

# Sequencing of Methyl Methacrylate/Vinylidene Chloride Copolymers by NMR Spectroscopy

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**ABSTRACT:** Methyl methacrylate/vinylidene chloride (M/V) copolymers of different monomer concentrations were prepared by photopolymerization using the uranyl ion as photosensitizer. The copolymer composition was determined by chlorine estimation of the copolymers. The complete assignment of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of these copolymers is made by comparison with the spectra of poly(methyl methacrylate) and observing the changes in the intensities of the resonances with copolymer composition. The quaternary carbon of V- and M- center resonances were used for determining the sequence in terms of the distribution of V- and M- centered triads. The triad fractions thus obtained were compared with theoretically determined triad concentrations. The Monte Carlo simulation method was also used for estimating the copolymerization behavior. The variation of V- and M- centered triad concentrations was reported as a function of fractional conversions. The comonomer reactivity ratios, determined by both Kelen Tudos and nonlinear error in variables methods are  $r_V = 0.26 \pm 0.04$  and  $r_M = 2.88 \pm 0.23$ . © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 373–381, 1998

**Key words:** vinylidene chloride; methyl methacrylate; NMR

## INTRODUCTION

To understand the polymerization processes and the macroscopic characteristic, one needs to determine the sequence distribution, tacticity, and the composition of the concerned copolymer.  $^{13}\text{C}$  NMR spectroscopy is the most reliable technique<sup>1,2</sup> for such determination. In our earlier work, we had reported the microstructure of vinylidene chloride-acrylate copolymers.<sup>3,4</sup> Herein, we report the microstructural studies on methyl methacrylate/vinylidene chloride copolymer using  $^{13}\text{C}$  NMR spectroscopy. Chiang and colleagues<sup>5</sup> worked on vinylidene chloride/methyl methacrylate and developed a new method for maintaining the constant composition monitored

by chromatographic analysis and also proposed a new graphical method<sup>6</sup> to understand the variations in the reactivity ratios observed. Infrared spectroscopy and thermal studies have also been reported on this copolymer to relate the effect of sequence length.<sup>7</sup> In this article, the complete assignment of all the carbon resonances has been made by comparison with the spectrum of poly(methyl methacrylate)<sup>8</sup> and the variation of the signal intensities with copolymer composition. Previously, such compositional and configurational assignments of triads based on  $^{13}\text{C}$  NMR spectra have been made for the copolymers of methyl methacrylate with acrylonitrile,<sup>9</sup> vinyl acetate,<sup>10</sup> and styrene.<sup>11</sup>

## EXPERIMENTAL

Vinylidene chloride and methyl methacrylate monomers distilled under reduced pressure were used for the polymerization. Uranyl nitrate in ace-

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**Table I Copolymer Composition, the % Conversion, the % Chlorine Content, and the Molecular Weights of Methyl Methacrylate/Vinylidene Chloride (M/V) Copolymer**

No.	Monomer Content in Feed (mol fraction)		Copolymer Composition (mol fraction)		% Chlorine	% Conversion	$\overline{M}_n \times 10^{-4}$ g/mol	$\overline{M}_w \times 10^{-4}$ g/mol
	$f_V$	$f_M$	$F_V$	$F_M$				
1.	0.40	0.60	0.18	0.82	13.07	3.3	2.2	6.0
2.	0.70	0.30	0.43	0.57	30.87	6.3	1.9	3.9
3.	0.75	0.25	0.47	0.53	33.90	1.8	1.2	2.2
4.	0.80	0.20	0.54	0.46	38.65	2.9	0.5	0.6
5.	0.85	0.15	0.62	0.38	44.98	2.6	1.0	2.1
6.	0.90	0.10	0.68	0.32	49.62	2.3	0.9	1.9
7.	0.93	0.00	0.79	0.21	57.48	3.7	0.5	0.9

$\overline{M}_n$  = number average molecular weight;  $\overline{M}_w$  = weight average molecular weight.

tone was used as a initiator, and the reaction was carried in a sealed tube under a nitrogen atmosphere. Conversions were kept below 5% by precipitating the copolymers in excess of methanol.

Composition of the copolymers was determined by the Schoneger technique,<sup>12</sup> and gel permeation chromatography was used to estimate the molecular weight averages using polystyrene as a narrow standard. The <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker-DPX-300 spectrometer under standard conditions.<sup>8</sup> The Lorentzian curve fitting was done using a nonlinear least square curve-fitting program.<sup>13</sup> The fitted and the experimental curves were taken when  $\chi^2$  was < 1.

