

Reactivity ratios and microstructure determination of vinyl acetate–ethyl methacrylate copolymers

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Vinyl acetate–ethyl methacrylate (VAc–EMA, V/E) copolymers have been prepared by solution polymerization using benzoyl peroxide as initiator. The composition of the copolymers has been calculated using ^1H nuclear magnetic resonance (n.m.r.) spectroscopy. Comonomer reactivity ratios have been calculated from the Kelen–Tüdös method, error-in-variables method and $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra of copolymers. The triad sequence distributions in terms of V- and E-centred triads have been obtained from $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra of copolymers. Homonuclear ^1H two-dimensional (2D) COSY (correlation spectroscopy) and 2D NOESY (nuclear Overhauser enhancement correlation spectroscopy) n.m.r. spectra were recorded to find the coupling between different protons in the copolymer. The copolymerization behaviour of the V/E copolymers as a function of conversion is also reported. Copyright © 1996 Elsevier Science Ltd.

(Keywords: VAc–EMA copolymers; reactivity ratios; $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectroscopy)

INTRODUCTION

Determination of the microstructure in copolymers is of great value in establishing structure–property relationships. ^{13}C n.m.r. spectroscopy is one of the most powerful and reliable techniques for the characterization of polymer structure^{1,2}. Brar *et al.*³ reported the sequence in vinyl acetate–ethyl methacrylate (VAc–EMA, V/E) copolymers prepared by emulsion polymerization (semi-continuous batch process) using ^{13}C n.m.r. spectroscopy. They did not report the reactivity ratios because the conversion was 100%. Sengupta *et al.*⁴ have reported the reactivity ratios $r_V = -$ and $r_E = 142.0$. Greenley⁵ recalculated the values of the reactivity ratios using the data of Sengupta *et al.*⁴. The recalculated values are $r_V = 0.767$ and $r_E = 131.8$. Perusal of the literature shows that the reactivity ratios of these monomers have not been widely investigated. This may be due to the very large difference in their reactivity ratios and the errors involved in their estimation. In our earlier publications^{6,7} we have reported the triad concentrations calculated from n.m.r. and other methods, in which the values of the reactivity ratios were of equal order and the uncertainty was less. In such systems a good agreement was observed between the experimentally observed and theoretically calculated values of triad concentrations. In this paper we report the reactivity ratios of solution-polymerized vinyl acetate–ethyl methacrylate (V/E) copolymers estimated using the Kelen–Tüdös (KT) method⁸ and error-in-variables method (EVM)⁹ using the RREVM¹⁰ computer program. The reactivity ratio values thus obtained have been compared with those

determined from $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra. The triad sequence distributions in terms of V- and E-centred triads have been obtained from the $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra of copolymers. Homonuclear ^1H two-dimensional correlation spectroscopy (2D COSY) and two-dimensional nuclear Overhauser enhancement correlation spectroscopy (2D NOESY) n.m.r. spectra were recorded to find couplings between protons in the copolymer. The effect of degree of conversion on the copolymer composition will also be reported.

EXPERIMENTAL

Vinyl acetate (VAc) and ethyl methacrylate (EMA) monomers were washed successively with 10% aqueous NaOH and distilled water, dried over anhydrous Na_2SO_4 and distilled *in vacuo*. Benzoyl peroxide (BPO) recrystallized from chloroform/methanol was used as initiator.

A mixture of monomers was taken in a glass tube and 0.5% (w/w) BPO in benzene was added. The reaction was allowed to proceed at 60°C for an hour. The reaction was stopped at a conversion of less than 5% by precipitating the copolymer in excess n-hexane. A series of copolymers containing different amounts (mol %) of ethyl methacrylate (from 1.6 to 13 mol %) in the feed were prepared.

^1H n.m.r. spectra of the copolymers were recorded on JEOL FX-100 NMR spectrometer in CDCl_3 at room temperature using tetramethylsilane (TMS) as internal standard. $^{13}\text{C}\{^1\text{H}\}$ n.m.r. for all the copolymer samples were recorded on a Bruker AMX 400 MHz spectrometer in CDCl_3 at room temperature. The details of measuring the fractional peak area using a Lorentzian curve-fitting computer program have been described elsewhere^{11,12}.

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Table 1 Copolymer composition data and intrinsic viscosities of vinyl acetate–ethyl methacrylate (V/E) copolymers prepared by solution polymerization

Sample	f_V^a	f_E^a	F_V^b	F_E^b	$[\eta]$ (dl g ⁻¹)
EV1	0.87	0.13	0.19	0.81	0.35
EV2	0.93	0.07	0.32	0.68	0.36
EV3	0.95	0.05	0.49	0.51	0.35
EV4	0.97	0.03	0.62	0.38	0.41
EV5	0.98	0.02	0.80	0.20	–

^a f_V and f_E are the mole fractions of V and E comonomers, respectively, in the feed

^b F_V and F_E are the mole fractions of V and E comonomers in the copolymer, respectively, determined from ¹H n.m.r. spectroscopy

The intrinsic viscosities of the copolymers were determined at 30 ± 0.1 °C using an Ubbelohde viscometer with benzene as solvent (Table 1).

