

Reactivity Ratios and Microstructure of Vinyl Acetate–Butyl Methacrylate Copolymers: NMR Study

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SYNOPSIS

Vinyl acetate/butyl methacrylate (V/B) copolymers were prepared by free-radical solution polymerization in benzene. Compositions of the copolymers have been obtained from ^1H -NMR spectroscopy. Kelen–Tüdös (KT), the nonlinear error in variables method (EVM), and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the copolymers were utilized to calculate the comonomer reactivity ratios. The reactivity from different methods are $r_V = 0.06 \pm 0.02$, $r_B = 26.34 \pm 8.49$ (KT); $r_V = 0.06 \pm 0.01$, $r_B = 26.88 \pm 3.59$ (EVM); and $r_V = 0.06$, $r_B = 18.20$ (^{13}C -NMR spectroscopy). The microstructure in terms of V- and B-centered triad fractions was obtained using $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of copolymers. The copolymerization behavior of V/B copolymers as a function of conversion was also studied. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Earlier, we reported the microstructure and reactivity ratios of the vinyl acetate/methyl methacrylate¹ and vinyl acetate/ethyl methacrylate² copolymers. In continuation of work on the reactivity ratios and microstructure of vinyl acetate/alkyl methacrylate copolymers in our laboratory, we report the reactivity ratios and microstructure of vinyl acetate/butyl methacrylate copolymers. Kapur and Brar³ reported the microstructure for 100% conversion of vinyl acetate/butyl methacrylate (V/B) copolymers prepared by emulsion polymerization (semicontinuous batch process) and did not report the reactivity ratios. In this work, reactivity ratios were obtained from Kelen–Tüdös (KT),⁴ nonlinear error in variables method (EVM)⁵ using the RREVM program,⁶ and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of copolymers. The microstructure was obtained in terms of V- and B-centered triad sequence distributions from $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra. The effect of degree of conversion on the copolymer composition shall also be reported.

EXPERIMENTAL

A series of vinyl acetate/butyl methacrylate (V/B) copolymers containing different mol % of butyl methacrylate (from 11.0 to 2.6 mol %) in the feed were prepared by solution polymerization in benzene at 60°C using benzoyl peroxide as the initiator. The conversion was kept below 5% by precipitating the copolymer in *n*-hexane.¹

The details of recording the ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the copolymer have been described in our earlier publications.^{1,2,7,8} The intrinsic viscosities of all the copolymer samples were measured in benzene at $30 \pm 0.5^\circ\text{C}$ using an Ubbelohde viscometer and are given in Table I.

RESULTS AND DISCUSSION

The ^1H -NMR spectrum of the V/B copolymer (V = 56.5 mol % in the copolymer) along with the assignment of various resonance signals is shown in Figure 1. The copolymer compositions were calculated from the relative intensities of the —CH (V-unit) and —OCH₂ (B-unit) resonances in ^1H -NMR using the following expression:

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

Sample	f_V	f_B	F_V	F_B	$[\eta]$ dL/g
BV5	0.974	0.026	0.655	0.345	0.38
BV4	0.964	0.036	0.565	0.435	0.42
BV3	0.953	0.047	0.510	0.490	0.33
BV2	0.922	0.078	0.324	0.676	0.43
BV1	0.890	0.110	0.265	0.735	—

f_V and f_B are the mol fractions of V and B comonomers, respectively, in the feed. F_V and F_B are the fractions of V and B comonomers, respectively, in the copolymer.

$$F_V = \frac{[2I(-\text{CH})_V]}{[2I(-\text{CH})_V + I(-\text{OCH}_2)_B]} \quad (1)$$

where F_V is the mol fraction of vinyl acetate in the copolymer and $I(-\text{CH})_V$ and $I(-\text{OCH}_2)_B$ are the intensities of the $-\text{CH}$ (V-unit) and $-\text{OCH}_2$ (B-unit) proton resonances, respectively.