## RESULTS AND DISCUSSION

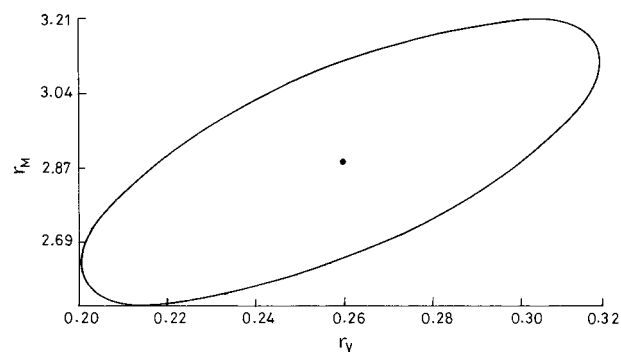
### Determination of Copolymer Composition, Reactivity Ratios, and Molecular Weight

The chlorine content of the copolymers prepared was estimated using the oxygen flask method,<sup>12</sup> wherein the combustion of the copolymer sample and then the estimation of the chlorine was conducted by titration methods. Table I shows the comonomer mole fractions in the feed, in the copolymer, the percent conversions, and the percentage of chlorine in the copolymer. This composition data were used to estimate the reactivity ratios by Kelen Tudos and nonlinear error in variables method.<sup>14</sup> The values obtained from both methods are  $r_V = 0.26 \pm 0.04$  for vinylidene chloride and  $r_M = 2.88 \pm 0.23$  for methyl methacrylate. A 95% joint confidence interval plot for the methyl methacrylate/vinylidene chloride comono-

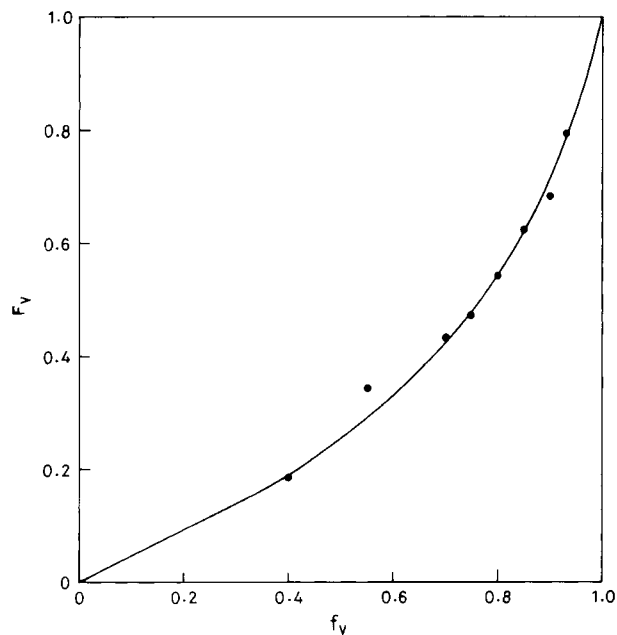
mer pair is shown in Figure 1. This plot shows that any reactivity ratios within this plot is within the 95% confidence level and is valid for this system. The theoretical composition curve obtained from the copolymer composition equation, using reactivity ratios  $r_V = 0.26$  and  $r_M = 2.88$  and the experimentally determined copolymer composition, is shown in Figure 2. The molecular weight averages determined by gel permeation chromatography are reported in Table I.

### <sup>13</sup>C NMR Studies

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of methyl methacrylate/vinylidene chloride copolymers ( $F_V = 0.43$ ) dissolved in CDCl<sub>3</sub> is shown in Figure 3. The quaternary carbon of the vinylidene chloride monomeric unit (V), gives several signals downfield in the range  $\delta$  83.0–90.0 ppm (Fig. 4), which are assigned by inspecting the intensity variations