RESULTS AND DISCUSSION

N.m.r. spectroscopy

The ¹H n.m.r. spectrum of vinyl acetate–ethyl methacrylate (V/E) copolymer (V = 32 mol % in the copolymer) along with the assignment of various resonance signals is shown in Figure 1. The copolymer compositions have been calculated from the relative intensities of the –CH (V unit) and –OCH₂ (E unit) resonances using the following expression:

$$F_V = \frac{2I(-CH)_V}{2I(-CH)_V + I(-OCH_2)_E}$$

where F_V is the mole fraction of vinyl acetate in the copolymer, and $I(-CH)_V$ and $I(-OCH_2)_E$ are the intensities of the –CH (V unit) and –OCH₂ (E unit) proton resonances, respectively. Copolymer composition data (Table 1) were used to calculate the terminal model reactivity ratios by the Kelen–Tüdös (KT) method and error-in-variables method (EVM) using the RREVM computer program. In the RREVM program the percentage error in measuring the comonomer composition

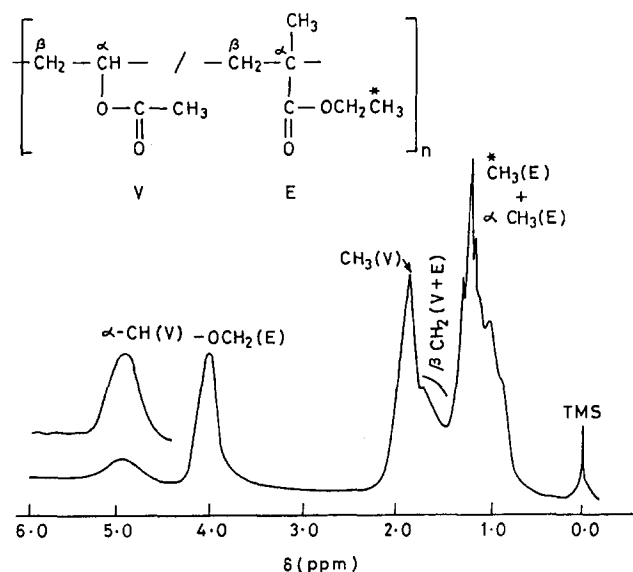


Figure 1 The 100 MHz ¹H n.m.r. spectrum of V/E copolymer (V = 32 mol % in copolymer) in CDCl₃ at room temperature

in the feed and in the copolymer was taken as 0.1 and 3% respectively. The values of reactivity ratios obtained from the KT method were used as the initial estimates of the values in the RREVM program. The reactivity ratios obtained by the KT method and RREVM program are $r_V = 0.09 \pm 0.02$, $r_E = 38.5 \pm 10.08$ and $r_V = 0.09 \pm 0.02$, $r_E = 39.24 \pm 9.48$ respectively.

A representative ¹³C{¹H} n.m.r. spectrum of V/E copolymer (V = 32 mol % in copolymer) along with the signal assignments is shown in Figure 2. The resonance signals of the carbonyl carbon of E and V monomeric units appear as multiplets in the regions $\delta = 178.15$ – 175.57 ppm and 170.40 – 169.70 ppm respectively, showing their sensitivity to compositional as well as configurational sequences. The quaternary carbon of the E unit also appears as a multiplet at around $\delta = 45.20$ – 42.50 ppm, showing its sensitivity to copolymer tacticity. Comparison of ¹³C{¹H} n.m.r. and ¹³C DEPT (distortionless enhancement by polarization transfer) n.m.r. spectra of a copolymer (V = 49 mol % in the copolymer) (Figures 3a and 3b) in the region $\delta = 54.50$ – 39.00 ppm shows that the quaternary carbon resonance signal in V/E copolymer is overlapped by one of the methylene carbon resonance signals of the E unit. After subtracting the contribution of the overlapping methylene carbon resonance signal, the E-centred triad distribution was calculated from the quaternary carbon resonance of the E unit. The quaternary carbon resonance of the E unit along with the carbonyl carbon resonances of the E as well as V units have been used to obtain information about the microstructure of the V/E copolymer. The expansion of the carbonyl carbon resonance in PEMA along with signal assignment to pentad level is shown in Figure 4. The expanded carbonyl carbon resonance of the E monomeric unit in V/E copolymer is shown in Figure 5a. Resonance signals in the region $\delta = 178.15$ – 175.57 ppm have been assigned by observing compositional variation in the intensity of the resonance signals as well as by comparison with the ¹³C{¹H} n.m.r. spectrum of PEMA. The intensity of the resonance signals around $\delta = 178.15$ – 177.38 ppm decreases with the decrease in concentration of the E unit in the copolymer and were assigned as EEE triad sequences. The region shows compositional as well as configurational sensitivity. The signal at $\delta = 177.54$ ppm decreases in intensity while the signals at $\delta = 177.70$ and 177.88 ppm increase in intensity with decrease in concentration of the E unit in the copolymer. The composition effect is highly pronounced for signals at $\delta = 177.70$ and 177.54 ppm. By comparison of the signals of this region ($\delta = 178.15$ – 177.38 ppm) and those of the *mrrm*, *mrrr* and *rrrr* pentad sequences of the carbonyl carbon of PEMA, the signals at $\delta = 178.11$, 177.88 and 177.54 ppm may be assigned to *mrrm*, *mrrr* and *rrrr* pentad sequences. The additional signals at $\delta = 177.96$ and 177.70 ppm, which are not observed in the homopolymer and show variation in intensity with change in copolymer composition, are assigned as EEEEEV and VEEEEV sequences.