Figure 2(a) shows a representative $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the V/B copolymer ($V = 56.5$ mol % in the copolymer) along with signal assignments. The expanded carbonyl carbon resonance

signal of the B-monomeric unit in the V/B copolymer is shown in Figure 2(b). Since the carbonyl carbon resonance in poly(butyl methacrylate) (PBMA) is sensitive to tacticity, the carbonyl carbon resonance of $\delta 175.55$ – 178.20 ppm exhibits configurational as well as compositional sensitivity. The signal at $\delta 178.20$ – 177.30 ppm decreases while the signal at $\delta 175.55$ – 176.30 ppm increases in intensity with decrease in concentration of the B-unit in the copolymer. Therefore, the most downfield signal at $\delta 178.20$ – 177.30 ppm is assigned to BBB triad sequences. The addition of the V-unit adjacent to the B-unit increases the shielding at the carbonyl carbon and is expected to shift the BBV and VBV signals upfield. The most upfield signal at $\delta 175.55$ – 176.30 ppm is assigned to VBV triad sequences. The contribution of $B_m B_m B$ triad sequences that appear around $\delta 175.8$ – 176.39 ppm to VBV has been neglected on the basis that fraction of the $B_m B_m B$ triad in PBMA is negligible. The resonance signal at $\delta 176.28$ – 177.06 ppm is due to overlapping of the $B_m B_r B$ sequence with VBB triad sequences. By comparison with PBMA, it is observed that 50% of BBB triad fractions overlap with VBB triad sequences. The relative fractions of various peak triads BBB, BBV, and VBV were obtained from peak area

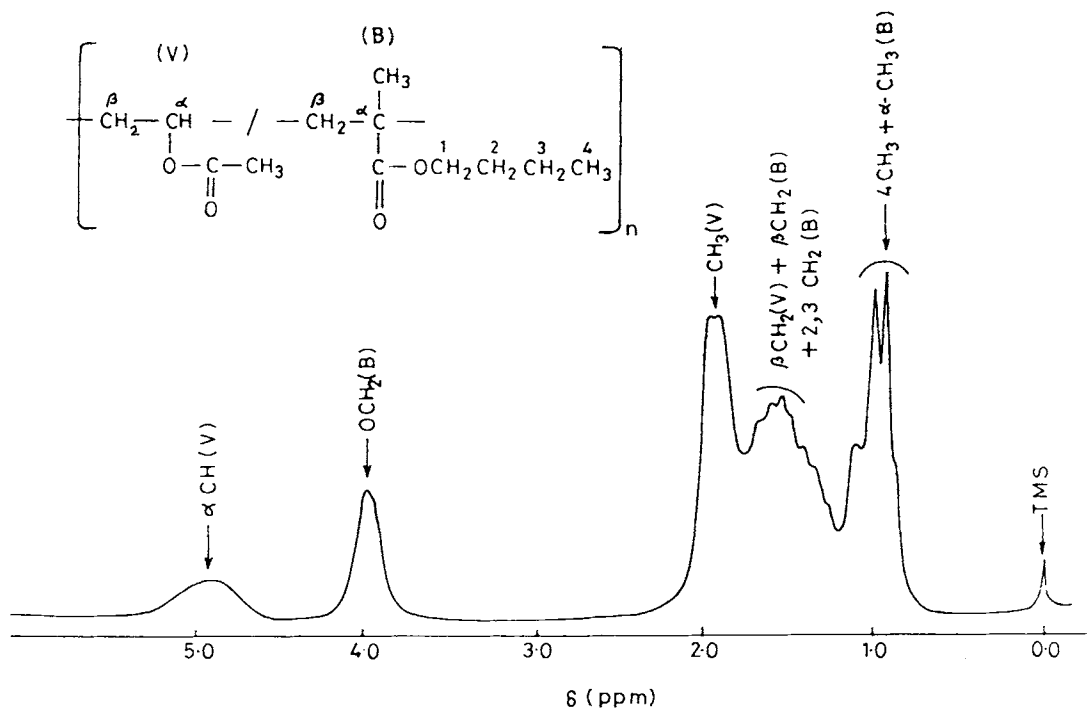


Figure 1 100 MHz ^1H -NMR spectrum of V/B copolymer ($V = 56.5$ mol % in the copolymer) in CDCl_3 at room temperature.