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



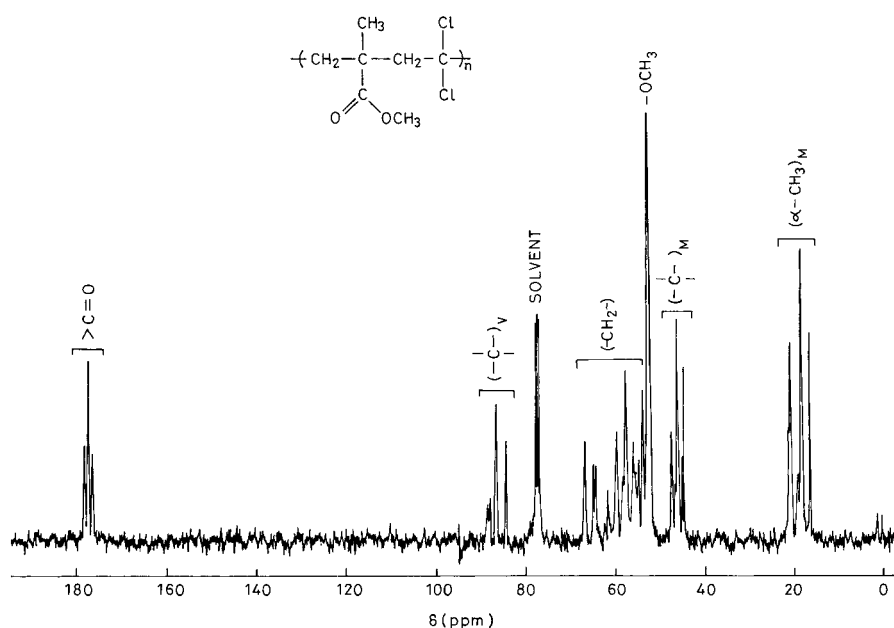
**Figure 2** Theoretical composition curve obtained using reactivity ratios  $r_V = 0.26$  and  $r_M = 2.88$ , along with experimentally determined copolymer composition (●).

with the composition. The resonance splitting herein is compositional sensitive and hence can be used for studying the copolymerization mechanism. In particular, it is observed that the signal at 84.0 ppm increases with an increase in the

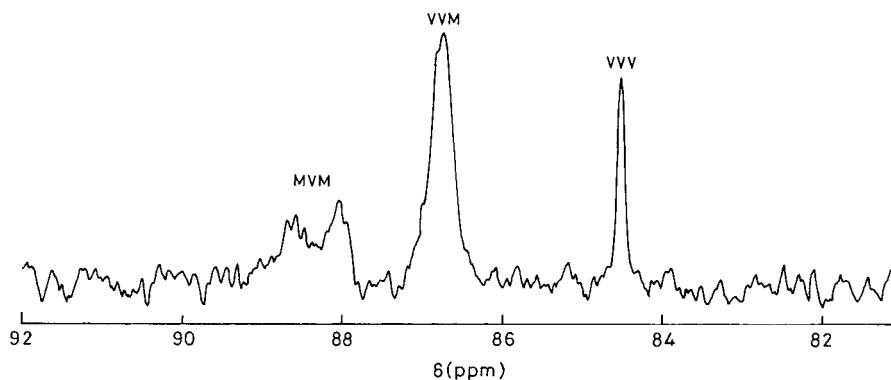
vinylidene chloride content and so is assigned to the VVV triad, whereas the resonating signals at 87.2 to 89.0 ppm that decrease with an increase in vinylidene chloride content are assigned to the MVM triad. The signal falling at 86.0–87.0 ppm whose intensity first increases and then decreases with increasing vinylidene chloride content is assigned to VVM triads. Further splitting observed in VVM and MVM triads may be due to tacticity effects. The methylene signals (Fig. 3), owing to the overlapping of V and M monomeric units, appear as dyads that are labeled as VV, VM, and MM and fall at 60.5–67.0 ppm, 55.0–60.5 ppm, and 52.8–55.0 ppm, respectively.

As to the triads centered on methyl methacrylate (M), although it is observed that all carbon resonances arising from the carbonyl, quaternary, and  $\alpha$ -methyl groups show a good splitting, not all of them could be studied because there are overlaps in the compositional sequences. Nevertheless, an attempt has been made to clearly assign these sequences.

The expanded quaternary carbon region of the M-unit of the copolymer ( $F_V = 0.43$ ), along with the corresponding quaternary carbon of the M-unit in poly(methyl methacrylate) is shown in Figure 5. For the copolymer spectra in this region, the peaks are sharp and well separated, and the complications due to tacticity are apparently unimportant. This is so because, in atactic poly(methyl methacrylate), the M-center triads of the

