

# Investigation of Microstructure of the *N*-Vinyl-2-pyrrolidone/Methyl Methacrylate Copolymers by NMR Spectroscopy

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**ABSTRACT:** The copolymers containing *N*-vinyl-2-pyrrolidone (V) and methyl methacrylate (M) units of different compositions were synthesized by free radical bulk polymerization. The copolymer composition of these copolymers was determined by CHN analysis. The distortionless enhancement by polarization transfer (DEPT) technique was used to resolve the methine, methylene, and methyl resonance signals in the V/M copolymer. Comonomer reactivity ratios were determined by the Kelen–Tudos (KT) and nonlinear least-square error-in-variable (EVM) methods.  $^1\text{H}$ – $^{13}\text{C}$  Heteronuclear shift quantum correlation spectroscopy (HSQC) and  $^1\text{H}$ – $^1\text{H}$  homonuclear total correlation spectroscopy (TOCSY) spectra were used for the resolution of the proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectrum of the V/M copolymers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1328–1336, 2002

**Key words:** *N*-vinyl-2-pyrrolidone; methyl methacrylate; copolymers; sequence distribution; microstructures; 1D and 2D NMR

## INTRODUCTION

The macroscopic properties of bulk polymers are fundamentally influenced by their chain level microstructures, which can be investigated by nuclear magnetic resonance (NMR) spectroscopy.<sup>1–3</sup> Because of the higher order compositional or configurational sequences, complicated split resonance signals are usually observed in high-resolution NMR spectra. Two-dimensional (2D) NMR spectroscopy, especially  $^1\text{H}$ – $^{13}\text{C}$  heteronuclear shift quantum correlation spectroscopy (HSQC) and  $^1\text{H}$ – $^1\text{H}$  homonuclear total correlation spectroscopy (TOCSY), is a powerful tool for the investigation of microstructure of copolymers in

terms of compositional<sup>4,5</sup> and configurational<sup>6–8</sup> sequences. The microstructural studies in copolymers are of immense help in establishing the structure–properties relationships.<sup>9,10</sup> *N*-Vinyl-2-pyrrolidone, being amphiphilic, is widely used as a comonomer in various copolymers of commercial interest.<sup>11,12</sup>

Poly(methyl methacrylate) (PMMA) and the copolymer of methyl methacrylate with *N*-vinyl-2-pyrrolidone are widely used as membranes for ultrafiltration and for fuel cells. In medical applications, these copolymers are used as soft contact lenses, as tablet coatings, as blood-compatible polymers, and as anticoagulant films. Brar et al. reported the sequence distributions in copolymers of methyl methacrylate with acrylonitrile,<sup>13</sup> methacrylonitrile,<sup>14</sup> vinylidene chloride,<sup>15</sup> etc. We reported the sequence distributions of *N*-vinyl-2-pyrrolidone with acrylonitrile<sup>16</sup> and glycidyl methacrylate<sup>17</sup> copolymers. The microstructure of

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**Table I** Copolymer Composition Data and Molecular Weight Averages of *N*-Vinyl-2-pyrrolidone/Methyl methacrylate (V/M) Copolymers<sup>a</sup>

Sample No.	Feed Mole Fraction		Copolymer Composition		$\bar{M}_w$ $\times 10^{-4}$	$\bar{M}_n$ $\times 10^{-4}$	$\bar{M}_z$ $\times 10^{-4}$	$\bar{M}_{z+1}$ $\times 10^{-4}$	<i>P</i>
	$f_V$	$f_M$	$F_V$	$F_M$					
VM7	0.98	0.02	0.66	0.34	8.31	7.14	9.76	11.55	1.16
VM8	0.96	0.04	0.55	0.45	9.00	7.81	10.34	11.89	1.15
VM9	0.94	0.06	0.50	0.50	7.69	6.48	9.00	10.86	1.14
VM10	0.92	0.08	0.43	0.57	6.48	5.78	7.51	9.13	1.12
VM11	0.90	0.10	0.33	0.67	5.82	5.28	6.69	8.14	1.10

<sup>a</sup> $f_V$  and  $f_M$  are the mole fractions of V and M comonomers, respectively, in feed;  $F_V$  and  $F_M$  are the mole fractions of V and M comonomers, respectively, in copolymers;  $\bar{M}_w$ ,  $\bar{M}_n$ ,  $\bar{M}_z$ , and  $\bar{M}_{z+1}$  are the weight average, number average, Z average and (Z+1) average molecular weights of copolymers, respectively; and P is the polydispersity

the *N*-vinyl-2-pyrrolidone/methyl methacrylate copolymer (V/M) system has not been reported. In this paper we report the complete assignment of <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of V/M copolymers in terms of compositional and configurational sequences from the results of analysis by carbon-13 distortionless enhancement by polarization (DEPT), HSQC, and TOCSY experiments.

## EXPERIMENTAL

*N*-Vinyl-2-pyrrolidone (Fluka) and methyl methacrylate (CDH) were distilled under reduced pressure and stored below 5 °C. *N*-Vinyl-2-pyrrolidone/methyl methacrylate (V/M) copolymers with different mole fractions (V/M) in feed were prepared by free radical bulk polymerization at 60 °C. Benzoyl peroxide (BPO) was used as an initiator. The percent conversion was kept <10% by precipitating the copolymer in petroleum ether (Qualigens). The copolymers were purified using chloroform/petroleum ether system.