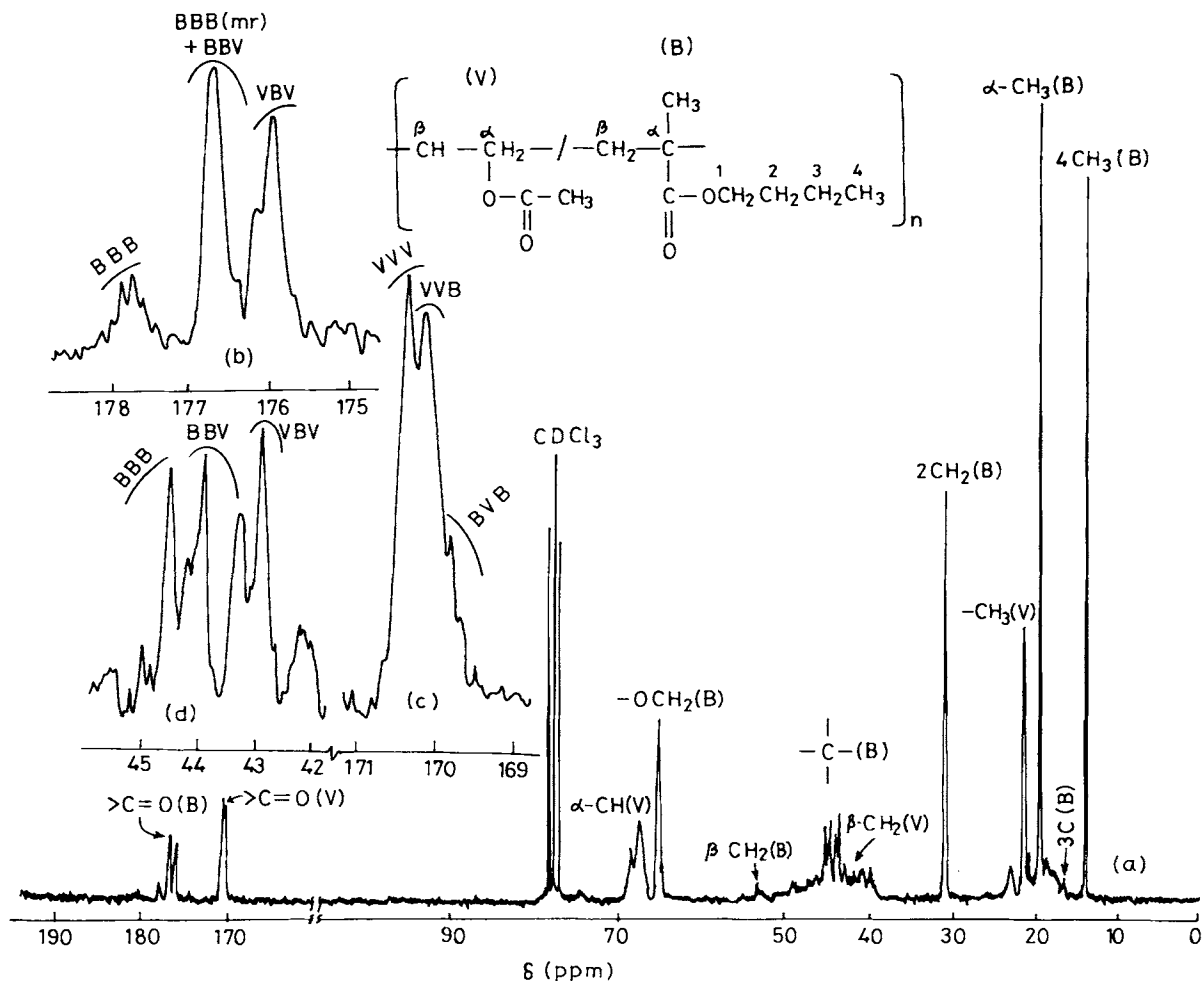


Figure 2 (a) 50 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of V/B copolymer (V = 56.5 mol % in the copolymer) in CDCl_3 at room temperature. (b) Expanded carbonyl carbon resonance of the B-monomeric unit. (c) Expanded carbonyl carbon resonance of the V-monomeric unit. (d) Expanded quaternary carbon resonance of the B-monomeric unit.

measurements. The region of $\delta 177.38\text{--}178.15$ ppm is further split up, showing pentad sensitivity. The signals at $\delta 178.11$, 177.85 , and 177.54 ppm are assigned to mrrm, mrrr, and rrrr pentad sequences, respectively, by comparison with PBMA. The additional signals at $\delta 177.70$ and 177.96 ppm do not appear in the PBMA spectrum and show compositional variation in intensity. The signal at $\delta 177.70$ ppm increases in intensity with decrease in concentration of the B-monomeric unit in the copolymer and is assigned to the VBBBBV pentad sequence, whereas the signal at $\delta 177.96$ ppm, which does not show significant variation in intensity with composition, is assigned to BBBBV pentad sequences.

The expanded quaternary carbon resonance of the B-monomeric unit in the V/B copolymer (V

= 56.5 mol % in the copolymer) is shown in Figure 2(d). Various signals have been assigned by observing the compositional variation of the intensities. The most downfield signals in the region of $\delta 45.20\text{--}44.65$ ppm, which decrease in intensity with decrease in concentration of the B-unit in the copolymer, have been assigned to BBB triad sequences, whereas the most upfield signal at $\delta 43.07$ ppm, which increases in intensity with decrease in concentration