

Sequence Determination of Vinyl Acetate–Methyl Acrylate Copolymers by NMR Spectroscopy

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SYNOPSIS

Vinyl acetate/methyl acrylate (V/M) copolymers were prepared by free-radical solution polymerization in benzene. Copolymer compositions were obtained from ^1H -NMR spectroscopy. Reactivity ratios for the copolymerization of V with M were calculated using the Kelen–Tudos (KT) and the nonlinear error in variables (EVM) methods. The reactivity ratios obtained from the KT and EV methods are $r_V = 0.04 \pm 0.03$ and $r_M = 7.28 \pm 2.88$ and $r_V = 0.04 \pm 0.01$ and $r_M = 7.28 \pm 0.37$, respectively. The microstructure was obtained in terms of the distribution of V- and M-centered triad sequences from $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of copolymers. Homonuclear ^1H -2D-COSY and 2D-NOESY NMR were used to determine the most probable conformer for the V/M copolymer. The copolymerization behavior of the V/M copolymers as a function of conversion is also reported. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

^{13}C -NMR spectroscopy is one of the most powerful and reliable techniques for the characterization of the polymer structure.^{1,2} The microstructure of vinyl acetate/methyl acrylate (V/M) has not been reported in detail. Florjanczyk et al.³ investigated the comonomer sequence in V/M copolymers prepared using ethylaluminum chloride catalysts. They assigned the M-centered triads but did not determine the triad sequences quantitatively. In this article, we report the comonomer sequence distribution in terms of various V- and M-centered triads using methine resonance signals of V- as well as M-monomeric units. The resonance signals due to the methine carbon of the M-monomeric unit and the methylene carbons of the V-monomeric unit were differentiated using the ^{13}C -NMR DEPT technique. This technique was not earlier used by Florjanczyk et al.³ for differentiating the resonance signals of triad sequences due to the methine carbon of the M-monomeric unit from those due to VV and VM

dyads. The experimental values of V- and M-centered triads from $^{13}\text{C}\{^1\text{H}\}$ triads were compared with the theoretical values from Harwood's⁴ statistical model using copolymerization reactivity ratios. The reactivity ratios for free-radical solution copolymerization of V with M were calculated using the Kelen–Tudos (KT)⁵ and the nonlinear error in variables (EVM)⁶ methods using the RREVM⁷ program. Homonuclear ^1H -2D-COSY and 2D-NOESY NMR of the copolymer sample were recorded for determining the interactions between different protons in the copolymer chain. The copolymerization behavior of V with M was also studied as a function of conversion.

EXPERIMENTAL

V and M monomers were washed successively with 10% aqueous NaOH and distilled water, dried over Na_2SO_4 , and distilled *in vacuo*. Benzoyl peroxide (BPO) recrystallized from chloroform/methanol was used as the initiator.

V and M monomers in different field ratios were taken in a glass tube and 0.5% (w/w) BPO in benzene was added. The tube was sealed and the reac-

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Table I Copolymer Composition Data and Intrinsic Viscosities of V/M Copolymers Prepared by Solution Polymerization

Sample	f_V	f_M	F_V	F_M	$[\eta]$ dL/g
VM1	0.97	0.03	0.75	0.25	0.75
VM2	0.95	0.05	0.63	0.37	0.77
VM3	0.92	0.08	0.44	0.56	0.98
VM4	0.90	0.10	0.37	0.63	1.02
VM5	0.82	0.18	0.31	0.69	1.56
VM6	0.69	0.31	0.23	0.77	—
VM7	0.62	0.38	0.16	0.84	1.82

f_V and f_M are the mol fractions of V and M comonomers, respectively, in the feed. F_V and F_M are the mole fraction of the V and M comonomers, respectively, in the copolymer.

tion was allowed to proceed at $60 \pm 1^\circ\text{C}$ for 1 h. The reaction was stopped at a conversion of $< 5\%$ by precipitating the copolymer in excess *n*-hexane. Intrinsic viscosities of prepared copolymer samples were measured in benzene as solvent using an Ubbelohde viscometer at $30 \pm 0.5^\circ\text{C}$ (Table I).

The details of recording the $^1\text{H-NMR}$ and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the copolymer samples and the fractional peak area measurement using a Lorentzian curve-fitting computer program were described elsewhere.^{8,9}

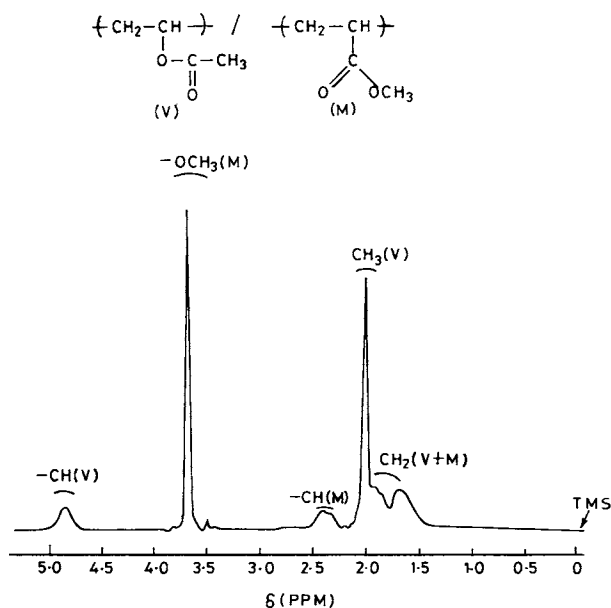


Figure 1 300 MHz $^1\text{H-NMR}$ spectrum of the V/M copolymer ($V = 44$ mol % in the copolymer) in CDCl_3 at room temperature.