The copolymer composition was calculated from the percentage of nitrogen in the copolymers. The C, H, and N analysis was performed on a Perkin Elmer 240C Elemental Analyzer. The various one-dimensional (1D) NMR experiments (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, DEPT) and 2D NMR (HSQC, TOCSY) experiments were performed in CDCl<sub>3</sub> on a Bruker DPX-300 NMR spectrometer using standard pulse sequences described in our previous papers.<sup>18,19</sup> The molecular weight averages were determined by gel permeation chromatography (GPC) using polystyrene as narrow standards, as given in Table I. The molecular weight determination was carried out on a Waters GPC

instrument (Styragel - HR4 column) attached to a refractive index detector.

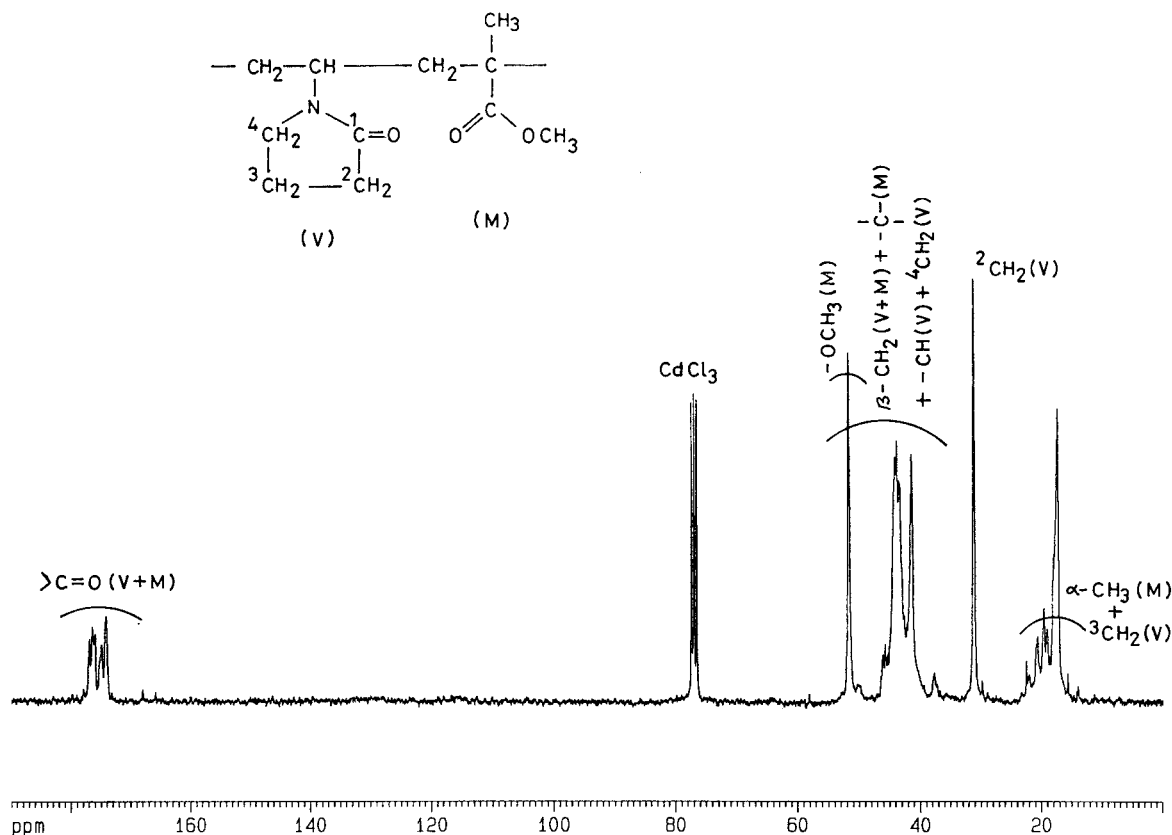
## RESULTS AND DISCUSSION

### Reactivity Ratio Determination

The compositions of V/M copolymers were determined from the percent nitrogen content of the copolymers. The feed mole fraction and the copolymer composition are shown in Table I. The copolymer composition data obtained from the CHN analysis were used to estimate the terminal model reactivity ratios by the Kelen–Tudos (KT)<sup>20</sup> method. The initial estimate of the reactivity ratios, along with the copolymer composition data, were used for the calculation of the reactivity ratios by the nonlinear least-square error in-variable (EVM)<sup>21</sup> method with the RREVM<sup>22</sup> computer program. The values of the reactivity ratios calculated from the KT and EVM methods are, respectively,  $r_V = 0.02 \pm 0.005$ ,  $r_M = 5.15 \pm 0.04$  and  $r_V = 0.027$ ,  $r_M = 5.05$ . These reactivity ratio values are in good agreement with the values reported in the literature.<sup>23</sup>

### <sup>13</sup>C{<sup>1</sup>H} NMR Studies

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the V/M copolymer along with the complete signal assignments ( $F_V = 0.50$ ) in CDCl<sub>3</sub> are shown in Figure 1. The carbon signals around  $\delta 177.70$ – $173.50$  ppm are assigned to carbonyl carbon (>C=O) resonances of both V and M units. The carbonyl carbon signals of both V and M units appear as a multiplet, indicating that they are sensitive to composi-



**Figure 1** The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (75.5 MHz) of a V/M copolymer ( $F_V = 0.50$ ) in  $\text{CDCl}_3$ .