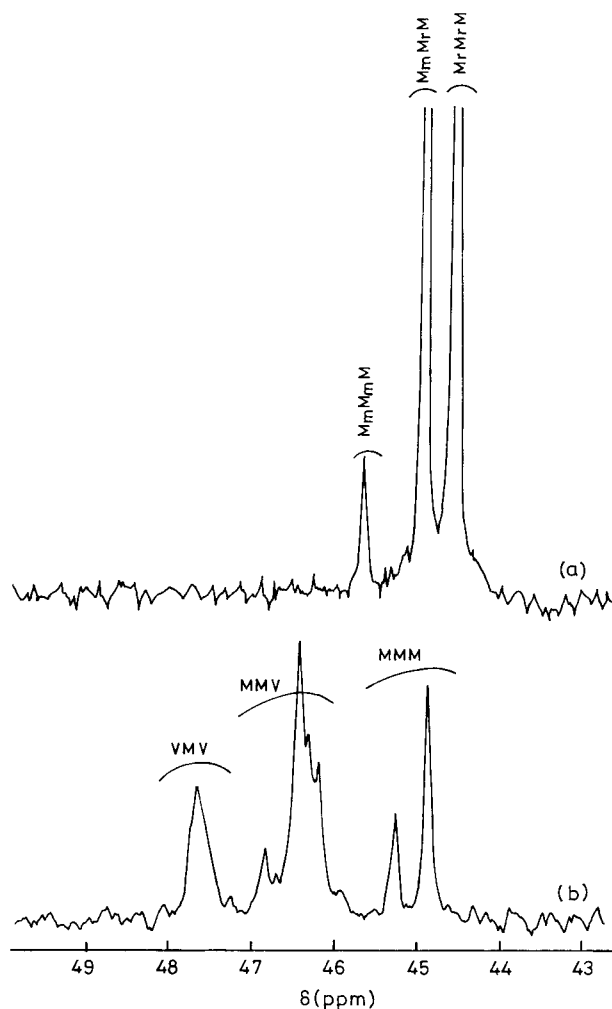


**Figure 3** 75 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the M/V copolymer ( $F_V = 0.43$ ).



**Figure 4** Expanded quaternary carbon resonance region of the V- monomeric unit of the M/V copolymer.

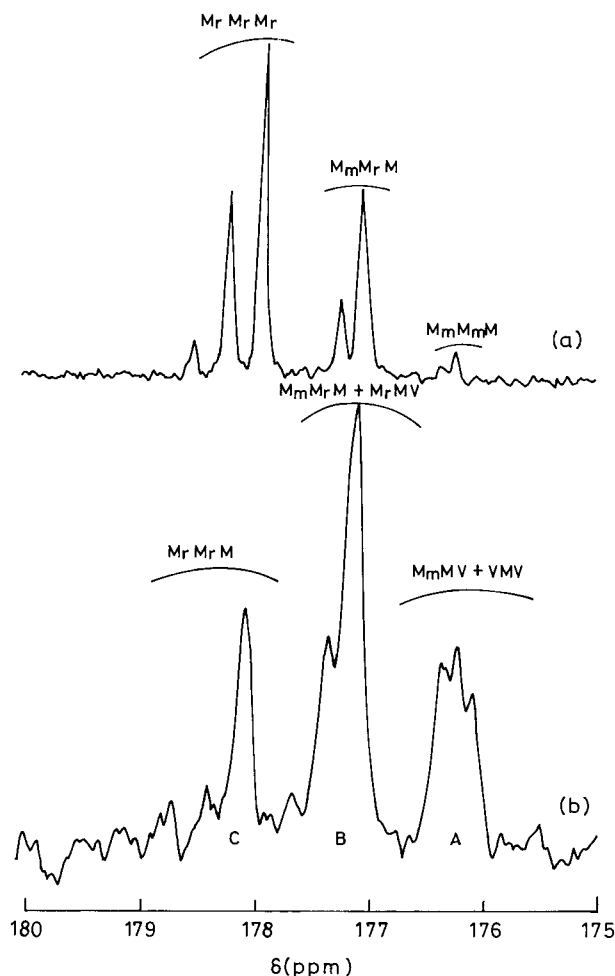
quaternary carbons are limited to the 44.5–45.6 ppm region [Fig. 5(a)]. By following the compositional trends in the series of spectra, the various



**Figure 5** Expanded quaternary carbon resonance region for (a) poly(methyl methacrylate) and (b) M- monomeric unit of the M/V copolymer ( $F_V = 0.43$ ).

groups of peaks were assigned to the three methyl methacrylate centered triads as indicated herein. The MMM triad in the copolymer is assigned to the signals at 44.0–45.6 ppm, in comparison with the poly(methyl methacrylate) spectrum and also on the fact that this group of resonances decreases with an increase in vinylidene chloride content. The VMV triad is assigned to 46.8–47.5 ppm resonances, whose intensities increase with an increase in vinylidene chloride content. Finally, the intermediate region at 45.6–46.8 ppm is assigned to the MMV triad, because it first increases and then decreases with variation in the composition.