Table II Reactivity Ratios for V/M Copolymers

	r_V	r_M	Refs and Remarks
(1)	0.5 0.401	3 2.578	Avetisyan et al. ¹² Recalculated by Greenley ¹⁰
(2)	0.1 0.033	9 6.382	Mayo et al. ¹¹ Recalculated by Greenley ¹⁰
(3)	0.04 ± 0.03	7.28 ± 2.88	Our data (KT method)
(4)	0.04 ± 0.01	7.28 ± 0.37	Our data (RREVM program)

RESULTS AND DISCUSSION

The $^1\text{H-NMR}$ spectrum of the V/M copolymer ($V = 44$ mol % in the copolymer) with the signal assignments is shown in Figure 1. The copolymer composition was calculated using the expression

$$F_V = \frac{[3I(-\text{CH})_V]}{[3I(-\text{CH})_V + I(-\text{OCH}_3)_M]}$$

where F_V is the mole fraction of V in the copolymer and $I(-\text{CH})_V$ and $I(-\text{OCH}_3)_M$ are the intensities

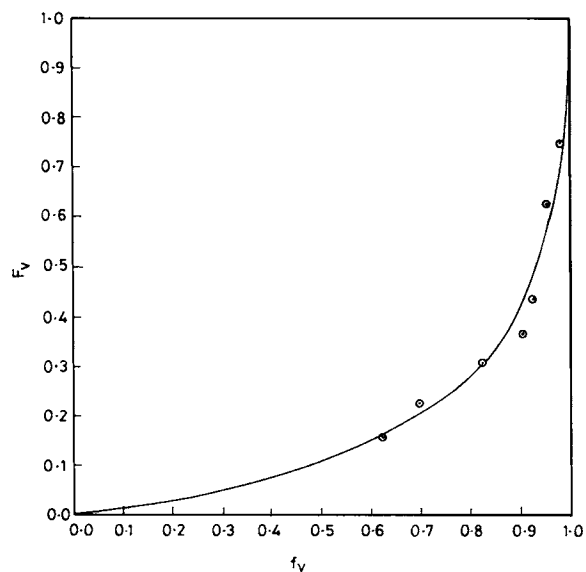


Figure 2 The theoretical curve obtained using reactivity ratios $r_V = 0.04$ and $r_M = 7.28$ in the copolymer composition equation along with experimental points (O).