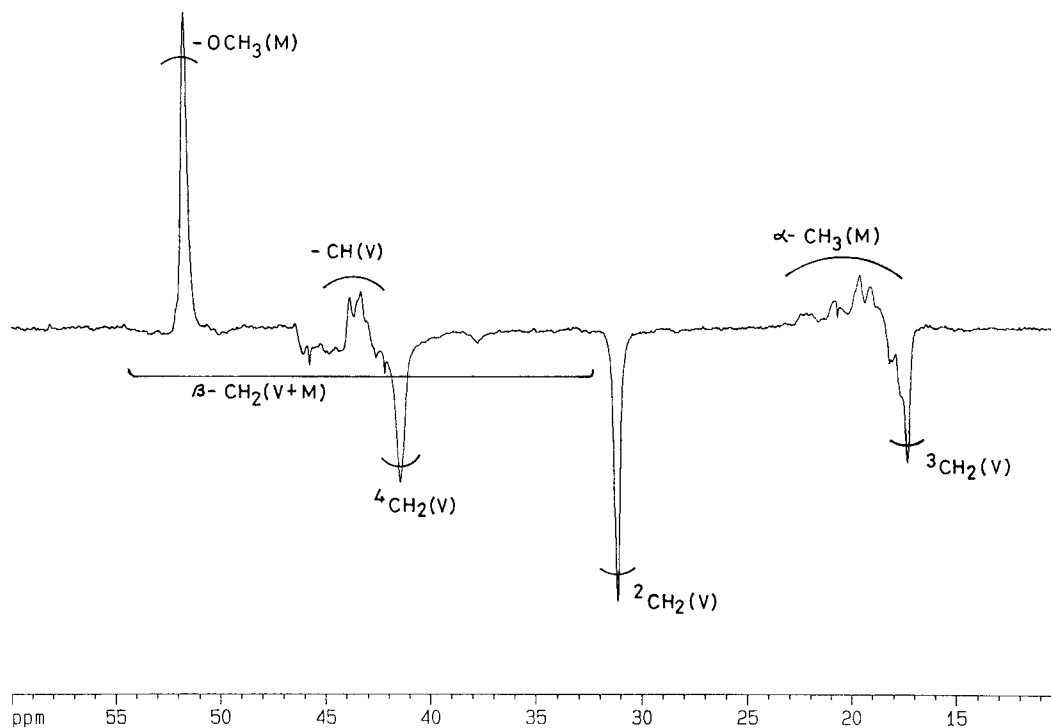
tional and configurational sequences. The spectral region around  $\delta 13.00$ – $55.00$  ppm is quite complex and overlapping. This region can be assigned to aliphatic carbon resonances in the backbone and the side chain of the V/M copolymer. In comparison with the homopolymer spectrum, there is a considerable amount of overlap between the quaternary and  $\beta$ - $\text{CH}_2$  carbon of M unit with the methine,  $\beta$ - $\text{CH}_2$ , and  $^4\text{CH}_2$  carbons of the V unit. Similarly, there is a considerable overlap between the  $\alpha$ -methyl of M and the methylene ( $^3\text{CH}_2$ ) of the pyrrolidone ring carbons. The extent of the overlap of these carbon signals can not be ascertained from the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum alone. These overlapping regions can be resolved by DEPT and HSQC NMR experiments.

The DEPT-135 NMR spectrum ( $F_V = 0.50$ ) in  $\text{CDCl}_3$  of the V/M copolymer, where the methine and methyl carbon resonances are in positive phase and methylene carbon resonances are in negative phase, is shown in Figure 2. The side chain ring methylene carbon signals are assigned around  $\delta 41.46$  ( $^4\text{CH}_2$ ),  $\delta 31.15$  ( $^2\text{CH}_2$ ), and  $\delta 17.34$  ( $^3\text{CH}_2$ ) ppm.

These assignments are made by comparison with the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of poly(*N*-vinyl-2-pyrrolidone).<sup>19</sup> All the methylene carbon resonances of the pyrrolidone ring are singlet, showing that they are insensitive to compositional and configurational sequences.

The  $-\text{OCH}_3$  carbon signals of M unit resonates around  $\delta 51.79$  ppm, as determined by comparison with the spectrum of PMMA.<sup>24</sup> The  $\beta$  methylene carbon of both the V and M units resonate around  $\delta 32.00$ – $54.00$  ppm. The signals around  $\delta 42.76$ – $45.8$  ppm and  $\delta 15.00$ – $24.00$  ppm are assigned to the methine carbon resonances of the V unit and the methyl carbon resonances of the M unit respectively, in copolymer.

