

Compositional Sequence Determination of 4-Vinylpyridine/ Ethyl Methacrylate Copolymers by One- and Two- Dimensional NMR Spectroscopy

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ABSTRACT: 4-Vinylpyridine/ethyl methacrylate (V/E) copolymers of different compositions were prepared by bulk polymerization using benzoyl peroxide as an initiator. The copolymer composition was determined from proton NMR spectra. The reactivity ratios for V/E copolymers were calculated using Kelen-Tudos method (KT) and non-linear error in variables method (EVM). The reactivity ratios obtained from KT and EVM methods are $r_V=0.48$, $r_E=0.82$, and $r_V=0.49\pm 0.15$, $r_E=0.83\pm 0.08$ respectively. The V- and E- centered triad concentrations were calculated from $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of copolymers and compared with those calculated from Harwood's program using terminal model reactivity ratios determined from EVM method. The complete spectral assignments in terms of compositional and configurational sequences of these copolymers were done with the help of distortionless enhancement by polarization transfer (DEPT), two dimensional heteronuclear single quantum coherence spectroscopy (HSQC). Total correlated spectroscopy (TOCSY) experiment was used to assign the various three bond ^1H - ^1H coupling in copolymers.

KEY WORDS 4-Vinylpyridine/Ethyl Methacrylate Copolymer/NMR/Spectroscopy/Two Dimensional Heteronuclear Single Quantum Coherence Spectroscopy (HSQC)/Distortionless Enhancement by Polarization Transfer (DEPT)/Total Correlated Spectroscopy (TOCSY)/Reactivity Ratios/Sequence Determination/

4-Vinylpyridine polymers are having very important applications in electrical field, polymer reagents, polymer supports in reaction catalysis, such as oxidation and reduction reactions and in polyelectrolyte.¹ The porous vinylpyridine polymers cross-linked with divinylbenzene are used as column packing material in gas chromatography and are particularly effective in the separation of mixture of amines. It is well known that NMR spectroscopy is probably the most effective method for characterizing the structure of polymers because the chemical shift is sensitive to configurational sequences.^{2,3} Two dimensional NMR experiments^{4,5} have been used as the most reliable method for determining the compositional^{6,7} and configurational⁸ sequences of the copolymers.

Natansohn *et al.*⁹ have reported the microstructure of 4-vinylpyridine/methyl acrylate copolymers by proton NMR spectroscopy. The microstructure of ethyl methacrylate copolymers with various monomers has been reported earlier.^{10,11} To the best of our knowledge the microstructure of 4-vinylpyridine/ethyl methacrylate (V/E) copolymer has not been reported so far. In this communication, we report the microstructure of V/E copolymers, prepared by free radical bulk polymerization. The reactivity ratio of the comonomers were calculated using linear Kelen-Tudos (KT) method¹² and non-linear least square error in variables method using RREVM program.¹³ The triad sequence distribution in terms of V- and E- units were obtained from NMR and compared with those calculated from statistical models using reactivity ratios obtained from RREVM program. The highly

complex and overlapped ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these copolymers have been assigned completely with help of distortionless enhancement by polarization transfer (DEPT)-135, DEPT-90, two dimensional heteronuclear single quantum coherence spectroscopy (HSQC), and total correlated spectroscopy (TOCSY) (low mixing time) experiments. The α -methyl, $^2\text{CH}_3$, methylene and methine carbon signals of V/E copolymers were sensitive to compositional and configurational sequences. The various sequences were assigned to triad, tetrad and pentad sequences with the help of various 2D experiments. The 2D TOCSY spectra of V/E copolymers show excellent splitting in aromatic region which shows the sensitivity toward the compositional and configurational sequences.

EXPERIMENTAL

Ethyl methacrylate (Merck), 4-vinylpyridine (Merck) were distilled under reduced pressure and stored below 5°C . A series of 4-vinylpyridine (V) and ethyl methacrylate (E) copolymers of different compositions were prepared by bulk polymerization using benzoyl peroxide as an initiator at 60°C . The percent conversion was kept below 10%. The copolymer was precipitated in petroleum ether. The copolymers were further purified from chloroform / petroleum ether system. All one- and two-dimensional NMR spectra were recorded in CDCl_3 at 24°C on a Bruker 300 MHz DPX spectrometer at a frequency of 300.13 and 75.5 MHz respectively. Two dimensional heteronuclear single quantum coherence (HSQC), DEPT-90, DEPT-135, TOCSY at 4 ms were recorded using standard pulse sequences.¹⁴ The relative area of dif-

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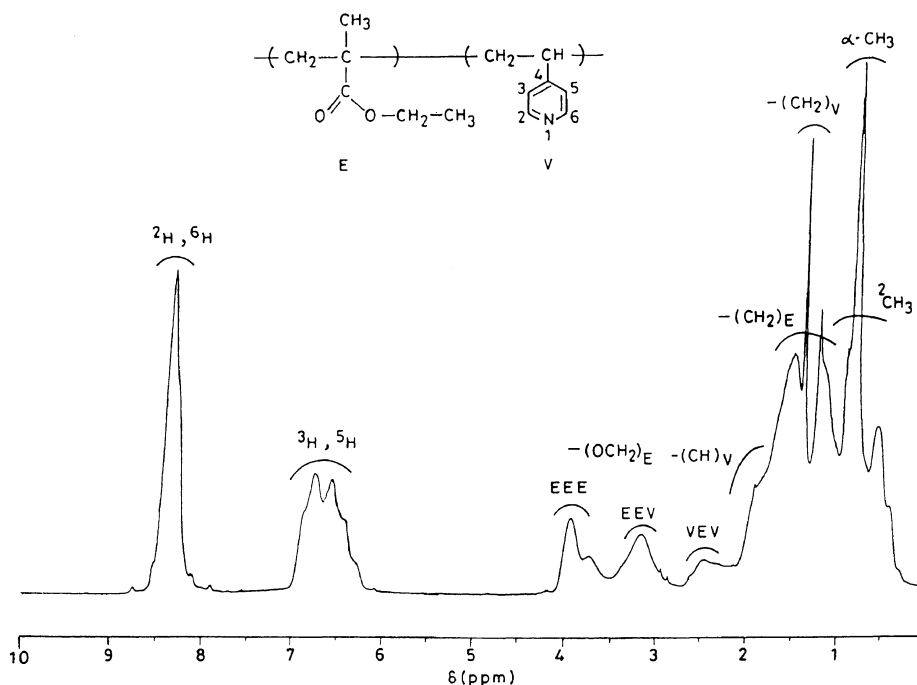


Figure 1. The ^1H NMR spectrum of 4-vinylpyridine/ethyl methacrylate (V/E) copolymer ($F_V=0.44$) in CDCl_3 .

ferent resonance signals was determined using a non-linear least square lorentzian line shape deconvoluting program.