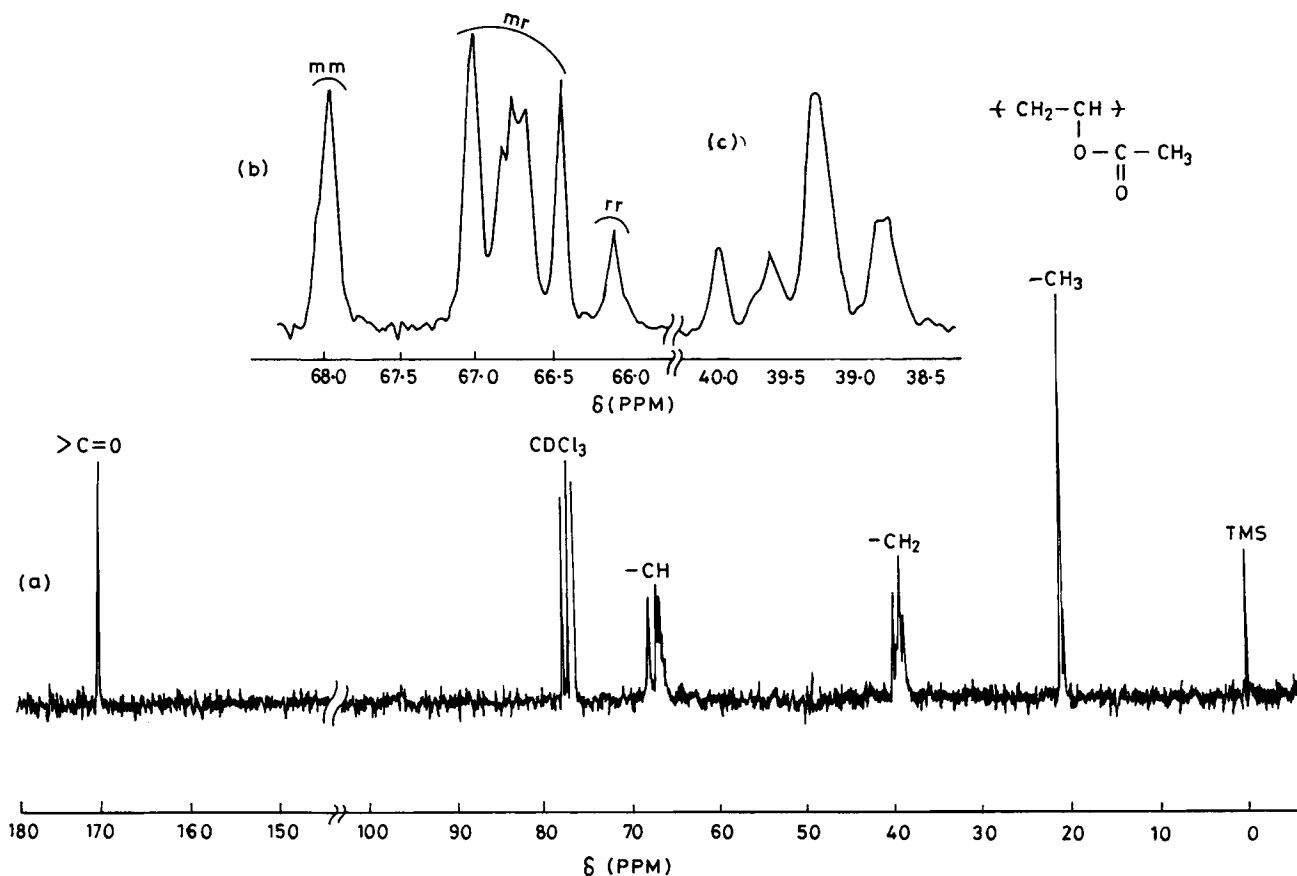


Figure 3 (a) 75 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of PVAc in CDCl_3 at room temperature. (b) Expanded methine carbon resonance signal. (c) Expanded methylene resonance signal of PVAc.

of methine and methoxy proton resonance signals due to V- and M- monomeric units, respectively. The comonomer mol fractions in feed and in the copolymers are given in Table I.

Copolymer composition data were used to calculate the terminal model reactivity ratios by the Kelen-Tudos⁵ and the nonlinear error in variables (EVM)⁶ methods using the RREVM⁷ computer program. The reactivity ratios estimated, from these methods, by us are in good agreement with the values of reactivity ratios obtained by Greenley¹⁰ using the reactivity ratios values reported by Mayo et al.¹¹ (Table II). The theoretical composition curve obtained from copolymer composition equation using reactivity ratios $r_V = 0.04$ and $r_M = 7.28$ and the experimental data are shown in Figure 2. The experimental curve is in good agreement with the theoretical one.

$^{13}\text{C}\{^1\text{H}\}$ -NMR of poly(vinyl acetate) [Fig. 3(a)] has four main signals: Methine (δ 66.1–67.9 ppm) and methylene resonances (δ 38.7–39.9 ppm) show

well-resolved splittings due to stereochemical or tacticity sensitivity [Fig. 3(b) and (c)]. The methine signals have been assigned to *mm* (δ 67.9 ppm), *mr* (δ 66.4–67.0 ppm), and *rr* (δ 66.1 ppm) triad sequences from low to high field [Fig. 3(b)].

$^{13}\text{C}\{^1\text{H}\}$ -NMR of poly(methyl acrylate) (PMA) (Fig. 4) also shows four resonance signals. The methoxy (δ 51.6 ppm) and carboxy resonances (174.7 ppm) are unaffected by the polymer tacticity. The methylene resonances (δ 34.0–35.9 ppm) as a multiplet and the methine (δ 41.0–41.2 ppm) resonances are stereochemically sensitive.

Figure 5 shows the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the V/M copolymer ($V = 44$ mol % in the copolymer). The carbonyl carbon resonances of the V as well as the M-monomeric units appearing, respectively, at δ 170.41 and 175.15 ppm are singlets and do not show any tacticity or sequence distribution effect. The methyl carbon of the V-monomeric unit and methoxy carbons of the M-monomeric unit that appear at δ 20.90 and 51.80 ppm, respectively, are