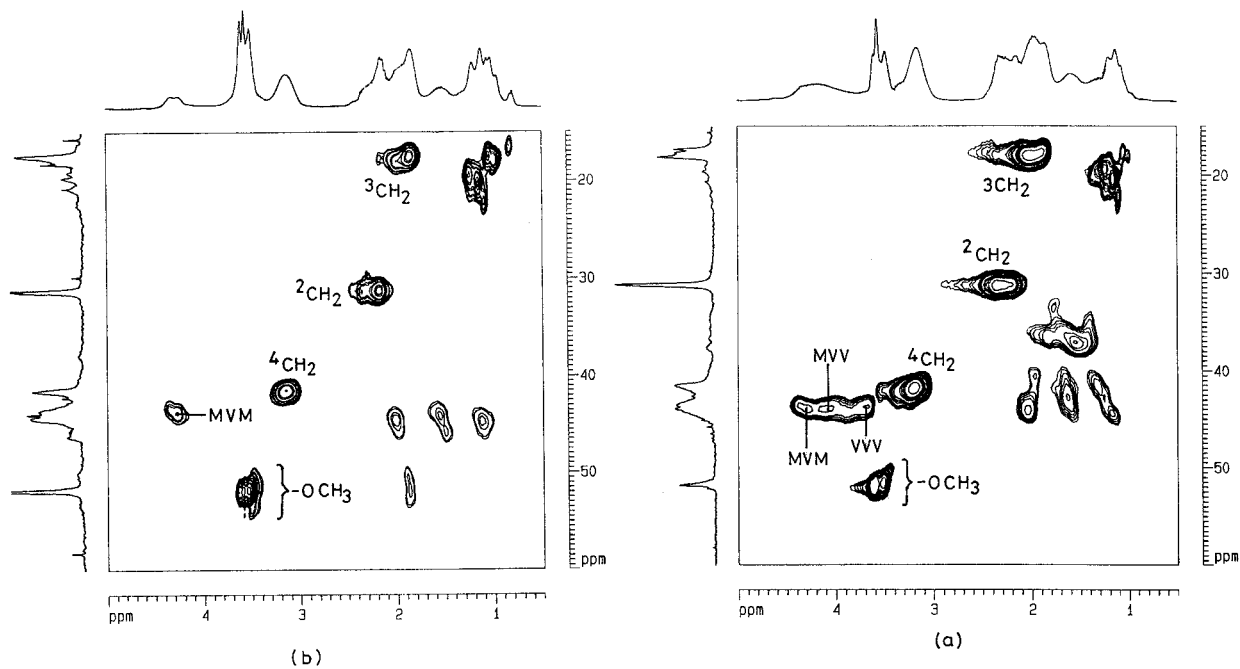
The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of methine carbon resonance (V) was resolved with the help of the 2D HSQC NMR spectrum (Figure 3). The cross peaks around  $\delta 43.9/4.30$ ,  $\delta 43.8/4.10$ , and  $\delta 43.5/3.70$  ppm are assigned to MVM, MVV, and VVV triads compositional sequences, respectively, on the basis of the change in intensity with the change in composition of copolymer.



**Figure 2** The DEPT-135 spectra of a V/M copolymer ( $F_V = 0.50$ ) in  $\text{CDCl}_3$ .

The  $\beta\text{-CH}_2$  region of V/M copolymers due to its symmetry is sensitive to dyad, tetrad, etc. sequences. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of

$\beta$ -methylene are quite complex and overlapped and can be resolved with the help of 2D HSQC NMR spectra (Table II). This region is divided



**Figure 3** The 2D HSQC NMR spectrum of V/A copolymer in  $\text{CDCl}_3$  [ $F_V =$  (a) 0.66 (b) 0.33].

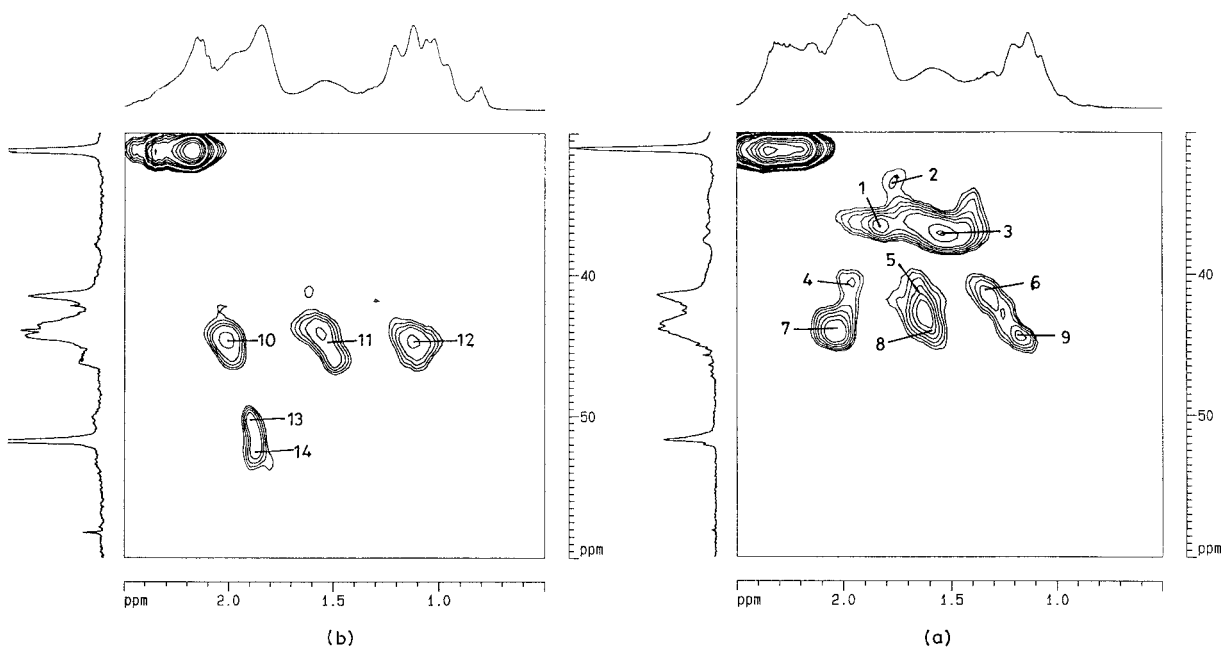
**Table II** Compositional and Configurational Assignment of Methylene Carbon ( $\beta$ -CH<sub>2</sub>) signals of the V/M Copolymers from 2D HSQC NMR Spectrum (Figure 4)