RESULTS AND DISCUSSION

Determination of Copolymer Composition and Reactivity Ratios

The ^1H NMR spectrum of 4-vinylpyridine/ethyl methacrylate (V/E) copolymer ($F_V=0.44$ mole fraction in copolymer) along with the assignment of various resonance signals is shown in Figure 1. The copolymer composition was calculated from the relative intensities of 2,6 aromatic protons signal of V- unit and oxy methylene protons signal of E- unit in ^1H NMR using the following expression:

$$F_E = \frac{I(\text{OCH}_2)_E / 2}{I(\text{C}_5\text{H}_4\text{N } 2,6)_V / 2 + I(\text{OCH}_2)_E / 2}$$

i. e.,

$I(\text{OCH}_2)_E$ is the area under the resonance signal of $(\text{OCH}_2)_E$. $I(\text{C}_5\text{H}_4\text{N } 2,6)_V$ is the area under the resonance signal of 2,6 protons of aromatic ring and F_E is the mole fraction of E unit in the copolymers. Table I shows the copolymer composition of various V/E copolymers along with feed in composition. The copolymer composition data were used to calculate the terminal model reactivity ratios by KT method. The reactivity ratios calculated from KT method are $r_V=0.48$ and $r_E=0.82$. These reactivity ratios were used as the initial estimates for the calculation of reactivity ratios from non-linear error in variables method (EVM) using RREVM program. The reactivity ratios obtained from EVM method are $r_V=0.49 \pm 0.15$ and $r_E=0.83 \pm 0.08$. The comonomer reactivity ratios of the copolymerization of V and E are not reported in literature.

Table I. The feed in mole fraction and copolymer composition data for V/E copolymers

Sample	Feed in mol fractions		Mol fractions in copolymer	
	f_V	f_E	F_V	F_E
VEM 3	0.70	0.30	0.63	0.37
VEM 4	0.60	0.40	0.50	0.50
VEM 5	0.50	0.50	0.43	0.57
VEM 6	0.40	0.60	0.40	0.60
VEM 7	0.30	0.70	0.30	0.70
VEM 8	0.20	0.80	0.19	0.81
VEM 9	0.10	0.90	0.11	0.89

^1H NMR Studies

In the ^1H NMR spectrum of V/E copolymer (Figure 1), aromatic protons appeared as a set of two separate signals, one centered at around δ 8.40 ppm and another at δ 6.60 ppm. The broad signal at around δ 8.40 ppm is assigned to 2, 6 protons while that at δ 6.60 ppm is assigned to 3, 5 protons of the aromatic ring. The $-\text{OCH}_2$ protons of E- unit appeared as a triplet from δ 2.00 to 4.00 ppm. Based upon the variation in intensity of these signals with copolymer composition, it has been found that the resonance signal around δ 3.95 ppm can be assigned to EEE triad while at δ 3.17 and δ 2.60 ppm can be assigned to EEV and EVE triads respectively. The aliphatic proton region from δ 0.50 to δ 2.00 ppm is quite complex and overlapped which can be assigned to the combination of $\alpha\text{-CH}_3$, $^2\text{CH}_3$, $-\text{CH}_2$ (V), $-\text{CH}_2$ (E). The complicated ^1H NMR spectrum can be simplified with the help of DEPT and 2D -HSQC experiments.

$^{13}\text{C}\{^1\text{H}\}$ NMR Studies

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of V/E copolymer ($F_V=0.44$ mole fraction in copolymer) along with assignment of various resonance signals is shown in Figure 2. The aromatic carbons (C-3 and C-5, meta position) of the co-

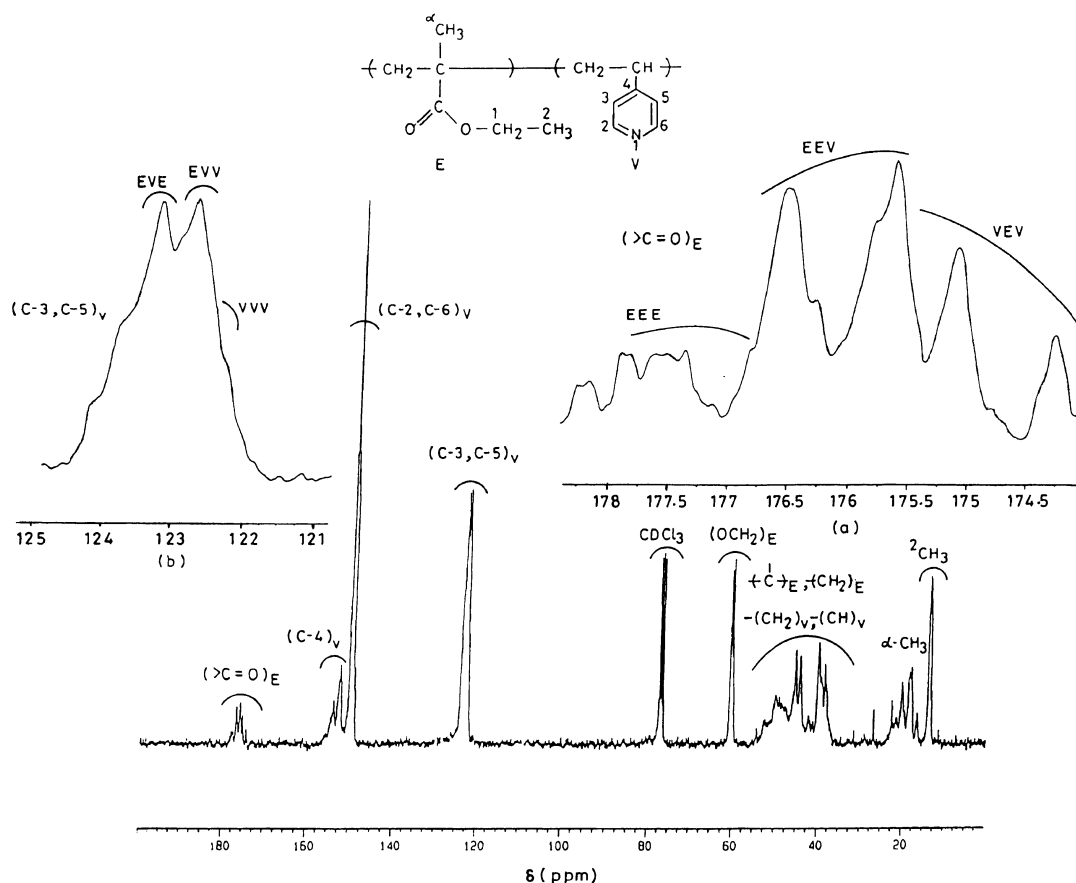


Figure 2. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of V/E copolymer ($F_V=0.44$) in CDCl_3 (a) the expanded region of carbonyl carbon of E- unit and (b) aromatic carbon (C-3, C-5) of V- unit.