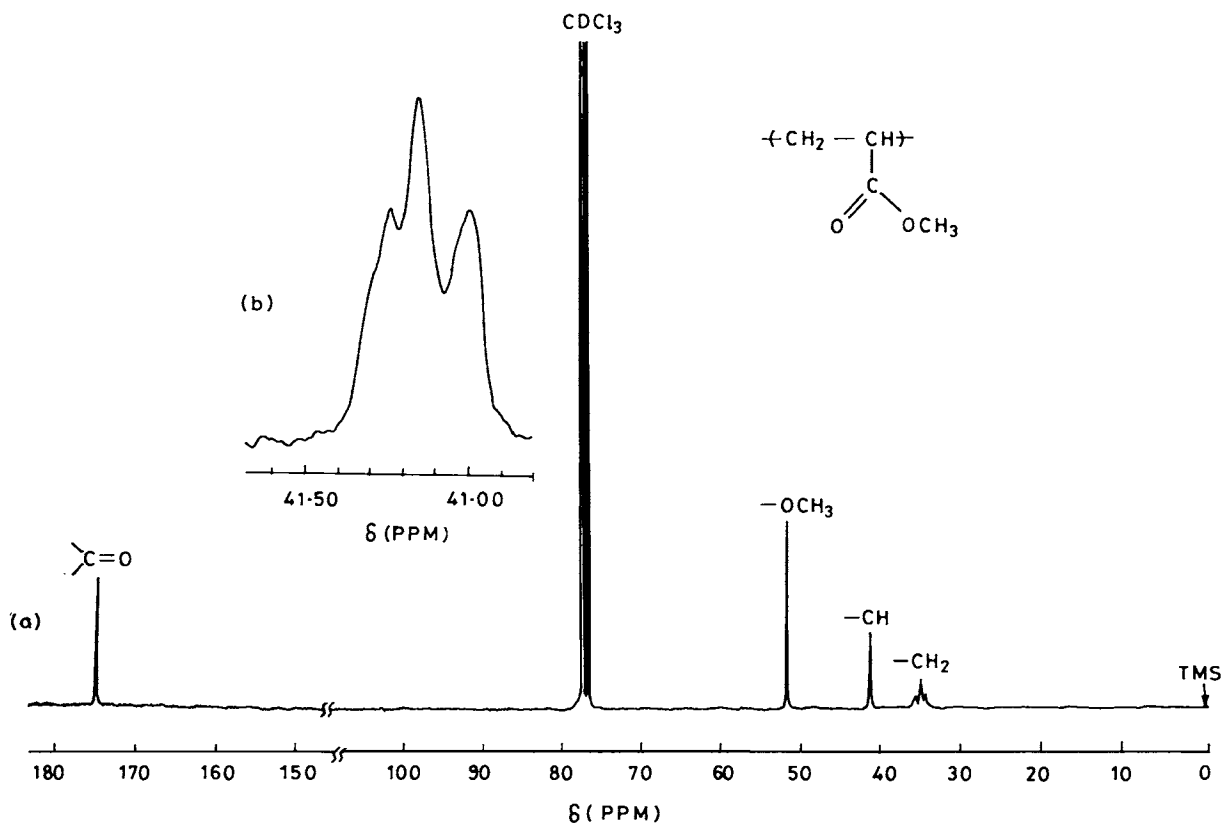


Figure 4 (a) 75 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of PMA in CDCl_3 at room temperature. (b) Expanded methylene carbon resonance spectra of PMA.

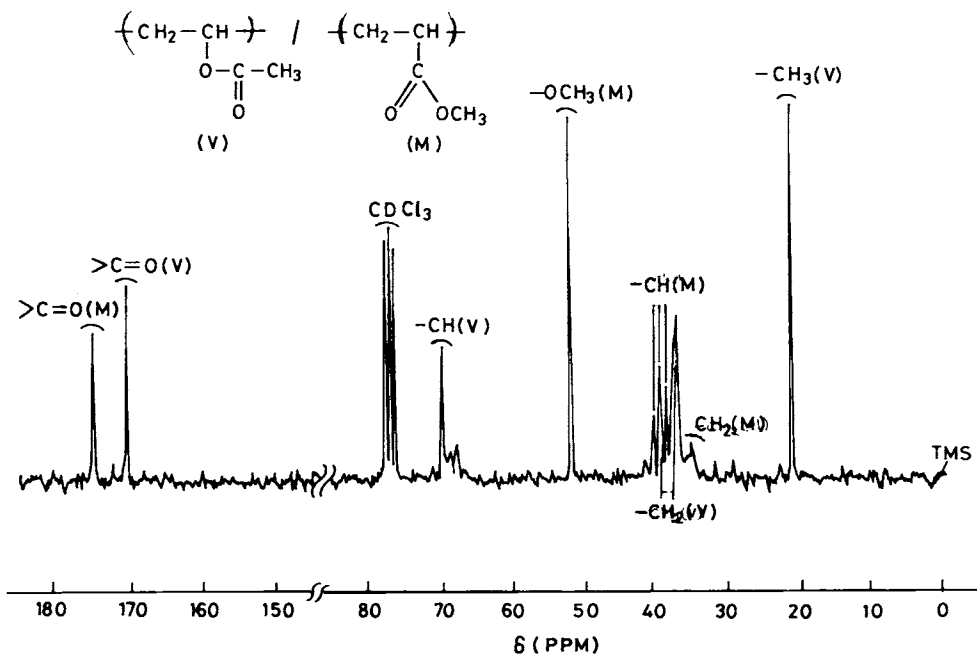


Figure 5 75 MHz $^{13}\text{C}\{^1\text{H}\}$ spectrum of the V/M copolymer (V = 44 mol % in the copolymer) in CDCl_3 at room temperature.