The resonance signal at $\delta = 175.90$ ppm, which increases in intensity with decrease in concentration of E unit in the copolymer, was assigned to VEV triad sequences. Comparison with the ¹³C{¹H} n.m.r. spectrum of PEMA shows that the resonance signals due to the $E_m E_m E$ triad sequences appear in the region $\delta = 176.40$ – 175.80 ppm. The contribution of $E_m E_m E$ triad sequences

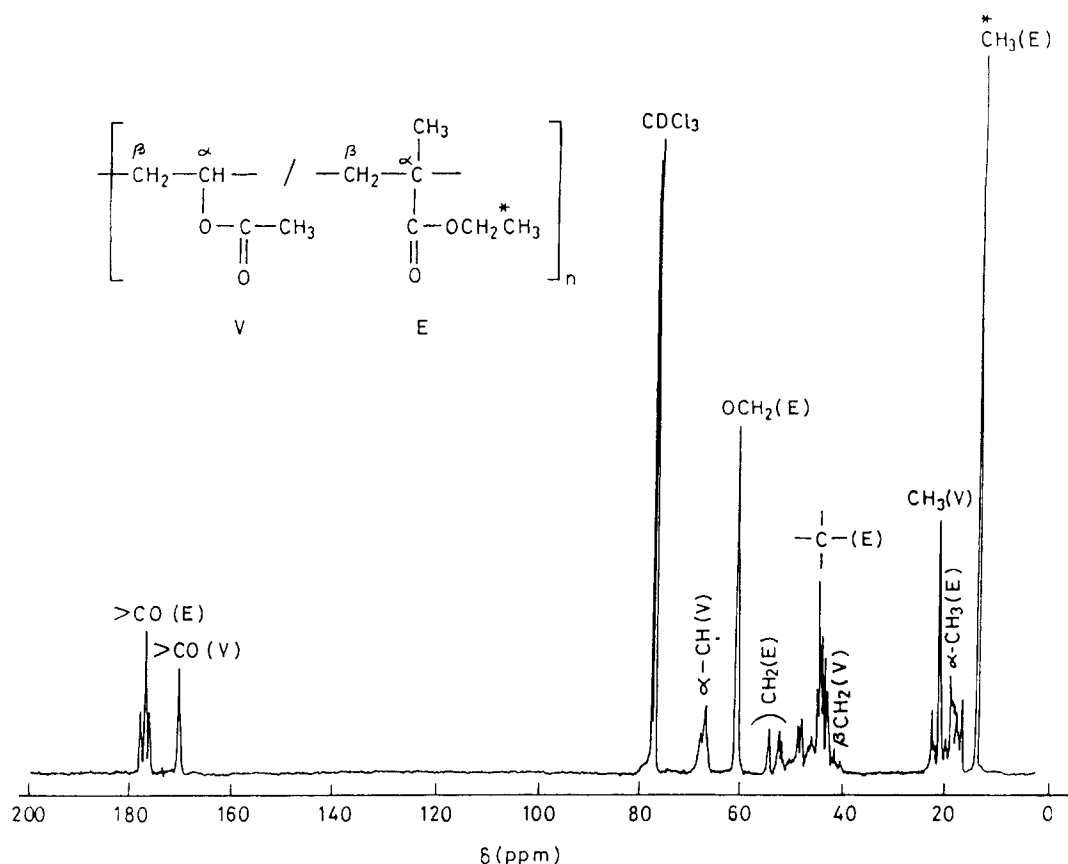


Figure 2 The 100 MHz $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum of V/E copolymer ($V = 32\text{ mol}\%$ in copolymer) in CDCl_3 at room temperature