polymer appeared at around δ 121.65–124.50 ppm while quaternary (C-4, para position), C-2 and C-6 (ortho position) carbons appeared around δ 151.75–156.00 and δ 148.70–150.85 ppm, respectively. The carbonyl carbon resonates around δ 174.00–178.50 ppm. Both of these carbon signals showed multiplet indicating their sensitivity to the compositional and configurational sequences and can be used for the assessment of the copolymerization mechanism. The methylene ($-\text{OCH}_2$) carbon of E- unit appeared as a multiplet around δ 59.0–62.0 ppm. The spectral region around δ 12.75–55.00 ppm is quite complex and overlapped, which can be assigned to the aliphatic carbons in the main and side chains of the copolymer. The extent of overlapping of various carbon signals cannot be ascertained from the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum alone. The overlapped carbon regions can be resolved by employing the DEPT-135 spectrum as shown in Figure 3. In this experiment, methylene carbon signal appear as a negative phase, while methine and methyl carbon signal appear as positive phase. The aliphatic region from δ 12.75 to 22.25 ppm can be assigned to methyl carbons of E- unit. The α - CH_3 of E- unit appeared as a multiplet around δ 16.00–22.25 ppm while the $^2\text{CH}_3$ of E- unit appeared as a multiplet around δ 12.75–14.50 ppm. The multiplet around δ 40.90–55.00 ppm can be assigned to the methylene carbons of E- and V- unit. On comparison with spectra of poly(4-vinylpyridine) and poly(ethyl methacrylate)¹⁵ (PEMA), the multiplet around δ 40.90–43.00 ppm and

around δ 46.85–55.00 ppm are assigned to methylene carbon of V- and E- unit, respectively. On comparison with PEMA, the resonance signal around δ 43.00–46.80 ppm can be assigned to quaternary carbon of E- unit. The multiplet centered around δ 40.0 ppm is assigned to methine carbon of V- unit, that can also be confirmed by DEPT-90 spectrum (Figure 4) which gives only methine carbon resonance around δ 38.25–41.25 ppm. The signal centered around δ 40.90 ppm increases in intensity with increase in the concentration of V- unit, can be assigned to VVV triad. On the similar basis, the signal centered around δ 40.50 ppm and δ 40.20–38.25 ppm can be assigned to VVE and EVE triads, respectively. In 2D-HSQC spectrum of methine region of V- unit as shown in Figure 5c, the cross peaks around δ 40.35/1.85, δ 40.50/2.18, and δ 38.70/2.40 ppm ($^{13}\text{C}/^1\text{H}$) are assigned to VVV, VVE, and EVE triads, respectively.

The α -methyl carbon of E- unit appeared as a multiplet around δ 16.00–22.25 ppm as shown in Figure 6a, indicating its sensitivity to the compositional and configurational sequences. This multiplet consists of three envelopes. The envelope centered around δ 16.00–18.00 ppm increases in intensity as the concentration of E- unit in the copolymer increases, can be assigned to EEE triad. The envelope centered around δ 20.00–22.25 ppm decreases in intensity with the increase in concentration of E- unit and can be assigned to VEV triad, while the central envelope around δ 18.00–20.00 ppm can be assigned to EEV triad. The further splitting

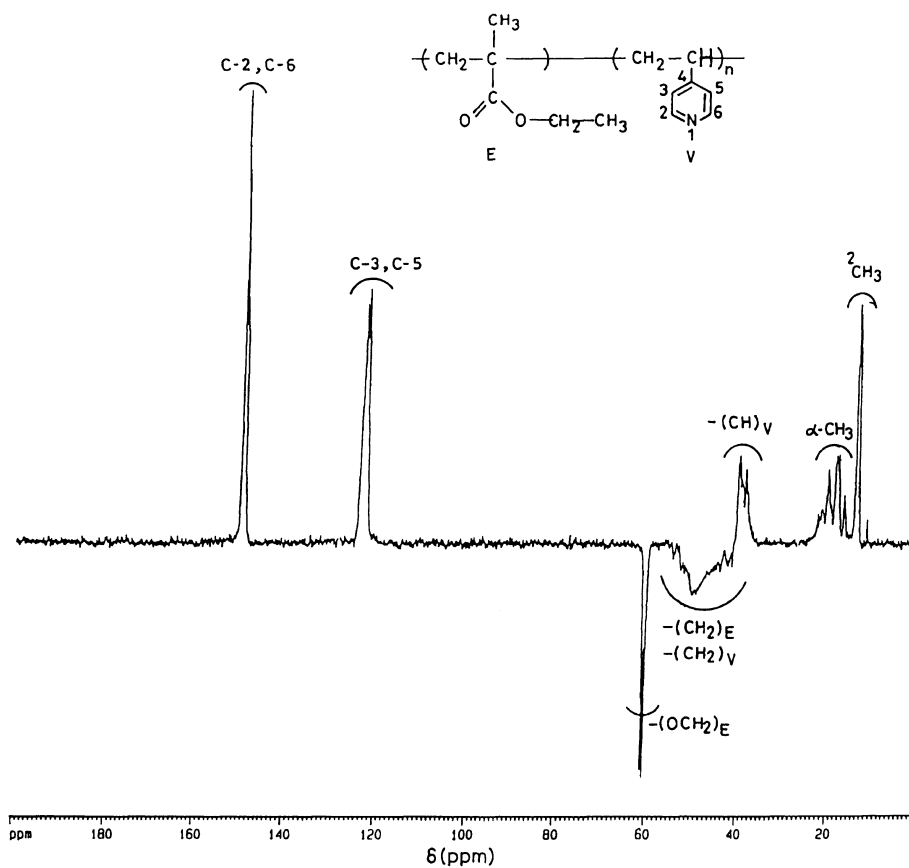


Figure 3. The DEPT-135 spectrum of V/E copolymer ($F_V=0.44$) in CDCl_3 .