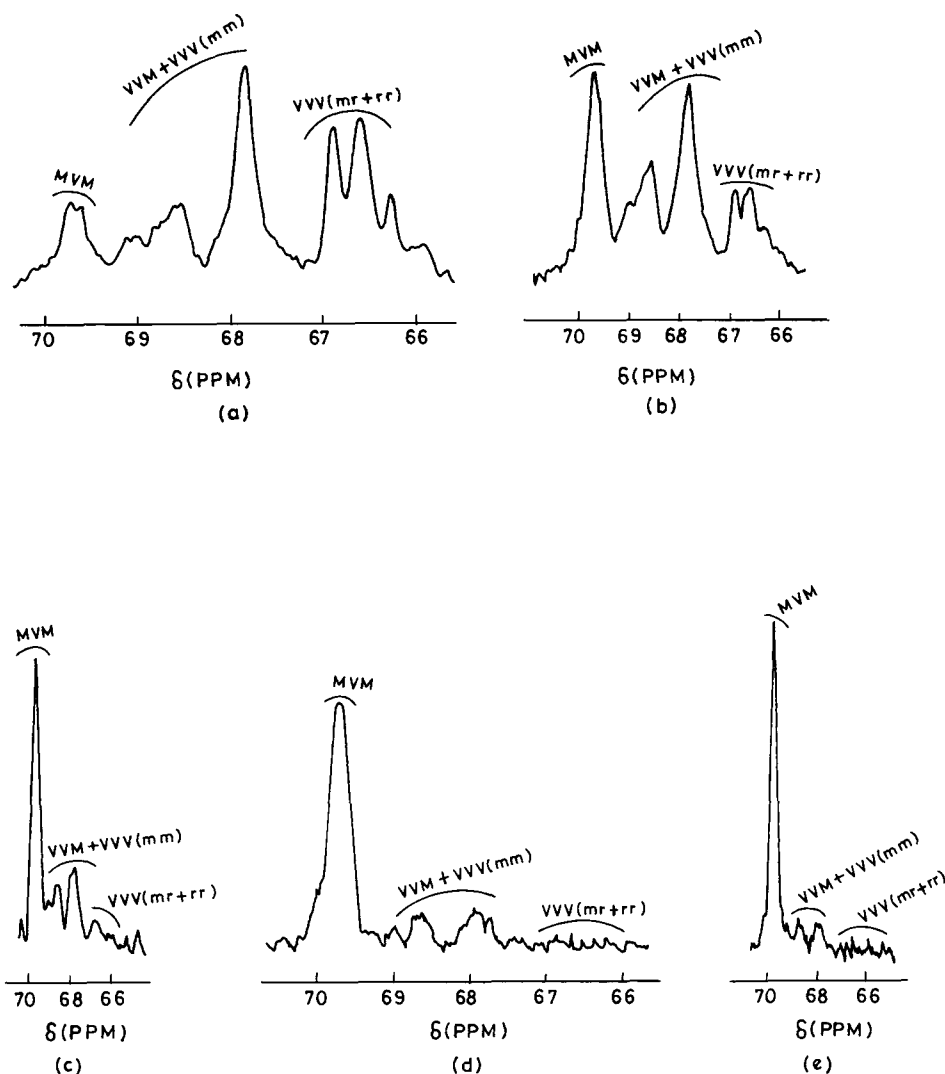


Figure 6 Expanded methine carbon resonance spectra of the V unit in the V/M copolymers: (a) 75.0; (b) 63.0; (c) 44.0; (d) 37.0; (e) 31.0 mol % V units in the copolymer.

sharp singlets and therefore insensitive to compositional as well as to configurational sequences. The methine carbon of the V-monomeric unit appears as a multiplet in the region δ 66.0–69.7 ppm and shows both configurational as well as compositional sensitivity. The methine carbon of the M-monomeric unit and the methylene carbons of the V- as well as the M-monomeric units appear in the region δ 34.0–41.3 ppm as a multiplet and are configurational as well as compositional-sensitive. This region can provide information about M-centered compositional triad sequences.

Figure 6(a)–(e) shows an expanded methine carbon resonance of the V-monomeric unit in the V/M copolymer. As the concentration of the V-mo-

nomeric unit in the copolymer decreases, the intensity of signal at δ 69.7 ppm increases, while those of the signals in the region δ 66.0–66.9 ppm decrease. Therefore, the signal at δ 69.7 ppm is assigned to MVM triad sequences, whereas, by comparison with $^{13}\text{C}\{^1\text{H}\}$ -NMR of poly(vinyl acetate) (PVAc) [Fig. 3(b)], the signals in the region δ 66.0–66.9 ppm are assigned to VVV (*mr + rr*) triad sequences. The signals at around δ 67.8–69.0 ppm are assigned to VVM + VVV (*mm*) triad sequences. The relative fractions of VVV, VVM, and MVM triad sequences were estimated by assuming that the *mm*/*mr + rr* ratio (0.248/0.752) of the VVV triads observed in the homopolymer is same as that for the copolymers.¹³ Experimental values of V-centered triads are