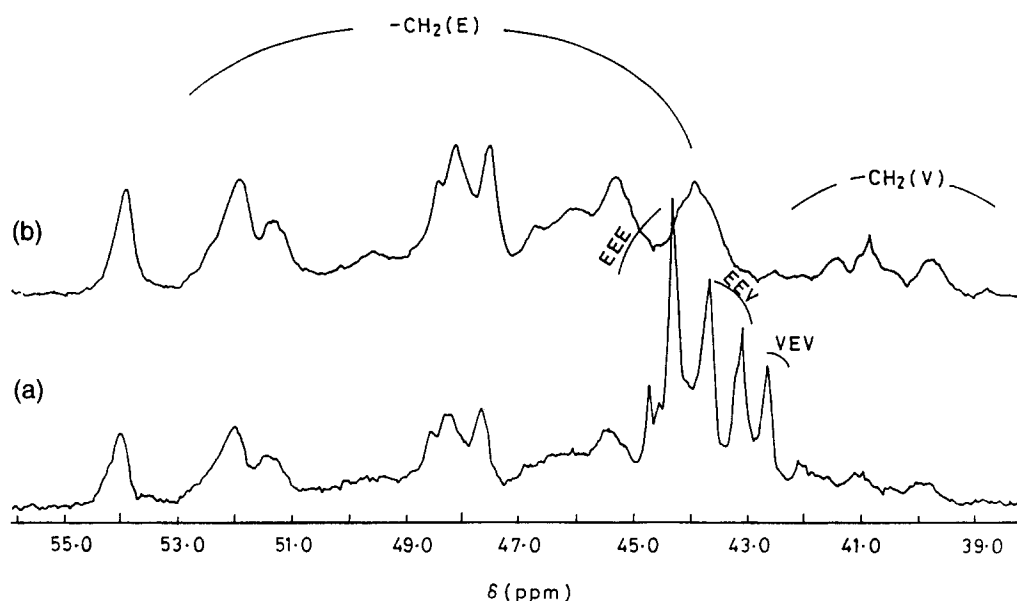


Figure 3 Comparison of (a) $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum and (b) ^{13}C DEPT n.m.r. spectrum of V/E copolymer ($V = 49\text{ mol}\%$ in copolymer) in the region $\delta = 54.5\text{--}39.0$ ppm to find the overlapping methylene resonance signal of the E unit with the quaternary carbon resonance of the same unit

to the intensity of the resonance signal at 175.90 ppm has been neglected on the basis that the fraction of $E_m E_m E$ triads in PEMA is negligible.

The resonance signals at $\delta = 176.92$, 176.68, 176.54 and 176.15 ppm are assigned to EEV sequences. Signals at $\delta = 176.92$ and 176.54 ppm are observed only in copolymers with higher E-unit content. These signals are therefore due to compositional sensitivity of EEV triad

sequences. The $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum of PEMA shows that $E_m E_r E$ configurational sequences resonate in the region $\delta = 177.10\text{--}176.40$ ppm and they contribute to the intensity of resonance signals due to EEV triads in V/E copolymer. It is found that 50% of EEE triad fractions overlap EEV triad sequences. The relative fractions of various triads (EEE, EEV, VEV) were obtained from resonance signal area measurements.

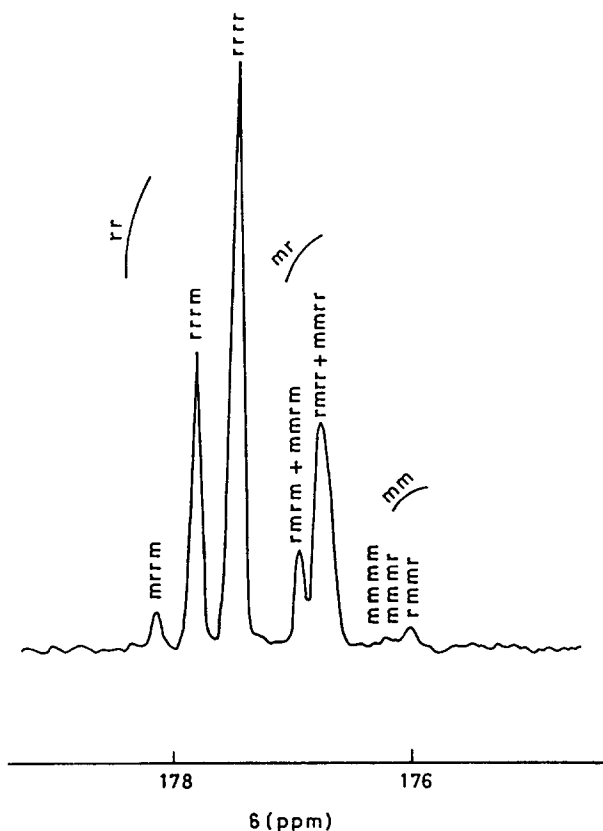


Figure 4 Expanded carbonyl carbon resonance signal of PEMA recorded in $CDCl_3$ at room temperature