As for carbonyl carbon and the  $\alpha$ -methyl carbon resonances, although the splitting pattern seems to be well separated and spread over a wide range of chemical shifts, the assignments to M- center triads is not so simple. This is because tacticity effects between two adjacent M- units bring a large chemical shift variation. In the carbonyl carbon region of poly(methyl methacrylate) [Fig. 6(a)], the MrMrM triad appears at 177.8–178.4 ppm, the MmMrM triad shifts upfield at 176.9–177.2 ppm, and the MmMmM triad (although its intensity is very low) goes most upfield at 176.2 ppm. It is observed from the methyl methacrylate/vinylidene chloride spectrum [Fig. 6(b)] that the carbonyl carbon resonances are distributed over three regions: 175.7–176.7 ppm (A); 176.7–177.7 ppm (B), and 177.7–178.7 ppm (C). In comparison with poly(methyl methacrylate), all three regions have the MMM triad sequence, predominantly in regions B and C. Region B is assigned to MrMrM, whereas C is assigned to the MmMrM tactic sequence. Now the addition of another comonomer vinylidene chloride (V) brings a further chemical shift variation for MMV and VMV triads. Because vinylidene chloride itself is tacticity insensitive because of its symmetry, the VMV triad

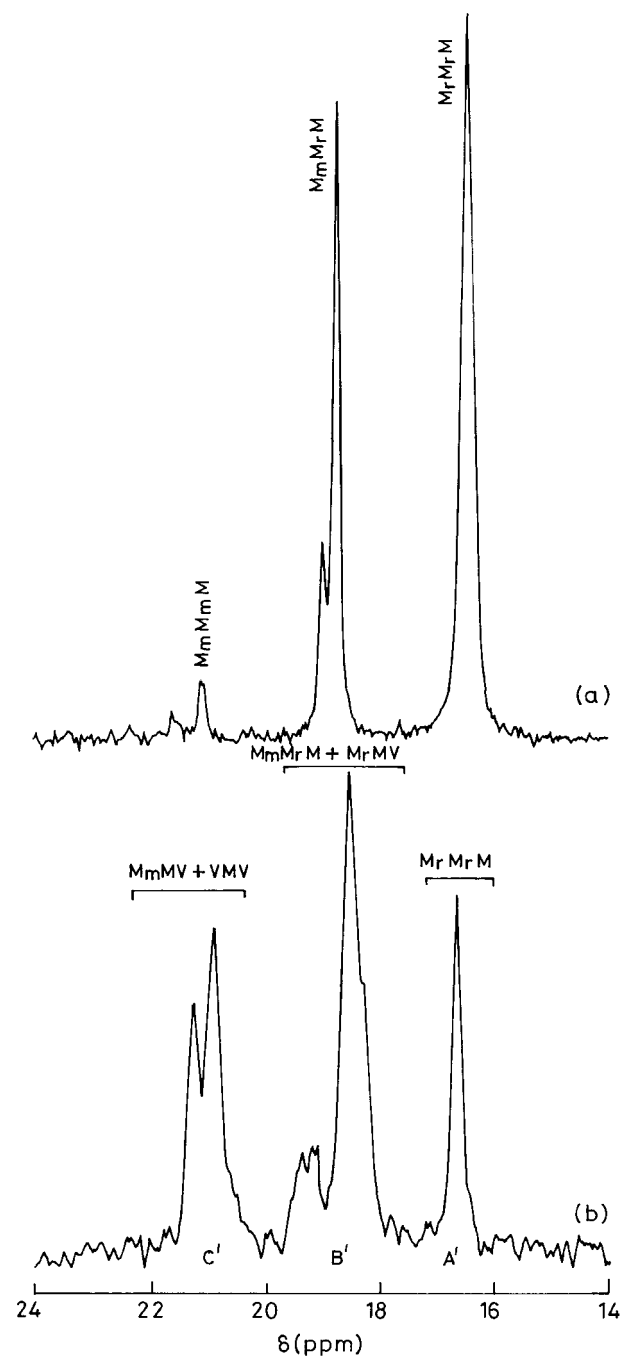


**Figure 6** Expanded carbonyl carbon resonance region for the (a) poly(methyl methacrylate) and (b) M-monomeric unit of the M/V copolymer ( $F_V = 0.43$ ).

is expected to appear at one position and is observed in region A. Considering the MMV triad, the tacticity effects between the two M- units affects the chemical shift and hence it appears in both region A (MmMV) and region B (MrMV).