of the B-unit in the copolymer, has been assigned to VBV triad sequences. The signals in the region of $\delta 43.44\text{--}44.35$ ppm have been assigned to VBB triad sequences. The relative fractions of BBB, BBV, and VBV triad sequences were obtained by resonance signal area measurements. The relative fractions of B-centered triads determined from a qua-

ternary carbon resonance signal are in good agreement with those obtained using a carbonyl carbon resonance signal (Table II).

Expanded carbonyl carbon resonance of the V-monomeric unit in the V/B copolymer (V = 56.5 mol % in the copolymer) is shown in Figure 2(c). By comparison with poly(vinyl acetate) (PVAc), signals in the region of δ 170.30–170.40 ppm, which increase in intensity with increase in concentration of V-unit in the copolymer, have been assigned to

Table II Calculated and Observed Fractions of V- and B-Centered Triads in V/B Copolymers

V (Mol Fraction) in Copolymer	Triad	Triad Fractions		
		Obs ^a		Ter ^b
		*	**	
0.27	BBB	0.44	0.48	0.48
	BBV	0.48	0.48	0.43
	VBV	0.08	0.04	0.10
	VVV	0.09	—	0.10
	VVB	0.46	—	0.43
	BVB	0.45	—	0.47
0.32	BBB	0.32	0.37	0.37
	BBV	0.53	0.52	0.48
	VBV	0.15	0.11	0.16
	VVV	0.14	—	0.16
	VVB	0.51	—	0.48
	BVB	0.35	—	0.36
0.51	BBB	0.24	0.26	0.22
	BBV	0.48	0.45	0.50
	VBV	0.28	0.30	0.28
	VVV	0.29	—	0.28
	VVB	0.49	—	0.50
	BVB	0.22	—	0.22
0.57	BBB	0.18	0.18	0.16
	BBV	0.46	0.52	0.48
	VBV	0.36	0.31	0.36
	VVV	0.37	—	0.36
	VVB	0.45	—	0.48
	BVB	0.16	—	0.16
0.66	BBB	0.12	0.10	0.11
	BBV	0.47	0.49	0.44
	VBV	0.41	0.41	0.45
	VVV	0.40	—	0.46
	VVB	0.49	—	0.44
	BVB	0.12	—	0.10

^a Triad fractions obtained using ¹³C-NMR: * carbonyl carbon resonance signal; ** quaternary carbon resonance.