Peak No.	HSQC		Assignment
	<sup>13</sup> C{ <sup>1</sup> H} ppm	<sup>1</sup> H ppm	
1, 3	36.4	1.85, 1.55	V <sub>m</sub> V
2	33.0	1.75	V <sub>r</sub> V
4, 6	41.5	1.98, 1.34	VV <sub>m</sub> MV
5	41.5	1.63	VV <sub>r</sub> MV
7, 9	44.0	2.04, 1.18	MV <sub>m</sub> MV
8	44.0	1.59	MV <sub>r</sub> MV
10, 12	45.0	2.02, 1.12	MV <sub>m</sub> MM
11	45.0	1.52	MV <sub>r</sub> MM
13	50.5	1.88	M <sub>m</sub> M
14	52.6	1.87	M <sub>r</sub> M

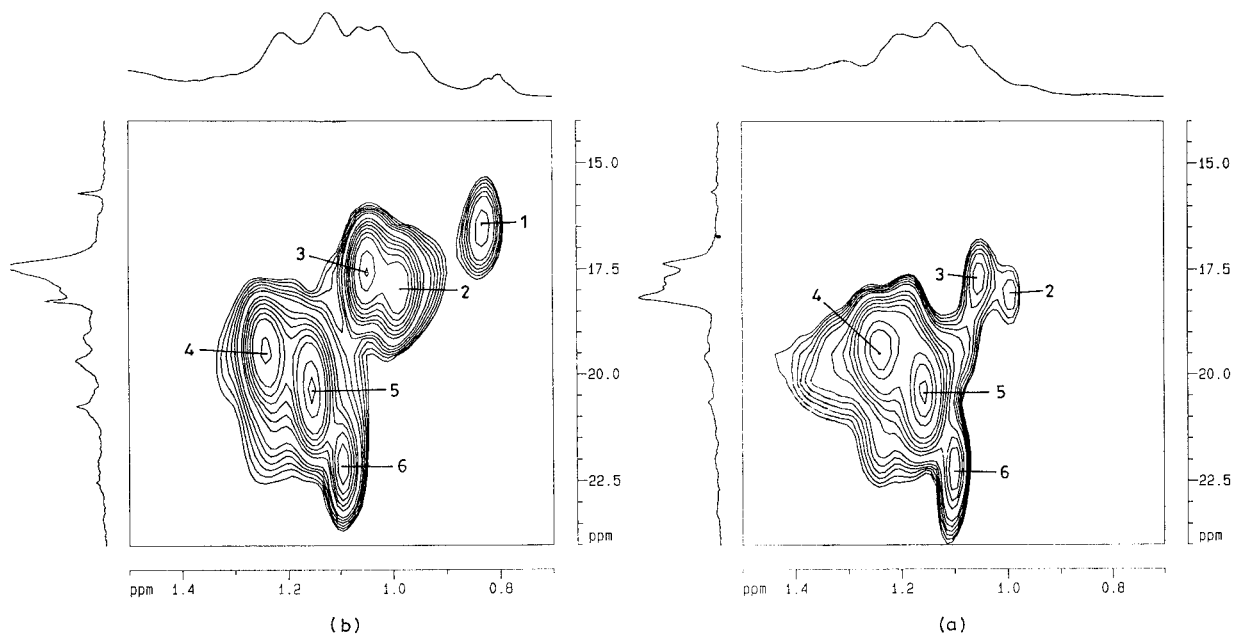
into three broad envelopes, VV, VM, and MM dyads, on the basis of change in intensity of signals with the change in composition of copolymer, as shown in Figure 4(a, b). These three dyads are assigned around  $\delta$ 32.50–39.00,  $\delta$ 39.00–48.50, and  $\delta$ 48.50–54.00 ppm, respectively. The VV and VM dyads show further splitting into three cross peaks along the proton axis due to the stereochemical configurations. The meso (*m*) configura-

tion gives two cross peaks due to two nonequivalent methylene protons, and the racemic (*r*) configuration gives one cross peak in between these two cross peaks, corresponding to meso configurations. In the VV dyad, the two cross peaks at  $\delta$ 36.4/1.85 (1) and  $\delta$ 36.4/1.55 (3) ppm are assigned to V<sub>m</sub>V because of the two inequivalent protons in the meso configuration and that at  $\delta$ 33.0/1.75 (2) ppm is assigned to V<sub>r</sub>V because of the racemic configuration, as determined by comparison with the HSQC NMR spectrum of poly(*N*-vinyl-2-pyrrolidone).<sup>19</sup>

In the VM region, the tetrads VVMV ( $\delta$ 41.0 ppm), MVMV (VVMM) ( $\delta$ 43.9 ppm), and MVMM ( $\delta$ 45.0 ppm) are assigned on the basis of change in intensity with the change in copolymer composition. Further splitting in these tetrads along the proton axis is assigned to meso (*m*) and racemic (*r*) configurational sequences, as in the VV dyad. The cross peaks around  $\delta$ 41.5/1.98 (4) and  $\delta$ 41.5/1.34 (6) ppm in the VVMV tetrad are assigned to two inequivalent protons in the meso (*m*) configuration, VV<sub>m</sub>MV, and the cross peak around  $\delta$ 41.5/1.63 (5) ppm is assigned to racemic (*r*) configuration VV<sub>r</sub>MV. In the MVMV(VVMM) tetrad, the cross peaks at  $\delta$ 44.0/2.04 (7) and  $\delta$ 44.0/1.18 (9) ppm are assigned to the MV<sub>m</sub>MV configuration, and the cross peak at  $\delta$ 44.0/1.59 (8) ppm is assigned to the MV<sub>r</sub>MV configuration. Similarly, in



**Figure 4** Expanded 2D HSQC NMR spectra showing the methylene resonances of the V/M copolymers with the compositions in CDCl<sub>3</sub> [ $F_V$  = (a) 0.66 (b) 0.33].