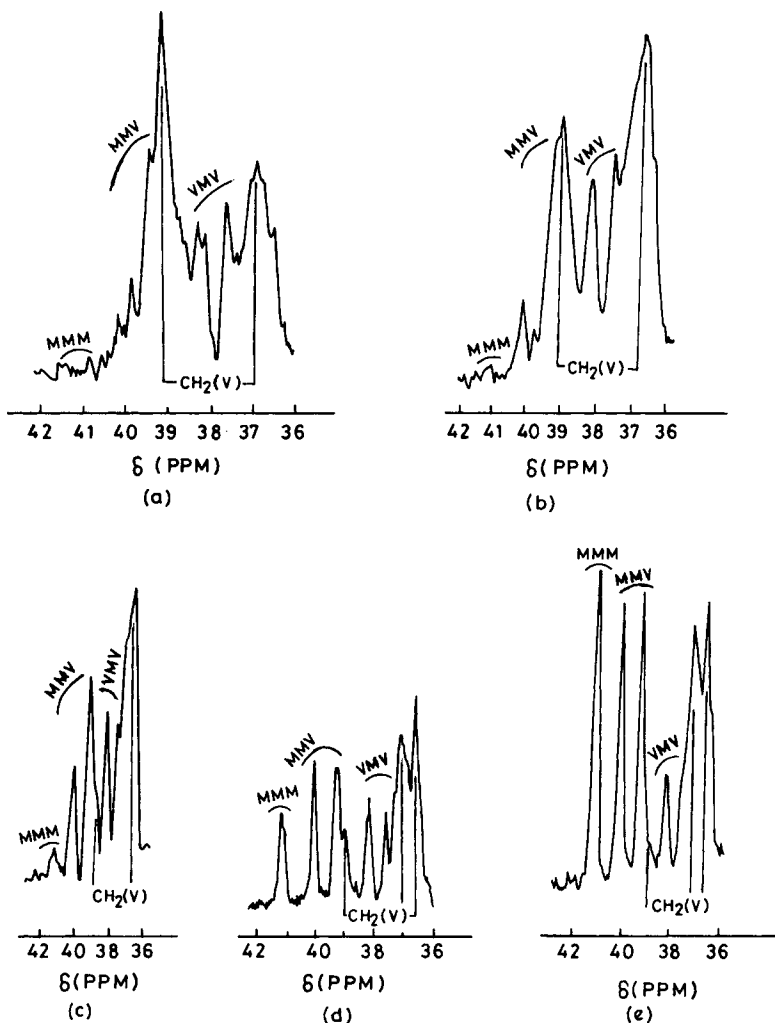


Figure 7 Expanded methine carbon resonance spectra of the M unit in the V/M copolymers: (a) 25.0; (b) 37.0; (c) 56.0; (d) 63.0; (e) 69.0 mol % M units in the copolymer.

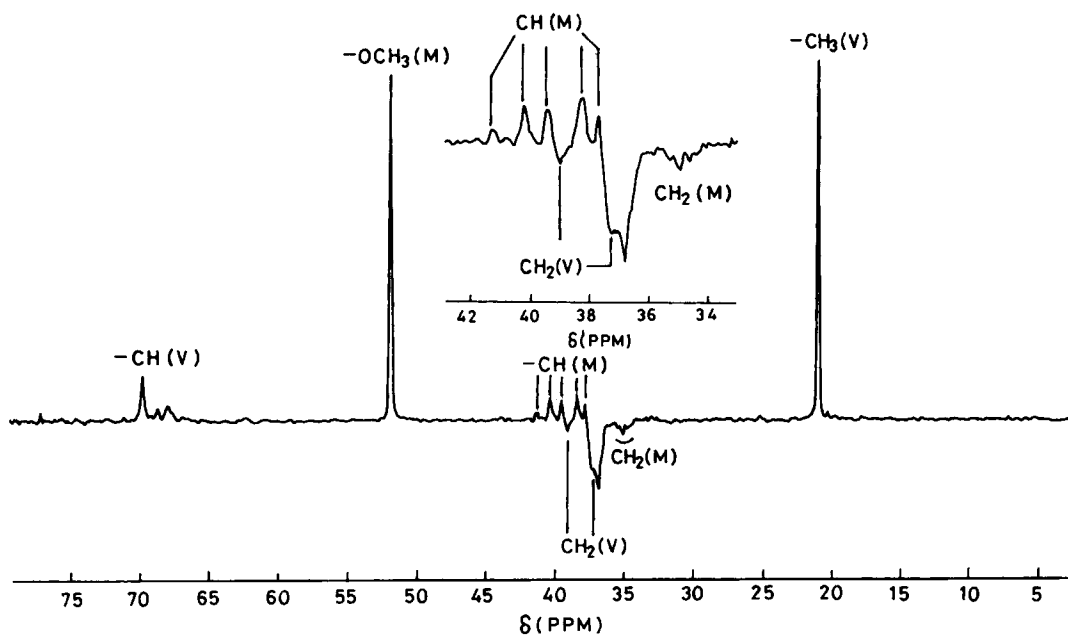


Figure 8 (a) ^{13}C -DEPT NMR spectrum of V/M (V = 44 mol % in the copolymer). (b) Expanded resonance region δ 36–41.3 ppm. Methylene resonances appear as negative peaks and methine and methyl carbon resonances appear as positive peaks.