The assignment of the  $\alpha$ -methyl resonance signals, 16.30–22.0 ppm in Figure 7 of the methyl methacrylate/vinylidene chloride copolymer is also made on the similar lines as done for the carbonyl resonating signals. The  $\alpha$ -methyl resonating signals also shows high chemical shift variation due to tacticity effects in the poly(methyl methacrylate) spectrum, but the order of tactic sequences is reversed with respect to the carbonyl sequences. The MrMrM triad appears the most upfield at 16.5 ppm; MmMrM at 18.8–19.1 ppm and MmMmM at 20.8–22.4 ppm in the poly(methyl methacrylate) spectrum [Fig. 7(a)]. Three regions are observed in the copolymer spec-

trum: 16.3–17.5 ppm (A'), 17.5–20.0 ppm (B'), and 20.0–22.0 ppm (C'). Thus, the MMM triad appears in all three regions, but predominantly in regions A' and B', because the MmMmM tactic sequence is very low. Regions A' and B' are thus assigned to MrMrM and MmMrM, respectively. The VMV triad is assigned only in region C',

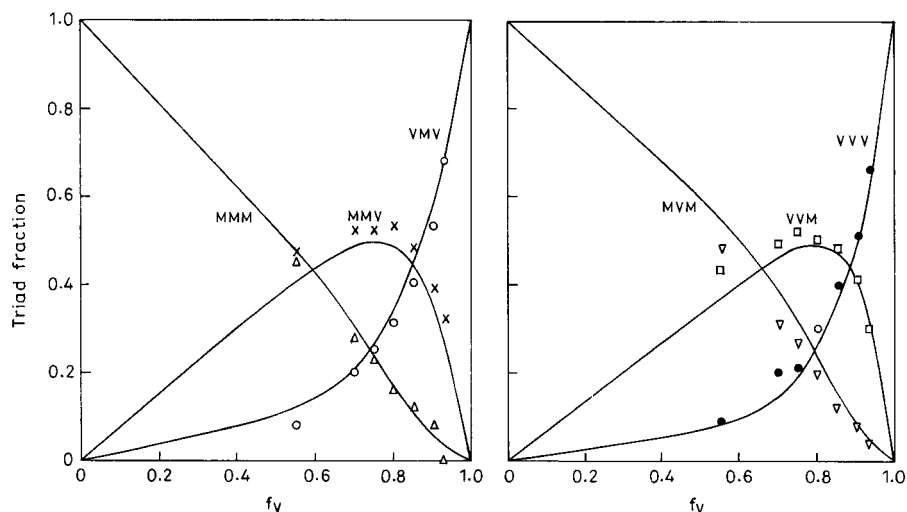


**Figure 7** Expanded  $\alpha$ -methyl carbon resonance region for the (a) poly(methyl methacrylate) and (b) M-monomeric unit of the M/V copolymer ( $F_V = 0.43$ ).

**Table II Comparison of the Triad Compositions Calculated from the Alfrey Mayo Model and the MC Simulation Method Using  $r_V = 0.26$  and  $r_M = 2.88$  with the Experimentally Determined Triad Fractions for the M/V Copolymer**

Signal No.	Copolymer Composition ( $F_V$ )	Triads	Triad Compositions <sup>a</sup>		
			Alfrey Mayo	NMR <sup>b</sup> $^{13}\text{C}\{^1\text{H}\}$	MC
1	0.2	VVV	0.02	0.04	0.01
		VVM	0.25	0.34	0.15
		MVM	0.73	0.62	0.84
		MMM	0.66	0.71	0.78
		MMV	0.30	0.29	0.21
		VMV	0.04	0.0	0.01
2	0.43	VVV	0.14	0.20	0.10
		VVM	0.47	0.49	0.44
		MVM	0.39	0.31	0.46
		MMM	0.31	0.28	0.33
		MMV	0.49	0.52	0.49
		VMV	0.20	0.20	0.18
3	0.48	VVV	0.19	0.21	0.15
		VVM	0.49	0.52	0.48
		MVM	0.32	0.27	0.37
		MMM	0.24	0.23	0.24
		MMV	0.50	0.52	0.50
		VMV	0.26	0.25	0.26
4	0.55	VVV	0.26	0.30	0.28
		VVM	0.50	0.50	0.50
		MVM	0.24	0.20	0.22
		MMM	0.17	0.16	0.12
		MMV	0.49	0.53	0.45
		VMV	0.34	0.31	0.43
5	0.62	VVV	0.36	0.40	0.45
		VVM	0.48	0.48	0.44
		MVM	0.16	0.12	0.11
		MMM	0.11	0.12	0.07
		MMV	0.45	0.48	0.38
		VMV	0.44	0.40	0.55
6	0.71	VVV	0.49	0.51	0.61
		VVM	0.42	0.41	0.34
		MVM	0.09	0.08	0.05
		MMM	0.06	0.08	0.02
		MMV	0.37	0.39	0.26
		VMV	0.57	0.53	0.72
7	0.78	VVV	0.60	0.66	0.73
		VVM	0.35	0.30	0.25
		MVM	0.05	0.04	0.02
		MMM	0.03	0.00	0.01
		MMV	0.29	0.32	0.18
		VMV	0.68	0.68	0.81

<sup>a</sup> V- and M- centered triad fractions add up to unity.<sup>b</sup> Triad fractions determined using quaternary carbon resonance signals of V- and M- centered triads of  $^{13}\text{C}$  NMR.