**Figure 5** Expanded 2D HSQC NMR spectra showing the methyl resonances of M unit of V/M copolymers with the compositions in  $\text{CDCl}_3$  ( $F_V =$  (a) 0.66 (b) 0.33).

the MVMM tetrad, the cross peaks at  $\delta 45.0/2.02$  (10) and  $\delta 45.0/1.12$  (12) ppm are assigned to  $MV_mMM$ , and the cross peak at  $\delta 45.0/1.52$  (11) ppm to  $MV_rMM$  configurational sequences. In the MM dyad region, the two cross peaks around  $\delta 50.5/1.88$  (13) and  $\delta 52.6/1.87$  (14) ppm are assigned to  $M_mM$  and  $M_rM$  configurational sequences, respectively, by comparing with the PMMA, as shown in Figure 4(b). The assignments 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10, 11, 12, 13, 14 are done according to Figure 4a ( $F_V = 0.66$ ), and Figure 4b ( $F_V = 0.33$ ), respectively. The remaining peaks may be due to higher configurational or compositional sequences. All the assignments in the  $\beta\text{-CH}_2$  are shown in Table II.

The  $\alpha$ -methyl region of the M unit in the 1D ( $^{13}\text{C}\{^1\text{H}\}$  and  $^1\text{H}$  NMR) spectra is quite complex and overlapped and can be assigned only with the help of the 2D HSQC NMR spectrum, which is shown in Figure 5(a, b), which shows both compositional as well as configurational sensitivity. The  $\alpha$ -methyl carbon region of the M unit is divided into three broad envelopes, MMM, MMV, and VMV, on the basis of change in intensity of signals with the change in copolymer composition. Further splitting within these compositional triads can be assigned to configurational or higher order compositional sequences. The cross peaks at  $\delta 16.50/0.83$  (1) and  $\delta 18.00/0.98$  (2) ppm are assigned to  $M_rM_rM$  and  $M_rM_mM$  configura-

tional sequences on the basis of the assignments made in the 2D HSQC NMR spectrum of PMMA.<sup>24</sup> Similarly, the other cross peaks at  $\delta 17.68/1.45$  (3) and  $\delta 19.50/1.24$  (4) ppm, which do not show relative change in the intensity with the change in copolymer composition, are assigned to  $M_rM_rV$  and  $M_rM_mV$  configurational sequences, respectively, as shown in Figure 5. The intensity of  $M_mM_mM$  configurational sequence is less and merges with the  $V_rM_rV$  sequence, which is assigned to the cross peak around  $\delta 20.35/1.15$  (5) ppm by comparing with the spectrum of PMMA.<sup>24</sup> The cross peak around  $\delta 21.20/1.09$  (6) ppm is assigned to  $V_rM_mV$  configurational sequences. Further splitting may be due to higher compositional sequences. All these assignments are shown in Figure 5a ( $F_V = 0.66$ ) and Figure 5b ( $F_V = 0.33$ ). The various  $\alpha$ -methyl assignments are shown in Table III.

The  $^1\text{H}$  NMR spectrum of the V/M copolymer ( $F_V = 0.50$ ) in  $\text{CDCl}_3$  with all the assignments is shown in Figure 6. The overlapped proton signals completely assigned by the one-to-one correlation between the carbon and proton signals in the 2D HSQC NMR spectrum (Figure 3). The methine proton signals of V unit are assigned to compositional triad sequences with the help of 2D HSQC NMR spectra, as discussed earlier. The main chain methylene proton signals of both the V and M unit resonate around  $\delta 2.15\text{--}0.90$  ppm, which

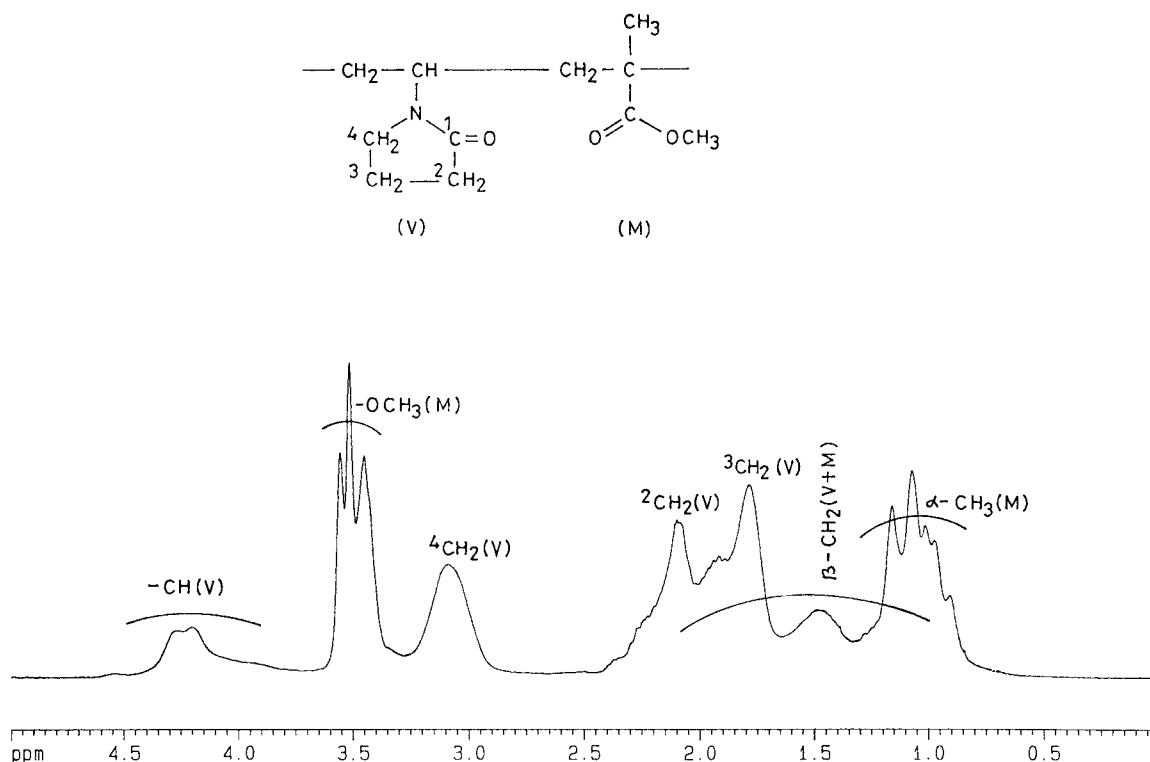
**Table III** Compositional and Configurational Assignment of Methyl Carbon Region of V/M Copolymers from 2D HSQC Spectrum (Figure 5)