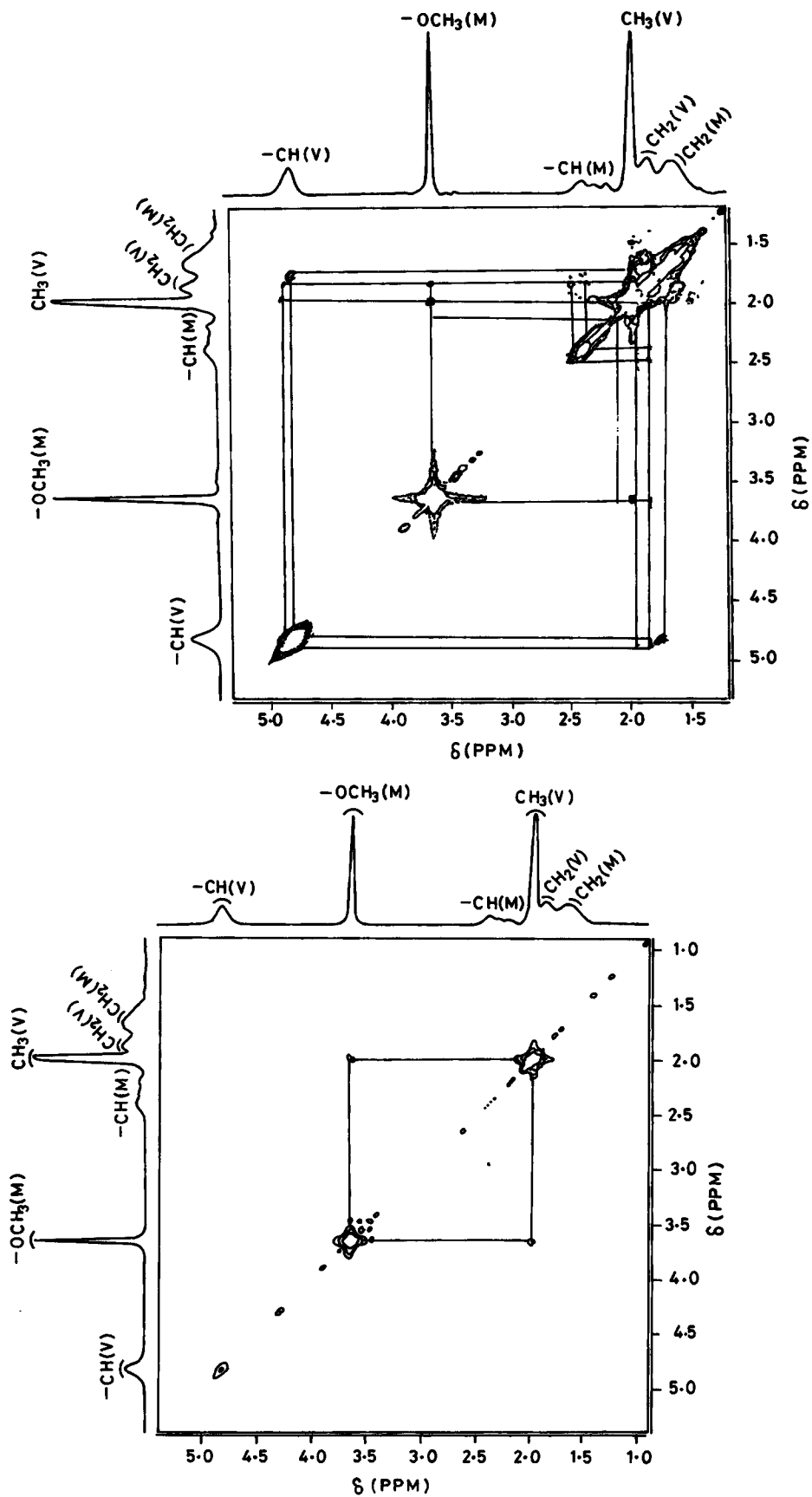


Figure 9 (a) 300 MHz $^1\text{H-NMR-2D-COSY}$ spectrum of the V/M copolymer (V = 63 mol % in the copolymer) recorded at room temperature in CDCl_3 . (b) 300 MHz $^1\text{H-NMR-2D-NOESY}$ spectrum of the V/M copolymer (V = 63 mol % in the copolymer) recorded at room temperature in CDCl_3 .

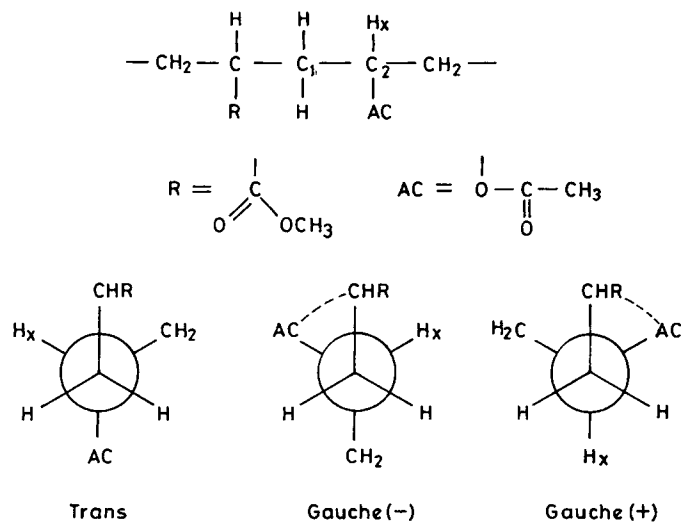


Figure 10 Newman projections illustrating the stable conformers along the $\text{C}_1\text{H}_2-\text{C}_2\text{H}_x$ bond in the V/M copolymer.

in good agreement with those obtained from Harwood's statistical model using reactivity ratios $r_V = 0.04$ and $r_M = 7.28$ (Table III).

The methine carbon of the M-monomeric unit and the methylene carbon of the V-monomeric units appear in the region δ 36.0–41.2 ppm [Fig. 7(a)–(e)]. The ^{13}C -DEPT-NMR spectrum (Fig. 8) of a copolymer sample ($V = 44$ mol % in the copolymer) was recorded in CDCl_3 to differentiate the resonance

signals due to methine and methylene carbons of M- and V-monomeric units, respectively. The signals at δ 41.3, 40.2, 39.43, 38.3, and 37.6 ppm can be attributed to the methine carbons of the M-monomeric unit and the signals at δ 39.02 ppm and at δ 36.8 ppm are attributed to the methylene carbons of the V-monomeric units. These assignments have been used to determine the relative fractions of M-centered triads.

