-HSQC NMR spectrum of the V/E copolymer ($F_V = 0.5$). (b) Expanded region of the 2D-HSQC NMR spectrum.

Table III Information Obtained from the 2D HSQC Spectrum

Region	Chemical Shift (ppm)		Assignment	Label in $^1\text{H-NMR}$
	$^{13}\text{C}\{^1\text{H}\}$	^1H		
Methyl	13.5–14.5	1.16–1.35	—	A
Oxymethylene of side chain	60.0–62.0	4.05–4.25	—	E
Methine	41.21, 40.99, 40.79	2.38	EEEE, VEEEE, VEEEV	C1
	40.61	2.98	EEEVE	C2
	40.48	2.90	EEEVV(VEEVE)	
	40.37	2.85	VEEVV	
	40.15	3.53	EVEVE	C3
	39.96	3.47	EVEVV(VVEVE)	
	39.74	3.39	VVEVV	
Methylene of main chain	35.02–35.96	1.56–2.1	EEEE	B
	36.0–37.0	—	EEEV (VEEE)	
	37.75–38.05	—	VEEV	
	49.25–49.80	2.1–3.2	EVEE	D
	50.20	—	EVEV(VVEE)	
	50.85–51.50	—	VVEV	
	61.73	3.8	EVVE	F
	62.08–62.51	3.57	EVVV(VVVE)	
62.61	3.39	VVVV		

garding the β -methylene protons. The methylene protons which are spread in three different regions are assigned, viz., δ 1.55–2.1 ppm for methylene protons incorporated between $-\text{CHCOO}-\text{CH}_2\text{CH}_3$ on both sides (labeled B), δ 2.1–3.2 ppm for methylene protons in between $-\text{CHCOO}-\text{CH}_2\text{CH}_3$ on one side and $-\text{CCl}_2$ on the other (labeled D), and δ 3.3–3.9 ppm for methylene incorporated between $-\text{CCl}_2$ on both sides (labeled F). 2D HSQC helps to assign the methylene protons on ^1H as tetrads, viz., δ 3.39 ppm for VVVV, δ 3.57 ppm for VVVE (EVVV), and δ 3.8 ppm for EVVE. All the tetrads of the VE and EE diad region are spread over δ 2.1–3.2 ppm and δ 1.56–2.10 ppm, respectively. Further splittings are seen for each of the tetrads on the ^1H , which indicates that $^1\text{H-NMR}$ is more sensitive than is $^{13}\text{C-NMR}$ for the methylene region. These splittings may be due either to higher compositional sequences or to configurational splittings.

The $^1\text{H-2D}$ COSY NMR of the V/E copolymer ($F_V = 0.5$) recorded in CDCl_3 is shown in Figure 10, which gives a better insight for studying the polymer structure. The cross peaks at δ 4.1/1.25 ppm show the coupling between the oxymethylene proton (OCH_2) of the side chain and the methyl (CH_3) proton. The methine (CH) protons, which

are triad-sensitive, show the J coupling with the methylene protons. In the VEV triad, the central methine proton is coupled to the same type of methylene protons (V type) on either side which appear at δ 3.53/3.05 ppm. The methine proton of the VEE (EEV) triad is coupled to both types of methylene protons, viz., V type (δ 2.90/3.08 ppm) and E type (δ 2.98/2.68 ppm). Another cross peak appearing at δ 2.38/2.75 ppm is due to the coupling of methine protons of the EEE triad with methylene protons of the E type on both sides.

The coupling between methylene protons is also very much evident in the COSY spectrum, which could be due either to head-to-head methylene–methylene couplings or because of coupling between unequivalent protons of the methylene in the unsymmetrical sequences. Since in the COSY spectrum no methine–methine coupling (CH—CH) cross peaks are seen, and for the two quaternary carbon ($\text{CCl}_2-\text{CCl}_2$) linked together, the COSY spectrum does not show cross peaks, therefore no such linkages are possible in the polymer chain.

CONCLUSIONS

The microstructure of V/E was determined with the help of $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy. The V/E

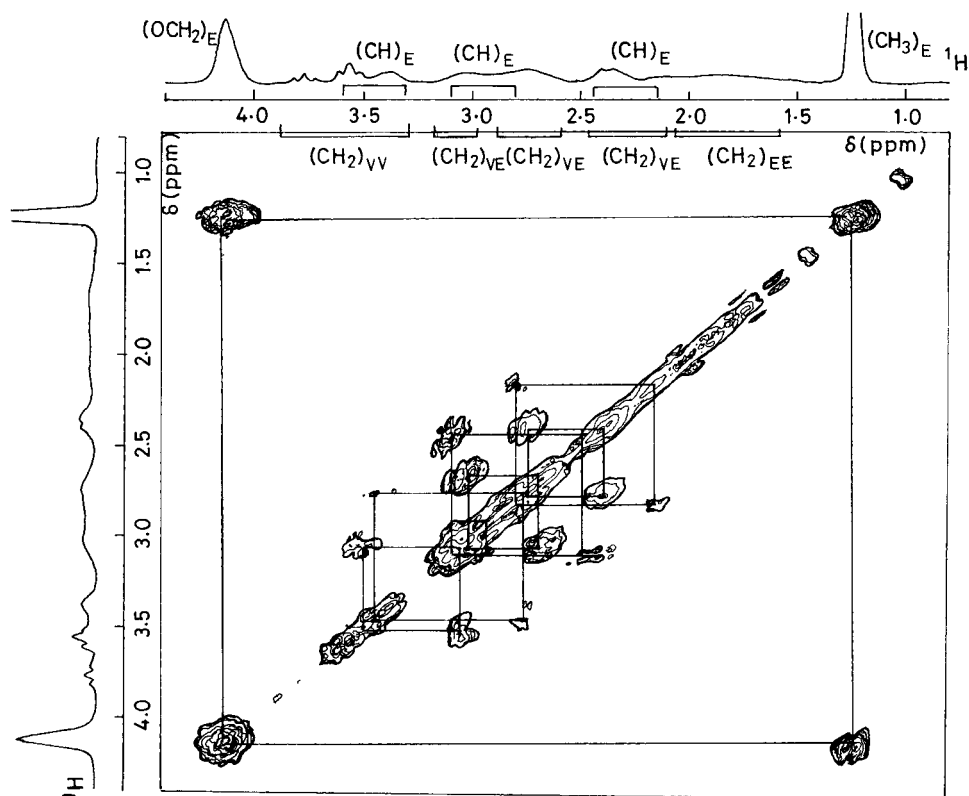


Figure 10 300 MHz ^1H -NMR 2D-COSY spectrum of V/E copolymer ($F_V = 0.5$).

copolymer system gives a good fit to the first-order Markov model and the triad fractions obtained from the NMR spectra are in good agreement to the theoretical models and MC simulations. The HSQC NMR spectrum was used to make unambiguous assignments of the ^1H -NMR spectra. The characterization of various signals were done from the tetrad to pentad level. It shows that the ^1H -NMR is more sensitive to the methylene signal than is the $^{13}\text{C}\{^1\text{H}\}$ -NMR. The 2D COSY experiment gave better insight into the feasibility of various structures of the polymer chain.

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