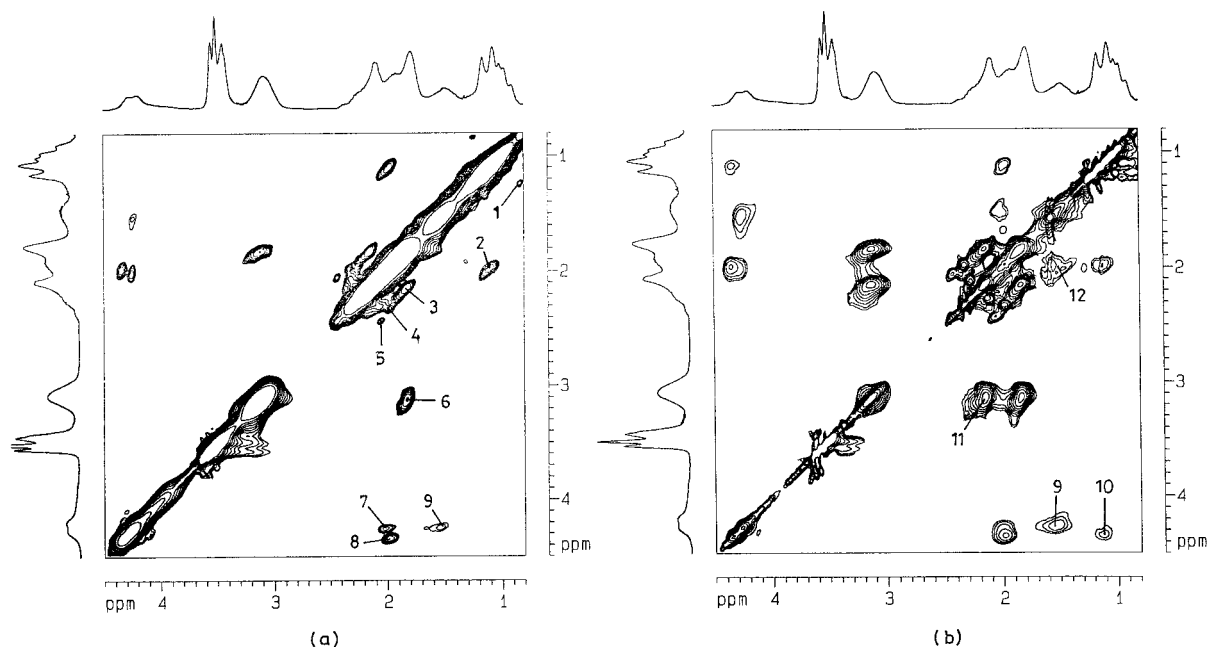
Peak No.	HSQC		Assignment
	$^{13}\text{C}\{^1\text{H}\}$ ppm	$^1\text{H}$ ppm	
1	16.50	0.83	$\text{M}_r\text{M}_r\text{M}$
2	18.00	0.98	$\text{M}_r\text{M}_m\text{M}$
3	17.68	1.45	$\text{M}_r\text{M}_r\text{V}$
4	19.50	1.24	$\text{M}_r\text{M}_m\text{V}$
5	20.35	1.15	$\text{V}_r\text{M}_r\text{V} + \text{M}_m\text{M}_m\text{M}$
6	21.20	1.09	$\text{V}_r\text{M}_m\text{V}$

are overlapping with different types of compositional and configurational sequences and thus difficult to assign. Similarly, the methyl ( $\alpha\text{-CH}_3$ ) proton signals ( $\delta 0.80\text{--}1.35$  ppm) are also overlapping with various types of compositional and configurational sequences. The three triad fractions are assigned as  $\delta 0.8\text{--}1.18$  ppm (MMM),  $\delta 1.02\text{--}1.35$  ppm (MMV), and  $\delta 1.05\text{--}1.20$  ppm (VMV).

The  $\text{--OCH}_3$  protons appear around  $\delta 3.15$  ppm and can be assigned by the cross peak around  $\delta 51.79/3.50$  ppm in the HSQC NMR spectrum.