The expanded carbonyl carbon resonance of the V monomeric unit in V/E copolymer is shown in Figure 5b. It is observed that signals centred at $\delta = 170.30$ – 170.40 ppm increase in intensity while those centred around $\delta = 169.70$ – 169.98 ppm decrease in intensity as the concentration of V unit in the copolymer increases. The resonance signals have been assigned to the carbonyl carbon of the central V unit of VVV ($\delta = 170.30$ – 170.40 ppm), VVE ($\delta = 170.05$ – 170.15 ppm) and EVE ($\delta = 169.70$ – 169.98 ppm) triad sequences from low to high field, by comparison with the $^{13}C\{^1H\}$ n.m.r. spectrum of PVAc and by observing the compositional variation in the intensities of the resonance signals. An attempt has been made to determine the relative abundance of V-centred triads (VVV, EVV/VVE, EVE) from signal area measurements under corresponding triads.

The expanded quaternary carbon resonance of the E-monomeric units in V/E copolymer is shown in Figure 5c. As the concentration of the E monomeric unit in the copolymer decreases, the intensity of the signal at $\delta = 43.07$ ppm increases whilst that of the signals in the region $\delta = 45.20$ – 44.65 ppm decreases. The signals in the region $\delta = 45.20$ – 44.65 ppm have been assigned to EEE triad sequences by comparison with PEMA. The signals in the region $\delta = 43.20$ – 44.65 ppm and at $\delta = 43.07$ ppm have been assigned to EEV and VEV triad sequences respectively. The relative fractions of EEE, EEV and VEV triad sequences were obtained from resonance signal area measurements by subtracting the contribution of the overlapping methylene carbon resonance signal of the E unit. The relative fractions of E-centred triads thus obtained were found to be in good