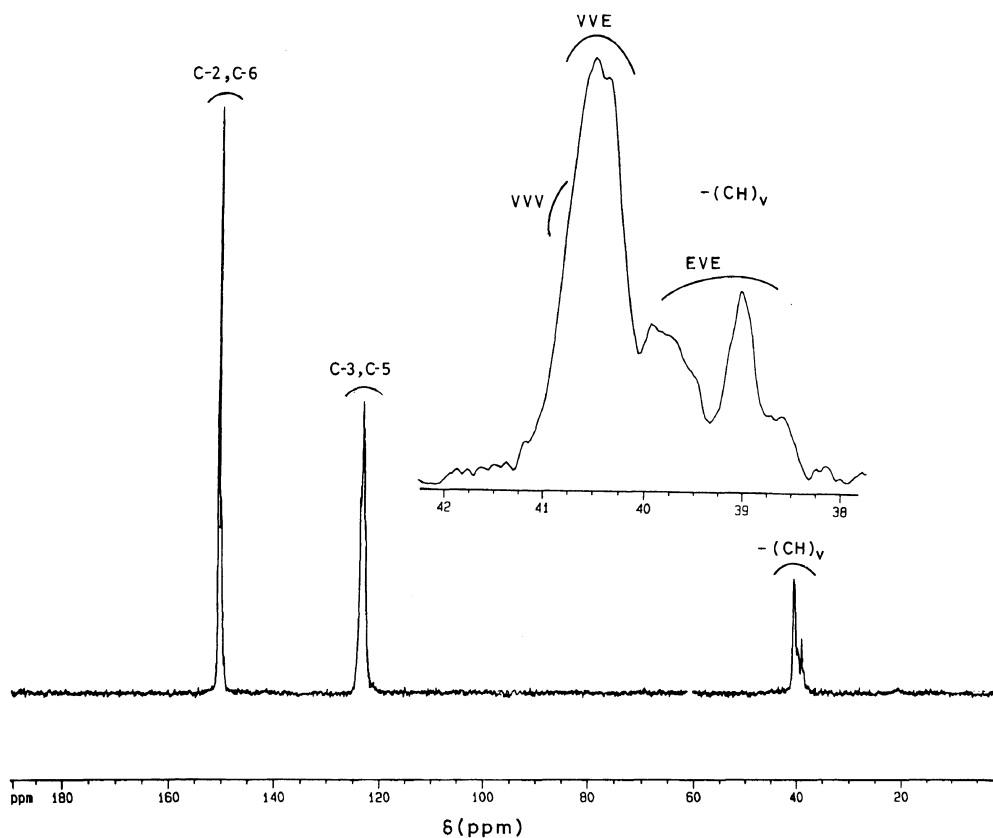


Figure 4. DEPT-90 spectrum of V/E copolymer ($F_V=0.44$) in CDCl_3 along with expanded methine region of V-unit.

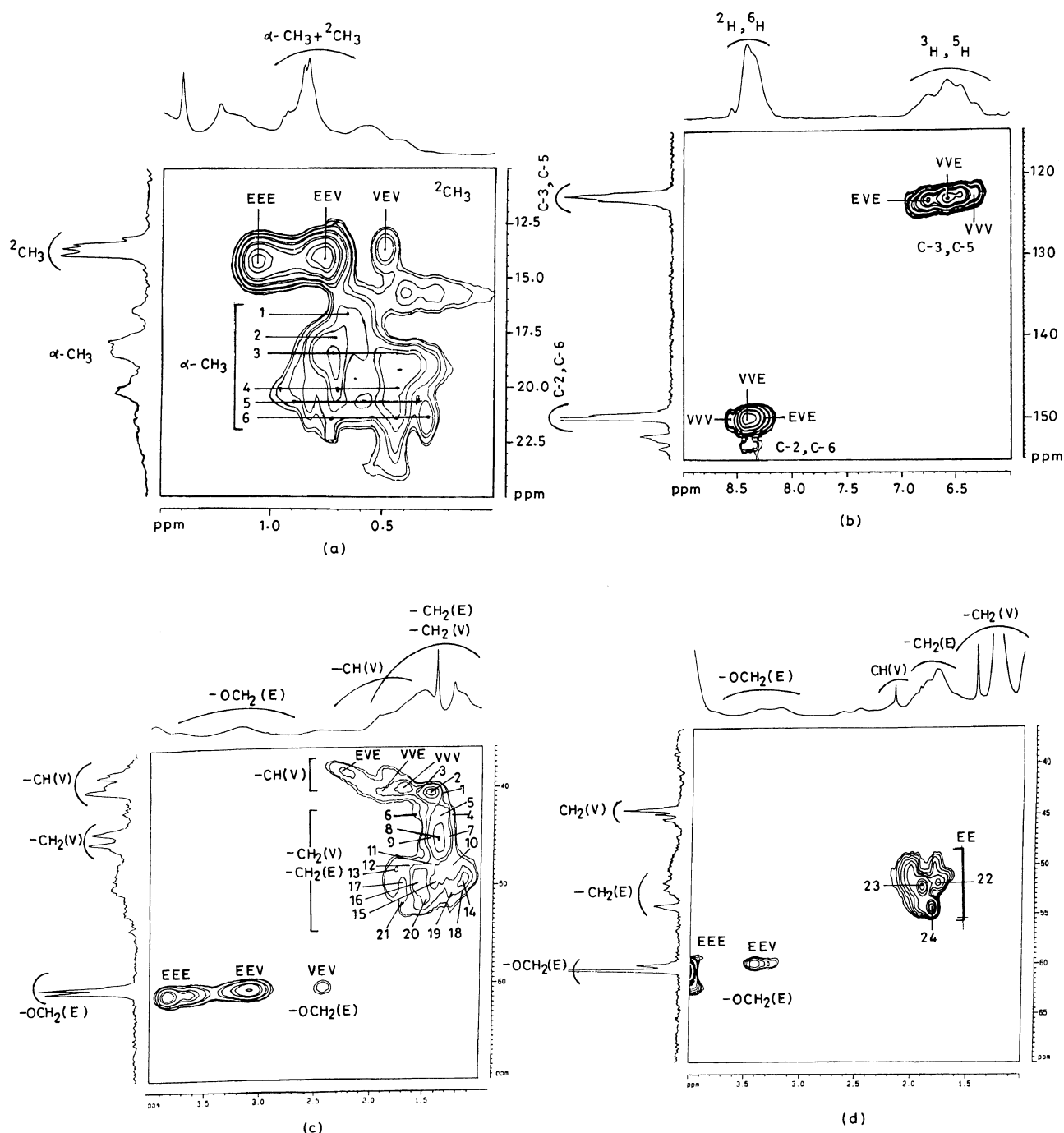


Figure 5. The 2D HSQC NMR spectrum of V/E copolymer ($F_V=0.44$) in CDCl_3 showing expanded $\alpha\text{-CH}_3$ region (a), $^2\text{CH}_3$ region (b), $-\text{OCH}_2$ region (c), expanded aromatic carbon (C-2 and C-6) region (d) and aromatic quaternary carbon region (e).