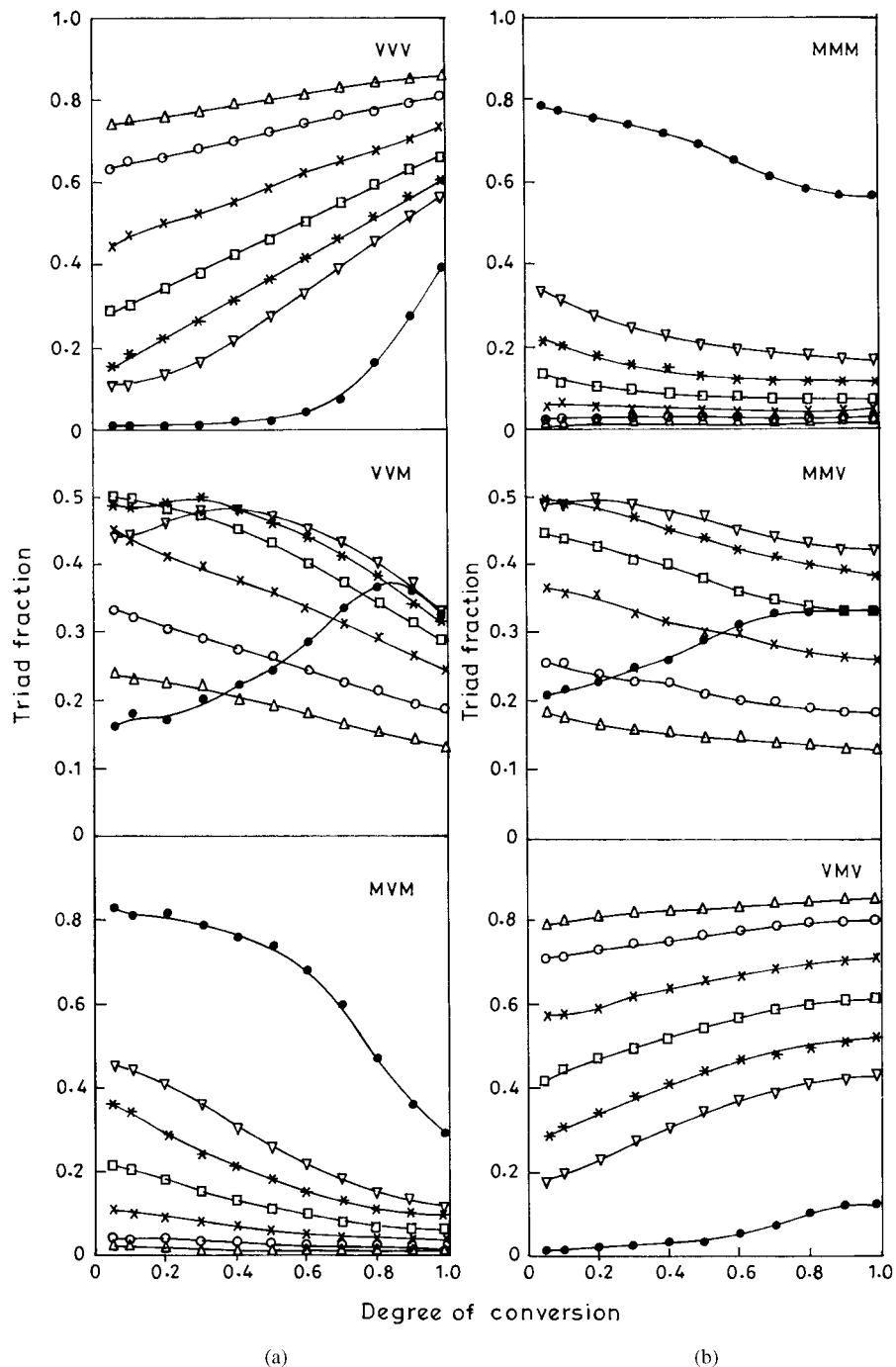
**Figure 8** Variation of V- and M- center triad fractions obtained from theoretical calculation (solid lines) and NMR spectroscopy (symbols) for the M/V copolymer plotted against feed mole fraction of vinylidene chloride ( $f_V$ ).