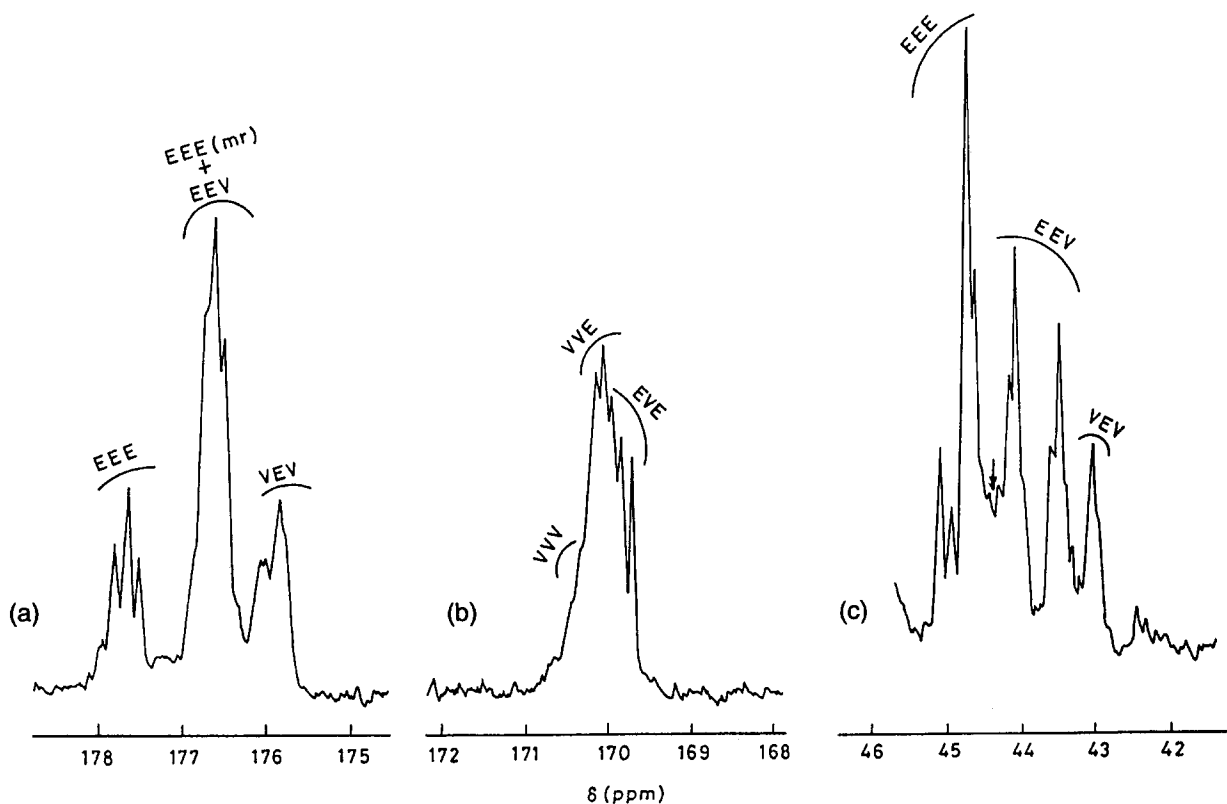


Figure 5 (a) Expanded carbonyl carbon resonance spectrum of the E unit. (b) Expanded carbonyl carbon resonance spectrum of the V unit. (c) Expanded quaternary carbon resonance spectrum of the E unit in V/E copolymer (V = 32 mol % in the copolymer). The contribution of one of the methylene signals of the E unit to the quaternary carbon resonance has been subtracted from the region marked by the arrow in the spectra

agreement with those determined using carbonyl carbon resonance signals and are given in Table 2.

The conditional probabilities P_{VE} and P_{EV} have been calculated by using the following equations:

$$P_{VE} = \frac{[EVE] + [EVV]/2}{[EVE] + [EVV] + [VVV]}$$

$$P_{EV} = \frac{[VEV] + [EEV]/2}{[VEV] + [EEV] + [EEE]}$$

where P_{VE} is the probability that a V-E unit comes about as a result of a V-growing chain end adding E, and P_{EV} is the probability that an E-V unit comes about as a result of an E-growing chain end adding V. The parameters in square brackets are the fractions of various triads determined by $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra. The terminal model reactivity ratios r_V and r_E have been calculated using the following equations:

$$r_V = \frac{f_E}{f_V} (1/P_{VE} - 1)$$

$$r_E = \frac{f_V}{f_E} (1/P_{EV} - 1)$$

where f_E and f_V are mole fractions of ethyl methacrylate and vinyl acetate in the feed, respectively. Reactivity

Table 2 Calculated and observed fractions of V- and E-centred triads in vinyl acetate-ethyl methacrylate (V/E) copolymers

V (mole fraction) in copolymer	Triad	Triad fractions ^a		Calc. (c)
		Obs.		
		(a)	(b)	
0.19	EEE	0.51	0.50	0.56
	EEV	0.42	0.47	0.38
	VEV	0.07	0.03	0.06
	VVV	0.06	-	0.08
	EVV	0.46	-	0.41
	EVE	0.48	-	0.51
0.32	EEE	0.36	0.38	0.38
	EEV	0.50	0.52	0.47
	VEV	0.14	0.10	0.15
	VVV	0.19	-	0.18
	EVV	0.46	-	0.49
	EVE	0.35	-	0.33
0.49	EEE	0.22	0.29	0.26
	EEV	0.53	0.57	0.50
	VEV	0.25	0.14	0.24
	VVV	0.27	-	0.28
	EVV	0.54	-	0.50
	EVE	0.19	-	0.22
0.62	EEE	0.13	0.21	0.15
	EEV	0.50	0.44	0.47
	VEV	0.37	0.35	0.38
	VVV	0.46	-	0.44
	EVV	0.43	-	0.45
	EVE	0.11	-	0.11
0.80	EEE	0.05	0.04	0.06
	EEV	0.39	0.46	0.37
	VEV	0.56	0.50	0.57
	VVV	0.64	-	0.62
	VVE	0.29	-	0.34
	EVE	0.07	-	0.05

^a Triad functions determined from observed ^{13}C n.m.r. spectra of copolymers using (a) carbonyl carbon resonance signal or (b) quaternary carbon resonance signal; or (c) from Harwood's¹⁴ terminal model program using $r_V = 0.06$ and $r_E = 20.0$

ratios r_V and r_E calculated using the above equations along with other copolymerization parameters of vinyl acetate-ethyl methacrylate (V/E) copolymers for different feed ratios are given in Table 3. The curves in Figure 6 describe the copolymer composition for reactivity ratios obtained by EVM, KT method and the use of $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectroscopy. It is well known that the uncertainties in the values of reactivity ratios are large when the values of r_1 and r_2 are very different¹³. Therefore there is a large error in the triad concentrations calculated using reactivity ratios estimated by the different methods. The observed fractions of V- and E-centred triads from $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra of copolymers are in good agreement with the values obtained using $r_V = 0.06$ and $r_E = 20.00$ in Harwood's¹⁴ terminal model program.