within these triads sequence indicates their sensitivity to higher compositional and configurational sequences as their intensities vary with the change in copolymer composition. The EEE triad sequence shows further splitting into three configurational sequences. On comparison with $\alpha\text{-CH}_3$ region (δ 16.0–19.0 ppm) in spectra of PEMA, the resonance signals around δ 16.50 and δ 17.75 ppm are assigned to ErErE and ErEmE triad sequences respectively. The fraction of EmEmE triad is negligible in comparison to above two triads. The further broadness within each resonance signal is due to higher order configurational sequences. The resonance signals around δ 18.35, δ 19.85, δ 20.45, and δ 21.50 ppm can

be assigned to ErErV, ErEmV, VrErV, and VrEmV triads respectively. The fraction of EmEmV and VmEmV are negligible in comparison to other triads as in case of homopolymers. The 2D -HSQC spectrum (Figure 5a) of α -methyl region also confirms that it can be assigned upto triad level. The three cross peaks centered around δ 16.00–18.00/0.45–0.75, δ 18.00–20.00/0.42–0.88, and δ 20.00–22.25/0.25–0.85 ppm are assigned to EEE, EEV, and VEV triads. All VEV and EEV centered triads show further splitting into three set of peaks, due to the presence of three protons of methyl group in different environment. This may be due to the hindrance to rotation of methyl group due to the presence of aromatic

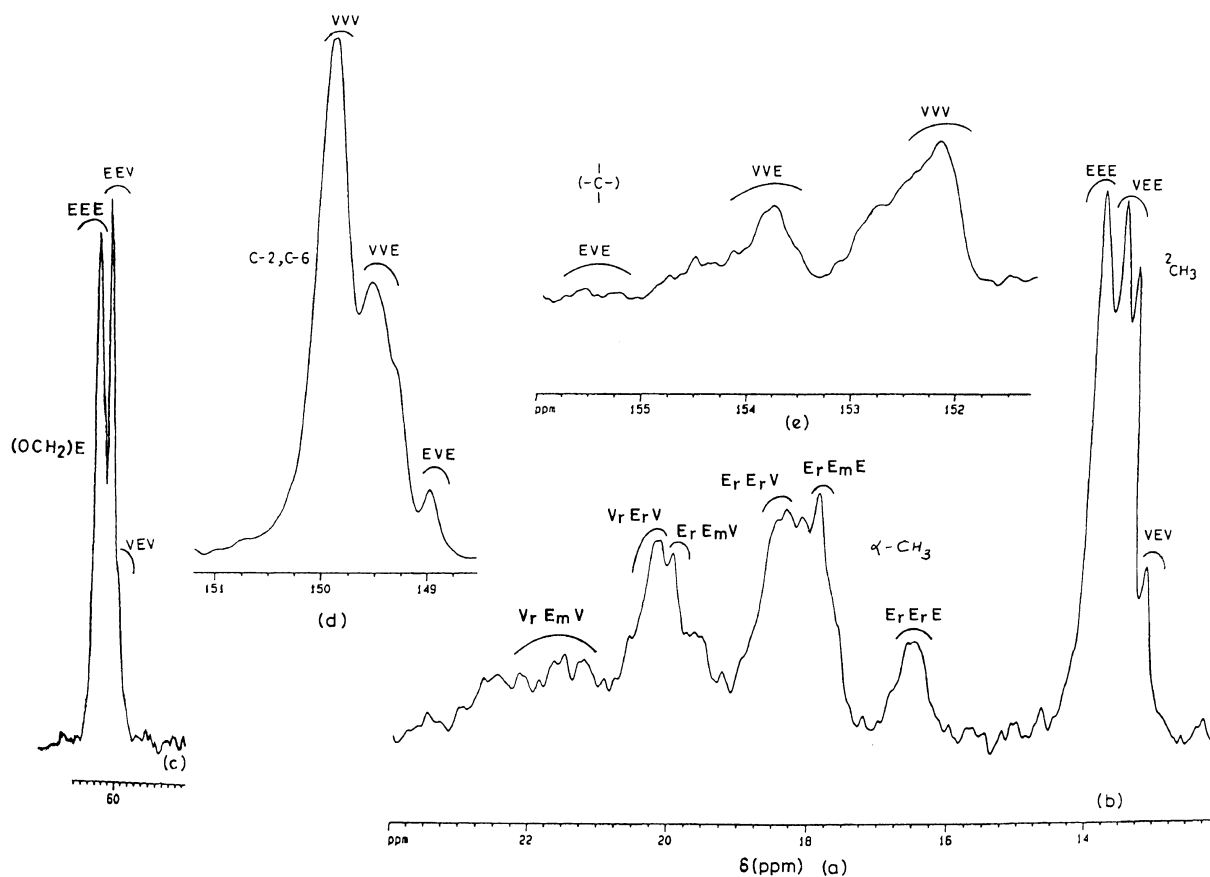


Figure 6. Expanded $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\alpha\text{-CH}_3$ (a), $^2\text{CH}_3$ (b), OCH_2 (c), carbon region of E-unit and C-2 and C-6 carbon of aromatic ring (d), and C-4 carbon of ring (e) of V-unit.

ring in these triads. The EEE centered triad does not show further splitting because there is no hindrance to rotation of methyl group due to the absence of aromatic ring hence three protons of methyl group appeared at the same position in different triads. The two sets of cross peaks in EEE triad around δ 16.50/0.62 (1) and δ 17.75/0.70 (2) ppm are assigned to ErErE and ErEmE triads respectively. The three cross peaks corresponding to same chemical shift of carbon but different chemical shift of protons, *i. e.*, around δ 18.35/0.40, δ 18.35/0.69, and δ 18.35/0.88 (3) ppm are assigned to three unequivalent protons present in $\alpha\text{-CH}_3$ group in ErErV triad and cross peaks around δ 19.85/0.42, δ 19.85/0.69, and δ 19.85/0.92 (4) ppm are assigned to three unequivalent protons in $\alpha\text{-CH}_3$ group in ErEmV triad. Similarly in VEV triad, the cross peaks around δ 20.45/0.32, δ 20.45/0.56, δ 20.45/0.92 (5) ppm, and δ 21.50/0.29, δ 21.50/0.43, δ 21.50/0.72 (6) ppm are assigned to three unequivalent protons in VrErV and VrEmV triads respectively. The spectral assignment based upon 1D $^{13}\text{C}\{^1\text{H}\}$ NMR and 2D-HSQC spectra of α -methyl region upto various triad level is given in Table II.