^b $r_V = 0.06$ and $r_B = 18.20$ in Harwood's terminal model.

VVV triad sequences. The signals in the region of δ 169.70–169.98 ppm, which decrease in intensity with decrease in concentration of the B-monomeric unit in the copolymer, have been assigned to BVB triad sequences. The relative fractions of VVV, VVB, and BVB triads were obtained by measuring peak areas under respective triad sequences.

From the results of the composition with respect to various V- and B-centered triads, the conditional probability P_{VB} that the V–B unit comes about as a result of the V-growing chain end adding B and P_{BV} , which is the probability that the B–V unit comes about as a result of the B-growing chain end adding V, were also calculated.⁹

Copolymer composition data (Table I) were used to calculate terminal model reactivity ratios by the KT and EVM methods using the RREVM program. Reactivity ratios from the KT method were taken as initial estimates in the RREVM program. The percentage errors in measuring the comonomer composition in the feed and in the copolymer were taken for the RREVM program as 0.1 and 3%, respectively. Terminal model reactivity ratios were obtained from ¹³C-NMR using conditional probabilities P_{VB} and P_{BV} in the following equations (see Table III):

$$r_V = \frac{f_B}{f_V} (1/P_{VB} - 1) \quad (2)$$

$$r_B = \frac{f_V}{f_B} (1/P_{BV} - 1) \quad (3)$$

where f_B and f_V are the feed in mol fractions of butyl methacrylate and vinyl acetate, respectively. Reactivity ratios obtained in this work are $r_V = 0.06 \pm 0.02$, $r_B = 26.34 \pm 8.49$ (KT); $r_V = 0.06 \pm 0.01$, $r_B = 26.88 \pm 3.59$ (RREVM program); and $r_V = 0.06$, $r_B = 18.20$ (¹³C-NMR) (Table III). Reactivity ratios estimated by various methods are different from each other and involve large uncertainties. This is also evident from the plot of the copolymer composition as a function of the monomer (vinyl acetate) mol fraction in the feed (Fig. 3) and shows that the V/B system is highly sensitive to even minor errors in the measurement of copolymer composition. However, the values of the reactivity ratios obtained in this work by KT and RREVM are in close agreement with those reported in the literature.^{10,11} Now it is well known that it is very difficult to determine the reactivity ratios correctly when the values of reactivity ratios are very much different from each other.¹² Also, the observed fractions of V-

Table III Copolymerization Parameters of V/B Copolymers Determined by ^{13}C -NMR Spectroscopy

Sample	V Mol Fraction in Copolymer	P_{VB}	P_{BV}	r_V	r_B	\bar{N}_V	\bar{N}_B
BV1	0.27	0.68	0.32	0.06	17.19	1.47	3.13
BV2	0.32	0.61	0.42	0.05	16.32	1.64	2.38
BV3	0.51	0.46	0.52	0.06	18.72	2.17	1.92
BV4	0.57	0.40	0.59	0.06	18.61	2.50	1.69
BV5	0.66	0.36	0.65	0.05	20.17	2.77	1.54
				0.06 ^a	18.20 ^a		

P_{VB} = probability of addition of monomeric unit B to a growing chain ending in V. P_{BV} = probability of addition of monomeric unit V to a growing chain ending in B. \bar{N}_V and \bar{N}_B = number-average sequence length of V and B units, respectively.