Table 3 Copolymerization parameters of vinyl acetate-ethyl methacrylate (V/E) copolymer determined by ^{13}C n.m.r. spectroscopy

Sample	V (mole fraction in copolymer)	P_{VE}^a	P_{EV}^b	r_V^c	r_E^c	\bar{N}_V^d	\bar{N}_E^d
EV1	0.19	0.71	0.28	0.06	17.21	1.41	3.57
EV2	0.32	0.58	0.39	0.06	19.29	1.72	2.56
EV3	0.49	0.46	0.49	0.06	19.78	2.04	2.17
EV4	0.62	0.33	0.62	0.06	19.82	3.03	1.61
EV5	0.80	0.22	0.76	0.06	23.92	4.55	1.32
Average				0.06	20.00		

^a P_{VE} = probability of addition of monomeric unit E to a growing chain ending in V

^b P_{EV} = probability of addition of monomeric unit V to a growing chain ending in E

^c Reactivity ratios

^d \bar{N}_V and \bar{N}_E are number-average sequence lengths of V and E units respectively

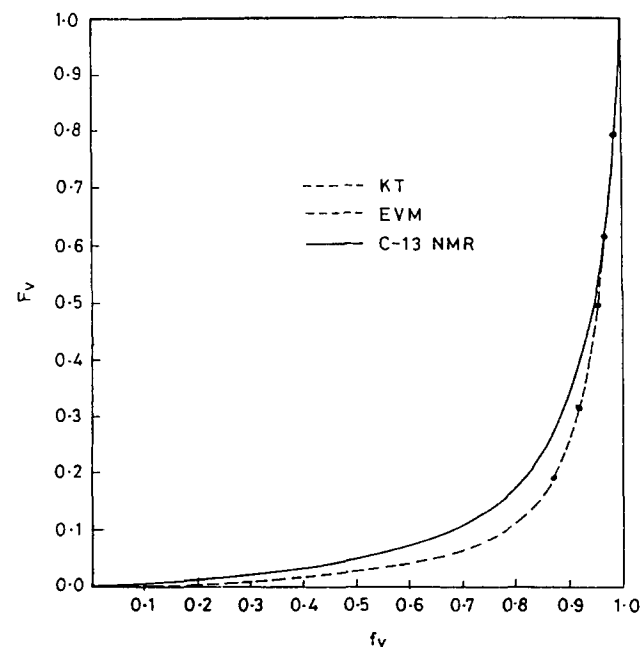


Figure 6 The theoretical composition curves obtained from the copolymer equation using reactivity ratios from EVM, KT method and ^{13}C n.m.r. spectroscopy along with experiment points (●). The curves from KT method and EVM are overlapping