The $^2\text{CH}_3$ of the side chain appeared as a multiplet around δ 12.75–14.50 ppm indicating its sensitivity to the compositional sequences as shown in Figure 6b. On the basis of the variation in the intensity of these signals with the copolymer composition, the signal around δ 12.75–13.30 ppm is assigned to VEV triad while the signals around δ 13.30–13.70 and δ 13.70–14.50 ppm are assigned to EEV and EEE triads respectively. The split-

Table II. The spectral assignment of $\alpha\text{-CH}_3$ region based upon 1D $^{13}\text{C}\{^1\text{H}\}$ NMR and 2D-HSQC spectra

Peak number	Peak assignment	Through 1D	Through 2D-
		$^{13}\text{C}\{^1\text{H}\}$ NMR ppm	HSQC ppm
1	ErErE	16.50	16.50/0.62
2	ErEmE	17.75	17.75/0.70
3	ErErV	18.35	18.35/0.40–0.88
4	ErEmV	19.85	19.85/0.42–0.92
5	VrErV	20.45	20.45/0.32–0.92
6	VrEmV	21.50	21.500/0.29–0.72

ting of $^2\text{CH}_3$ resonance signal up to triad level is confirmed by HSQC spectrum (Figure 5a) also. The three cross peaks around δ 14.35/1.05, δ 14.00/0.75, and δ 13.75/0.48 ppm can be assigned to EEE, EEV, and VEV triads respectively.

The methylene carbon due to its symmetry, is sensitive to diad, tetrad, hexad etc. compositional sequences. The methylene region is quite complex and overlapped in both proton and Carbon-13 NMR spectra and can be resolved and assigned with the help of 2D HSQC spectra as shown in Figure 5c. The methylene resonance signal of E- and V- unit can be divided into three envelopes of diads EE, EV/VE, and VV in the region around δ 39.00–47.00/1.20–1.59, δ 47.50–51.50/1.00–1.90, and δ 51.50–55.00/1.75–1.95 ppm respectively, on the basis of the change in the intensity of these signal with copolymer composition. All VV centered tetrads show

the further splitting into three different sets of peaks due to the non equivalence of the protons in $-\text{CH}_2$ group of V- in meso and racemo configuration. The cross peaks around δ 40.75/1.32 (1) and δ 40.75/1.59 (3) ppm are assigned to VVmVV (H_a) and VVmVV (H_b) tetrad respectively, which is due to the deshielding of H_b proton in meso configuration while both protons in VVrVV tetrad appeared at the same position, *i. e.*, around δ 40.75/1.45 (2) ppm due to the presence of both protons in same magnetic environment. Similarly the cross peaks around δ 43.00/1.22 (4), δ 44.00/1.60 (6), δ 43.00/1.32 (5) ppm are assigned to protons in VVmVE (H_a), VVmVE (H_b), and VVrVE (H_a & H_b protons) respectively. The cross peaks around δ 45.30/1.25 (7), δ 45.30/1.49 (9) and δ 45.30/1.38 (8) ppm are assigned to EVmVE (H_a), EVmVE (H_b), and EVrVE (H_a & H_b) proton respectively. All VE centered tetrads show further splitting into four set of peaks due to the presence of H_a and H_b in non equivalent environment in meso and racemo configurations. The cross peaks around δ 48.25/1.28 (10), δ 48.25/1.79 (13) ppm are assigned to VVmEV (H_a) and VVmEV (H_b) respectively. The cross peaks around δ 48.25/1.46 (11) and δ 48.25/1.65 (12) ppm are assigned to VVrEV (H_a) and VVrEV (H_b) tetrads respectively. This is because H_a and H_b protons in racemo configuration are deshielded in comparison to H_a and H_b protons in meso configuration and hence H_a and H_b protons in racemic configuration appeared in between the position of H_a and H_b in meso configuration. Similarly the cross peaks around δ 49.85/1.18 (14) and δ 48.95/1.70 (17) ppm are assigned to VVmEE (H_a) and VVmEV (H_b) while the cross peaks around δ 49.85/1.41 (15) and δ 49.85/1.58 (16) ppm are assigned to VVrEE (H_a) and VVrEE (H_b) respectively. In EVEE tetrads, EVmEE (H_a), and EVmEE (H_b) are assigned to δ 51.00/1.12 (18) and δ 51.50/1.70 (21) ppm and EVrEE (H_a) and EVrEE (H_b) are assigned to δ 51.00/1.28 (19) and δ 51.50/1.49 (20) ppm respectively. The EE centered tetrads does not show further splitting into three or four set of peaks, because the concentration of mm triad in PEMA is negligible hence two protons in methylene group appeared at the same position. The three cross peaks in EE centered tetrads around δ 52.00/1.78 (22), δ 52.50/1.92 (23), and δ 54.50/1.81 (24) ppm are assigned to VEEV, EEEV+VEEE, and EEEE tetrads respectively as shown in Figure 5d. The assignment of various peaks in $-\text{CH}_2$ region of V- and E- unit in V/E copolymer upto tetrad level with the help of 2D-HSQC spectra is given in Table III. The $-\text{OCH}_2$ of E- unit appeared as a multiplet around δ 59.5–61.5 ppm as shown in Figure 6c. On the basis of variation in intensity of these signals with copolymers composition, the peak centered around δ 61.0 ppm is assigned to EEE triad while the peaks around δ 60.6 and δ 60.4 ppm are assigned to EEV and VEV triads respectively. The 2D-HSQC spectrum (Figure 5c) shows three cross peaks around δ 60.90/3.82, δ 60.75/3.08, and δ 60.50/2.42 ppm, can be assigned to EEE, EEV, and VEV triads respectively, on the basis of variation in intensity of these cross peaks with copolymer composition.

The aromatic carbon (C-3, C-5) appeared as a multiplet around δ 121.65–124.50 ppm. The signal around δ 122.20 ppm decreases in intensity with decrease in concentration of V- unit, can be assigned to VVV triad

Table III. The spectral assignment of $-\text{CH}_2$ region of E- and V- unit in V/E Copolymer based upon 2D-HSQC spectra

Peak number	Peak assignment	Peak position/ppm
1	VVmVV (H_a)	40.75/1.32
2	VVrVV (H_a & H_b)	40.75/1.45
3	VVmVV (H_b)	40.75/1.59
4	VVmVE (H_a)	43.00/1.22
5	VVrVE (H_a & H_b)	43.00/1.32
6	VVmVE (H_b)	43.00/1.60
7	EVmVE (H_a)	45.30/1.25
8	EVrVE (H_a & H_b)	45.30/1.38
9	EVmVE (H_b)	45.30/1.49
10	VVmEV (H_a)	48.25/1.28
11	VVrEV (H_a)	48.25/1.46
12	VVrEV (H_b)	48.25/1.65
13	VVmEV (H_b)	48.25/1.79
14	VVmEE (H_a)	49.85/1.18
15	VVrEE (H_a)	49.85/1.41
16	VVrEE (H_b)	49.85/1.58
17	VVmEE (H_b)	49.85/1.70
18	EVmEE (H_a)	51.00/1.12
19	EVrEE (H_a)	51.00/1.28
20	EVrEE (H_b)	51.50/1.49
21	EVmEE (H_b)	51.50/1.70
22	VEEV	52.00/1.78
23	VEEE	52.50/1.92
24	EEEE	54.50/1.81