^a Average values of reactivity ratios.

and B-centered triads are in good agreement with those calculated using $r_V = 0.06$ and $r_B = 18.20$ in Harwood's statistical model.¹³

The reactivity ratios $r_V = 0.06$ and $r_B = 18.20$ have been used to study the copolymerization behavior of V/B copolymerization. Using the Meyer-Lowry equation¹⁴ in conjunction with the instantaneous copolymer composition equations,¹⁵ the percentage mol conversion ($1 - M/M_0$) was obtained as a function of copolymer composition for different feed compositions. The percentage mol conversion-copolymer composition curves (Fig. 4) obtained are typical of such systems having large

differences in their reactivity ratios. It is observed from these curves that the tendency of vinyl acetate monomeric units to homopolymerize increases with increasing vinyl acetate content in the feed.

CONCLUSION

From our work on the reactivity ratios of vinyl acetate/methyl methacrylate (V/M),¹ vinyl acetate/ethyl methacrylate (V/E),² and vinyl acetate/butyl methacrylate (V/B) copolymers, we conclude that the alkyl chain length of the ester group has almost no effect on the reactivity ratios.

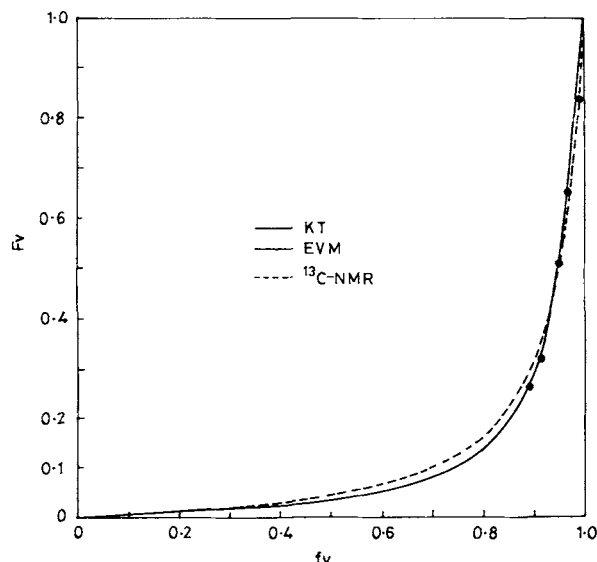


Figure 3 The theoretical composition curves obtained using reactivity ratios from EVM, KT, and ^{13}C -NMR spectroscopy along with experimental points (●). The curves from the EVM and KT methods are overlapping.

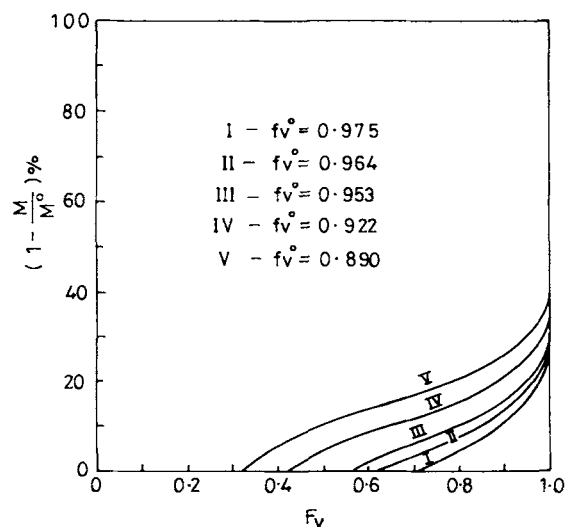


Figure 4 Percent mol conversion-copolymer composition curves for different concentrations (in mol %) of vinyl acetate in feed (f_v).

The authors thank the Department of Science and Technology, Government of India, for providing financial support during this work. The authors also thank Professor Harjit Singh, Guru Nanak Dev University, Amritsar, India, for recording the NMR spectra and Professor K. F. O'Driscoll of the University of Waterloo, Canada, for providing the RREVM program.

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Received April 27, 1993

Accepted July 3, 1993