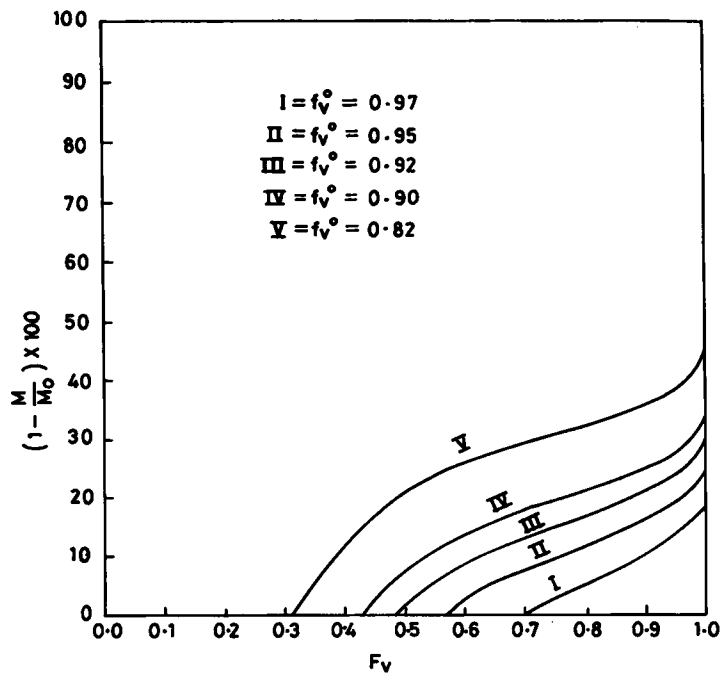


Figure 11 Percent mol conversion-copolymer composition curves for different concentrations (in mol %) of V in the feed (f_V).

Table III Experimental and Calculated Values of M- and V-centered Triads

Mol Fraction of V in the Copolymer	Triad	Triad Fractions	
		<i>a</i>	<i>b</i>
0.75	VVV	0.48	0.37
	VVM	0.41	0.48
	MVM	0.11	0.15
	MMM	0.02	0.03
	MMV	0.35	0.27
	VMV	0.63	0.70
0.63	VVV	0.22	0.18
	VVM	0.46	0.49
	MVM	0.32	0.33
	MMM	0.02	0.08
	MMV	0.43	0.40
	VMV	0.55	0.52
0.44	VVV	0.07	0.10
	VVM	0.43	0.44
	MVM	0.50	0.46
	MMM	0.13	0.17
	MMV	0.47	0.44
	VMV	0.40	0.39
0.37	VVV	0.03	0.07
	VVM	0.39	0.39
	MVM	0.58	0.55
	MMM	0.18	0.20
	MMV	0.51	0.50
	VMV	0.31	0.30
0.31	VVV	0.01	0.02
	VVM	0.22	0.26
	MVM	0.77	0.72
	MMM	0.31	0.37
	MMV	0.49	0.48
	VMV	0.20	0.15

Samples VM6 and VM7 (V = 23 and V = 16 mol % in the copolymer, respectively) could not be used for triad sequence determination because resolution was not good.

^a Triad fractions determined from ¹³C-NMR spectra of copolymers.

^b Triad fractions calculated using $r_V = 0.04$ and $r_M = 7.28$ in Harwood's statistical model.

¹³C{¹H}-NMR spectra of the copolymer sample in the region δ 36.0–41.5 ppm show that the signal at δ 41.3 ppm increases in intensity while the signals at δ 38.3 and 37.6 ppm decrease in intensity with increase in concentration of the M unit in the copolymer. By comparison with the ¹³C{¹H}-NMR spectrum of the homopolymer poly(methyl acrylate), the signal at δ 41.3 ppm has been assigned to MMM compositional triads, whereas compositional

variation in the intensity of the signals at δ 38.30 and 37.6 ppm shows that these signals can be assigned to VMV triad sequences. The signals at δ 40.2 and at 39.4 ppm have been assigned to MMV triad sequences. The relative fractions of MMM, MMV, and VMV triads were measured from peak area measurements under various resonance signals. Experimental values of M-centered triads are in good agreement with theoretical values obtained using $r_V = 0.04$ and $r_M = 7.28$ in Harwood's statistical model (Table III).

Homonuclear ¹H-2D-COSY and 2D-NOESY NMR of the V/M copolymer (V = 63 mol % in the copolymer) recorded in CDCl₃ are shown in Figure 9(a) and (b), respectively. Interactions from ¹H-2D-COSY shows that —CH(V) is correlated to —CH₂(M), —CH₂(V), and —CH₃(V). Also, —OCH₃(M) is correlated to —CH₂(V), —CH₃(V), and —CH(M). —CH(M) is correlated to —CH₂(V), but not much can be said about other correlations of —CH(M). The NOESY spectrum shows that —OCH₃(M) is space-coupled to CH₃(V); this shows that for the V/M copolymer the *gauche* conformer is more probable than is the *trans* form. Since COSY shows that —CH(V) is correlated to —CH₂(V) as well as to —CH₂(M) but not to —OCH₃(M), therefore the *gauche* (+) conformer seems more probable (Fig. 10).

The reactivity ratios $r_V = 0.04$ and $r_M = 7.28$ were used to study the copolymerization behavior of V/M copolymers. Using the Meyer-Lowry equation¹⁴ in conjunction with the instantaneous copolymer composition equation,¹⁵ the percentage mol conversion ($1 - M/M_0$) was obtained as a function of copolymer composition for different feed compositions. From the percentage mol conversion-composition copolymer composition curves (Fig. 11), it is observed that the tendency of V units to homopolymerize increases with increasing V content in the feed even at low conversions.

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