while the signal around δ 123.2 ppm increases in intensity with the decrease in concentration of V- unit, can be assigned to VEV triad. The central peak around δ 122.7 ppm is assigned to EVV triad. The expanded carbonyl carbon and C-3, C-5 aromatic carbon signals are shown in Figures 2a and 2b respectively. The aromatic carbon (C-2, C-6) appeared as a multiplet around δ 148.70–150.80 ppm (Figure 6d). On the similar basis of variation in intensity of resonance signal with copolymer composition, the signal around δ 150.00, δ 149.62, and δ 149.02 ppm are assigned to VVV, VVE, EVE triads respectively. The aromatic carbon (C-4) of V- unit appeared as a multiplet around δ 151.75–156.0 ppm (Figure 6e). On the similar basis of variation in intensity of resonance signals with copolymer composition, the signals around δ 152.25, δ 153.82, and δ 155.6 ppm are assigned to VVV, VVE, and EVE triads respectively. The presence of aromatic carbons in triad sequences is confirmed by HSQC spectrum (Figure 5b). The cross peaks around δ 122.5/6.35, δ 123.0/6.59, and δ 123.5/6.72 ppm in aromatic carbon region (C-3, C-5) are assigned to VVV, VVE, and EVE triads respectively, while the cross peaks around δ 150.02/8.55, δ 150.00/8.41, and δ 149.50/8.22 ppm in aromatic carbon region (C-2, C-6) are assigned to VVV, VVE, and EVE triads respectively.

In the carbonyl carbon resonance signal, *i. e.*, around δ 174.0–178.5 ppm, the signal around δ 177.0–178.5 ppm increases in intensity with the increase in concentration of E- unit in the copolymer while the signal around δ 174.0–175.5 ppm decreases in intensity. On the basis of variation in intensity of these resonance signals with copolymer composition, the resonance signal around δ 174.0–175.5, δ 175.5–177.0, and δ 177.0–178.5 ppm are assigned to VEV, EEV/VEE, and EEE triads respectively. On comparison with carbonyl carbon region of PEMA, *i. e.*, δ 178.25–175.75 ppm, the further splitting within EEE triad is assigned to higher order

Table IV. The triad concentration calculated from $^{13}\text{C}\{^1\text{H}\}$ NMR spectra and Alfrey–Mayo model For V/E copolymers

Sample	f_V	Triad concentration		
		Triads	Alfrey–Mayo model	NMR
VEM3	0.70	VVV	0.28	0.25
		VVE	0.50	0.50
		EVE	0.22	0.26
		EEE	0.07	0.09
		EEV	0.39	0.34
		VEV	0.54	0.57
VEM4	0.60	VVV	0.18	0.14
		VVE	0.49	0.56
		EVE	0.33	0.30
		EEE	0.13	0.12
		EEV	0.46	0.47
		VEV	0.41	0.41
VEM5	0.50	VVV	0.11	0.09
		VVE	0.44	0.46
		EVE	0.45	0.45
		EEE	0.20	0.22
		EEV	0.50	0.44
		VEV	0.30	0.34
VEM6	0.40	VVV	0.06	0.07
		VVE	0.37	0.41
		EVE	0.53	0.52
		EEE	0.31	0.28
		EEV	0.49	0.48
		VEV	0.20	0.24
VEM7	0.30	VVV	0.03	0.03
		EEV	0.28	0.28
		EVE	0.69	0.69
		EEE	0.43	0.46
		EEV	0.45	0.43
		VEV	0.12	0.11
VEM8	0.20	VVV	0.01	0.00
		VVE	0.19	0.16
		EVE	0.80	0.84
		EEE	0.59	0.59
		EEV	0.36	0.37
		VEV	0.05	0.04
VEM9	0.10	VVV	0.00	0.00
		VVE	0.10	0.08
		EVE	0.90	0.92
		EEE	0.78	0.79
		EEV	0.21	0.20
		VEV	0.01	0.00

configurational sequences. In PEMA, the multiplet around δ 178.25–177.0, δ 177.0–176.25 and δ 176.25–175.75 ppm are due to rr, rm, and mm triads respectively. The rm fraction of EEE triad compositional sequence appeared in EEV triad sequence region. The contribution of rm triad is calculated by considering the triad ratios in PEMA and this factor is included in triad concentration of EEE triad obtained from curve fitting in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The mm triad fraction is negligible in comparison to rr and rm triads in homopolymer so the contribution of mm triad is not included in EEE sequence. The signals around δ 176.25–175.5 and δ 174.5–175.5 ppm are not observed in homopolymer and show variation in intensity with change in copolymer composition and are assigned to EEV and VEV triads. Thus, the best suited resonance signals for the study of copolymerization mechanism are carbonyl carbon of E-unit and aromatic carbon (C-3, C-5) of V-unit. The experimental triad fractions are obtained by curve fitting of these resonance signals of $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The triad fractions thus obtained are then compared

with theoretical values obtained from Alfrey–Mayo model in Harwood's program,¹⁶ both are found to be in good agreement as given in Table IV.