because it is tactic insensitive. Then, the MMV triad goes in two regions (*viz.* B' and C') corresponding to MrMV and MmMV tactic sequences, respectively. Similar kinds of assignments were attempted and explained by Aerdtts and colleagues.<sup>11</sup>

Thus, the best-suited resonating signals for the study of the copolymerization mechanism are the quaternary carbon resonating signals of the V- and M- monomeric units, because they allow determination of the V- and M- centered triad fractions, respectively. The experimental triad fractions are obtained by curve-fitting of the resonance signals of these regions on the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum. The triad fractions thus obtained are then compared with the theoretically obtained triad fractions using the Alfrey Mayo model using the Harwood program.<sup>15</sup> The terminal model reactivity ratios used are  $r_V = 0.26$  and  $r_M = 2.88$ . The good agreement between these values is seen from Table II and can also be seen graphically in Figure 8. Figure 8 shows the variation of V- and M- center triad fractions against the mole fraction of vinylidene chloride, where the symbols represent the experimentally determined (NMR) triad fractions, and the solid lines represent the theoretically calculated (first-order Markov model) triad fractions. The correlation coefficient between the experimental and theoretical data is  $R = 0.98$ . It is observed from Fig. 8 that MMV and MVV reach the maximum value at 0.75 and 0.80 feed mole fraction of V, respectively.

The Monte Carlo (MC) simulation method<sup>16</sup> is also used to monitor the changes in copolymer sequence behavior during the course of the poly-

merization. The triad fractions obtained from MC methods are also found to be in good agreement with theoretical and experimental triad fraction values, as seen in Table II. The correlation coefficient between the simulated data (MC) and the experimental data (NMR) is 0.93. The MC method can also be used to calculate the triad concentrations at various degrees of polymerization. Figure 9(a,b) shows the variation of the V- and M- centered triad concentrations as a function of fractional conversions for different feed mole fractions. It is observed that, with the progress of copolymerization, the monomer with higher reactivity ratios (*i.e.*, methyl methacrylate) is consumed faster than the other one (vinylidene chloride). This is seen from Figure 9, where the VVV triad increases as conversion increases. At lower feed mole fractions, the triad fraction (VVV) increases only at higher conversions as methyl methacrylate is consumed faster than vinylidene chloride comonomer. Similarly, the MMM triad concentration decreases as fractional conversion increases, as expected. For  $f_V > 0.9$ , the decrease is very small, whereas there is a significant decrease when  $f_V < 0.9$ , as conversion increases. For the VVM and MMV triads, the concentration first increases, goes through a maxima, and then decreases as the conversion increases. Maxima shift toward higher conversion as  $f_V$  decreases. For  $f_V > 0.8$ , no maxima are seen; instead, there is a steady decrease of triad concentration as the degree of polymerization increases. For the MVM and VMV triads, the concentration decreases and increases, respectively, with an increase of frac-



**Figure 9** Variation of (a) V- and (b) M- centered triad fractions plotted as a function of fractional conversion for different feed mole fractions:  $f_V = 0.4$  (●),  $f_V = 0.70$  (▽),  $f_V = 0.75$  (\*),  $f_V = 0.80$  (□),  $f_V = 0.85$  (×),  $f_V = 0.90$  (○),  $f_V = 0.93$  (△).

tional conversion. The decrease in the MVM triad is much sharper for lower feed mole fraction ( $f_V$ ) at higher conversions. For the VMV triad at the lower feed mole fraction, concentration increases only at higher conversion as the reactivity ratio of vinylidene chloride is less than that of methyl methacrylate.

## CONCLUSIONS

Characterization of the monomer sequence distribution of methyl methacrylate/vinylidene chloride has been investigated. The complete assignment of the  $^{13}\text{C}$  NMR spectrum has been attempted. It is observed that the carbonyl and



$\alpha$ -methyl resonance signals, which are in the side chain of the polymer, show compositional and configurational variations over a larger chemical shift region, whereas the quaternary carbon resonances that form part of the main chain show tactic variations over a smaller chemical shift region. The quaternary carbons of V and M monomeric units that are used to study the copolymerization behavior give the best fit to the Alfrey Mayo model (first-order Markov model). The triad fractions determined for V- and M- centered triads changes with a change in degree of conversion.

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