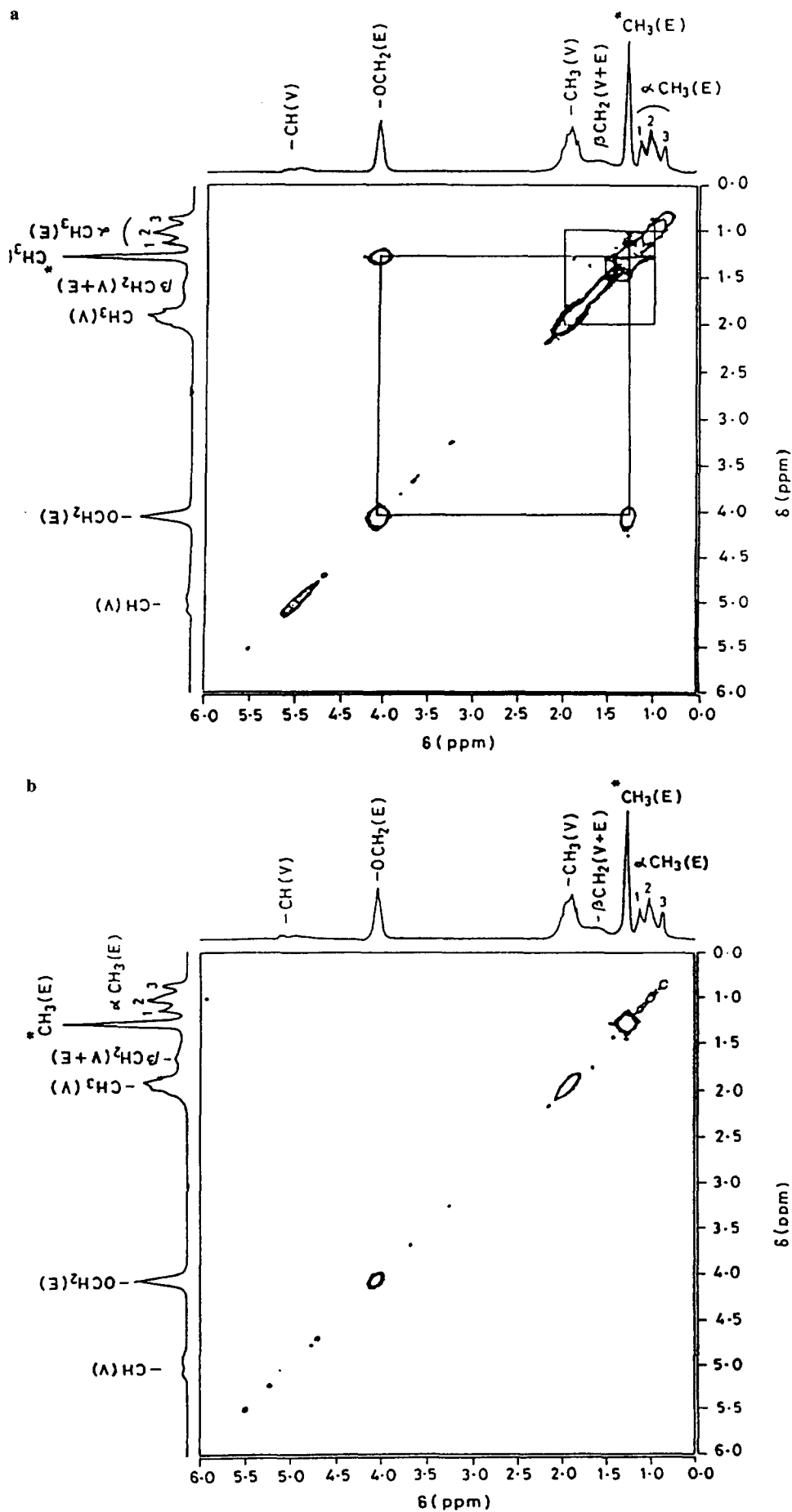


Figure 7 (a) The 300 MHz ^1H n.m.r. 2D COSY spectrum and (b) the 300 MHz ^1H n.m.r. 2D NOESY spectrum of V/E copolymer (V = 32 mol % in copolymer) recorded at room temperature in CDCl_3

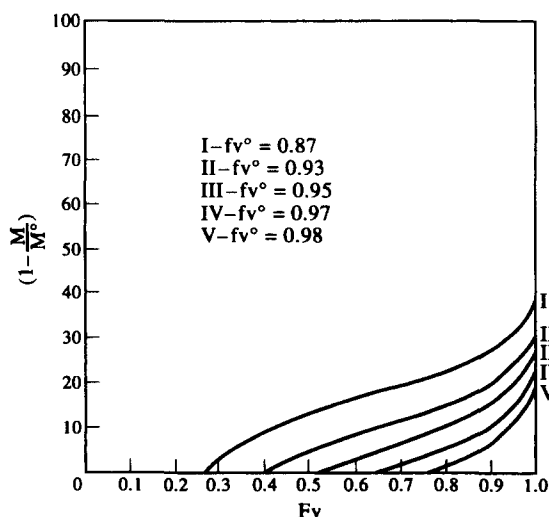


Figure 8 Mole per cent conversion-copolymer composition curve with initial feed in composition $f_V = 0.87$ (I), 0.93 (II), 0.95 (III), 0.97 (IV) and 0.98 (V) in V/E copolymer

Two-dimensional n.m.r.

Homonuclear ^1H 2D COSY n.m.r. and 2D NOESY n.m.r. spectra (Figures 7a and 7b) ($V = 49$ mol% in copolymer) were recorded to find the couplings in the V/E copolymer. It is seen from COSY that $-\text{OCH}_2(\text{E})$ is coupled to $^*\text{CH}_3(\text{E})$; $\beta\text{-CH}_2(\text{E})$ is also coupled to $^*\text{CH}_3(\text{E})$. Peak 2 of $\alpha\text{-CH}_3(\text{E})$ is coupled to $^*\text{CH}_3(\text{E})$ as well as $\text{CH}_3(\text{V})$. It is also linked to signal 1 and signal 3 of $\alpha\text{-CH}_3(\text{E})$. NOESY shows that no space coupling is present in the V/E copolymer.

Copolymerization behaviour

The reactivity ratios $r_V = 0.06$ and $r_E = 20.0$ were used to study the copolymerization behaviour of V/E copolymerization. Using the Meyer-Lowry equation¹⁵ in conjunction with the instantaneous composition equation¹⁶, the molar percentage conversion ($1 - M/M_0$) was obtained as a function of copolymer composition for different feed compositions. The molar percentage

conversion-copolymer composition curves (Figure 8) obtained are typical of such systems with very large difference in comonomer reactivity. With increasing vinyl acetate in the feed composition, a drift from homogeneity is observed as the degree of copolymer conversion increases.

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