2D-TOCSY Spectra Studies

In order to understand the connectivity and confirm the various couplings in the polymer chain, the TOCSY spectrum was recorded. The three bond coupling between the protons of different directly coupled groups in A/E copolymer can be clearly seen in TOCSY experiments in short mixing time (4 ms) while at longer mixing time cross peaks between the resonance of the protons from relayed coupling (AMX spin type system) through magnetization transfer are evident. The cross peak at δ 1.40/2.0 ppm (1) is due to the coupling between the protons of methylene and methine of V-unit of the main chain. The cross peak around δ 1.5/1.85 ppm (2) is due to the coupling between $-\text{CH}_2$ (E) and $-\text{CH}$ (V) unit while the cross peak around δ 1.85/2.20 ppm (3) is assigned to the coupling of $-\text{CH}$ of V-unit with $-\text{CH}$ of another V-unit. The various geminal coupling between the protons of $-\text{CH}_2$ (V), α - CH_3 (E), $^2\text{CH}_3$ (E), OCH_2 (E) are shown by the cross peaks around δ 1.25/1.40, δ 0.75/0.80, δ 1.05/1.25, and δ 3.15/3.35 ppm respectively. The coupling between the protons of OCH_2 (E) with $^2\text{CH}_3$ (E) is also possible. It appeared as a set of three cross peaks as shown in Figure 7a. On the basis of variation in intensity of these cross peaks with copolymer composition, the cross peaks around δ 4.00/1.20 (4), δ 3.40/0.95 (5), δ 3.20/0.95 (6) ppm are assigned to the coupling of $-\text{OCH}_2$ (E) in EEE, EEV, and VEV triads with $^2\text{CH}_3$ (E) protons respectively. The coupling within the aromatic protons (^2H - ^3H and ^5H - ^6H) of V-unit is also possible as shown in Figure 7b. It appeared as a multiplet around δ 8.20–8.48/6.25–6.95 ppm. This multiplet may be assigned to the coupling of aromatic protons in different configurational and compositional sequences. The assignment of various coupling in this region is carried out on the basis of variation in intensity of these signals with copolymer composition. The cross peaks around δ 6.25–6.45/8.20–8.35 ppm are assigned to the coupling of aromatic protons in VVV triads. The further splitting within this triad can be assigned to various configurational sequences on comparison with TOCSY spectrum of poly (4-vinylpyridine). The cross peaks around δ 8.20/6.28 (7), δ 8.35/6.35 (8) and δ 8.40/6.45 (9) ppm are assigned to the coupling in VrVrV, VrVmV, and VmVmV sequences respectively. The multiplet around δ 6.45–6.60/8.30–8.48 ppm and δ 6.70–6.90/8.38–8.48 ppm are assigned to the coupling in VVE and EVE triads respectively. The further splitting within these triads are assigned to higher compositional sequences, on the basis of variation in intensity of these cross peaks with copolymer composition. The cross peaks around δ 8.48/6.48 (10), δ 8.32/6.55 (11), and δ 8.45/6.60 (12) are assigned to the couplings in VVVEV, VVVEE, and EVVEE pentads while the cross peaks around δ 8.40/6.75 (13), δ 8.48/6.75 (14), and δ 8.39/6.85 (15) ppm are assigned to the coupling in VEVEV, VEVEE, and EEVEE pentads respectively. These all possible couplings are shown in Table V. Further four and five bond couplings are also possible in V/E copolymer which can be clearly seen in 80 ms TOCSY spectra.

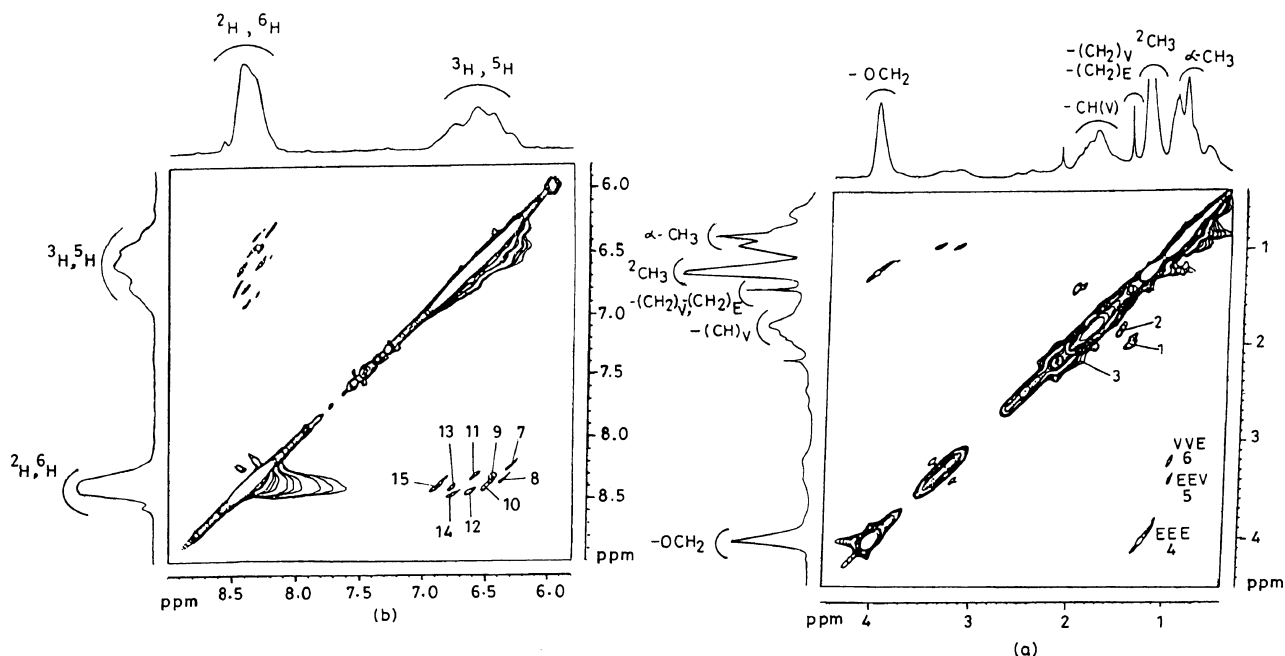


Figure 7. The 2D TOCSY NMR spectrum of V/E copolymer ($F_V=0.44$) in $CDCl_3$ showing expanded aliphatic region (a), expanded aromatic region (b).

Table V. TOCSY 1H - 1H shift correlation

Peak number	Type of proton (ppm)	Coupled to (ppm)
1	$CH_2(V)$ (1.4)	$CH(V)$ (2.0)
2	$CH_2(E)$ (1.50)	$CH(V)$ (1.85)
3	$CH(V)$ (1.85)	$CH(V)$ (2.20)
4	$OCH_2(E)$ in EEE triad (4.0)	$^2CH_3(E)$ (1.20)
5	EEV triad (3.4)	$^2CH_3(E)$ (0.95)
6	VEV triad (3.2)	$^2CH_3(E)$ (0.95)
	Aromatic 3H & 5H in	Aromatic 3H & 5H in
7	VrVrV (8.2)	VrVrV (6.25)
8	VrVmV (8.35)	VrVmV (6.32)
9	VmVmV (8.4)	VmVmV (6.4)
10	VVVEV (8.4)	VVVEV (6.48)
11	VVVEE (8.3)	VVVEE (6.55)
12	EVVEE (8.45)	EVVEE (6.59)
13	VEVEV (8.4)	VEVEV (6.75)
14	VEVEE (8.48)	VEVEE (6.75)
15	EEVEE (8.39)	EEVEE (6.85)

Due to these higher bond couplings TOCSY spectra at 80 ms is quite complex and overlapped.

CONCLUSIONS

The comonomer reactivity ratios of the copolymerization of V/E are $r_V=0.49$ and $r_E=0.83$. The overlapped and complex proton and carbon-13 spectra were well resolved with the help of DEPT-135, DEPT-90, and 2D HSQC spectra. The α -methyl carbon of E- unit were assigned upto pentad sequences. The methylene carbon of E- and V- unit were assigned upto diad and tetrad levels with help of HSQC spectra. The carbonyl and aromatic carbon signals were assigned upto triad levels. The copolymerization mechanism of V/E copolymers was found to follow the first order Markov model. The various type of couplings between different groups in V/E copolymer

were assigned by TOCSY experiments with mixing time of 4 ms.

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