The overlapping methylene protons of the side chain can be distinguished from the main chain methylene protons by 2D ( $^1\text{H}\text{--}^{13}\text{C}$ ) HSQC spectroscopy, as shown earlier. The side chain methylene proton signals can be assigned around  $\delta 3.10$  ( $^4\text{CH}_2$ ),  $\delta 2.12$  ( $^2\text{CH}_2$ ), and  $\delta 1.78$  ppm ( $^3\text{CH}_2$ ). These signals are assigned by the cross peaks at  $\delta 41.50/3.10$  ( $^4\text{CH}_2$ ),  $\delta 31.50/2.15$  ( $^2\text{CH}_2$ ), and  $\delta 17.50/1.81$  ppm ( $^3\text{CH}_2$ ) in the HSQC NMR spectrum. Thus, with the help of the 2D HSQC NMR spectrum, the overlapped  $^1\text{H}$  NMR spectrum is assigned completely.

**Figure 6** 300 MHz  $^1\text{H}$  NMR spectrum of a V/M copolymer ( $F_V = 0.50$ ) in  $\text{CDCl}_3$ .



**Figure 7** The 2D TOCSY NMR spectra of a V/M copolymer ( $F_V = 0.50$ ) in  $\text{CDCl}_3$  at (a) 4 ms and (b) 80 ms.

### 2D TOCSY NMR Studies

The various  $\text{CH}/\text{CH}_2$  proton couplings in the triad fractions can be assigned using the 2D TOCSY NMR spectrum. At a shorter mixing time (4 ms), one can easily see the direct coupling (AM spin type) between the bonded protons, whereas at a higher mixing time (80 ms), one can see the relay coupling (AMX spin type) through the magnetization transfer. The TOCSY (4 ms) NMR spectrum of the V/M copolymer ( $F_V = 0.66$ ) in  $\text{CDCl}_3$  is shown in Figure 7(a). The cross peak around  $\delta 1.14/0.85$  (1) ppm is assigned due to the geminal coupling in the  $\alpha\text{-CH}_3$  group. The cross peak at  $\delta 1.99/1.10$  (2) ppm appears due to coupling of  $\beta\text{-CH}_2$  of M unit with the  $\alpha\text{-CH}_3$  of M unit in the head-to-tail linkage, which is confirmed by comparing with PMMA.<sup>8</sup> The cross peaks around  $\delta 2.16/1.80$  (3),  $\delta 2.26/1.90$  (4), and  $\delta 2.36/2.00$  (5) ppm appear due to the coupling of  $^2\text{CH}_2$  with the  $^3\text{CH}_2$  of the pyrrolidone ring by comparing with the TOCSY NMR spectrum of the poly(*N*-vinyl-2-pyrrolidone).<sup>19</sup> Similarly, the cross peak at  $\delta 3.12/1.85$  (6) ppm is assigned due to the coupling of  $^4\text{CH}_2$  with the  $^3\text{CH}_2$  of the pyrrolidone ring. The cross peaks around  $\delta 4.25/2.02$  (7) and  $\delta 4.33/1.99$  (8) ppm are assigned due to the coupling of CH (V) with the  $\beta\text{-CH}_2$  of M unit. The cross peak  $\delta 4.35/1.53$  (9) is assigned due to the coupling of CH (V) with the  $\beta\text{-CH}_2$  of V unit in the main chain.

The four bond couplings are also possible, which are assigned in the 80 ms TOCSY spectrum (Figure 7b). The cross peak at  $\delta 4.35/1.12$  (10) ppm is assigned due to the coupling of CH (V) with the  $\alpha\text{-CH}_3$  of M unit. The cross peak around  $\delta 3.12/2.15$  (11) ppm is assigned due to coupling of  $^4\text{CH}_2$  with the  $^2\text{CH}_2$  of the pyrrolidone ring in the side chain. The cross peak at  $\delta 1.45/1.99$  ppm (12) is assigned due to coupling of  $\beta\text{-CH}_2$  of V unit with the  $\beta\text{-CH}_2$  of M unit, which confirms the head-to-tail linkage in the copolymer. All these possible couplings are shown in Table IV.

### CONCLUSIONS

The monomer reactivity ratios of the V/M copolymer are  $r_V = 0.027$  and  $r_M = 5.05$ . The overlapped and broad signals in carbon and proton spectra were assigned to various compositional and configurational sequences using 2D HSQC and TOCSY experiments. The methine carbon resonances of V unit were assigned to compositional triad sequences. The methyl carbon resonances of M unit were assigned to triad compositional and configurational sequences. The methylene carbon resonances were assigned to tetrad compositional and configurational sequences with the help of 2D HSQC NMR experiments.



**Table IV** 2D TOCSY  $^1\text{H}$ - $^1\text{H}$  Coherence of the V/M Copolymers

Peak No.	Proton (ppm)	Coupled to Proton (ppm)
1	$\alpha\text{-CH}_3$ (1.14)	$\alpha\text{-CH}_3$ (0.85) (geminal)
2	$\beta\text{-CH}_2$ of M (1.99)	$\alpha\text{-CH}_3$ of M (1.10)
3	$^2\text{CH}_2$ (2.16)	$^3\text{CH}_2$ (1.80)
4	(2.26)	(1.90)
5	(2.36)	(2.00)
6	$^4\text{CH}_2$ (3.12)	$^3\text{CH}_2$ (1.85)
7	CH (V) (4.25)	$\beta\text{-CH}_2$ in M (2.02)
8	(4.33)	(1.99)
9	CH (V) (4.25)	$\beta\text{-CH}_2$ of V (1.53)
10	CH (V) (4.35)	$\alpha\text{-CH}_3$ (1.12)
11	$^4\text{CH}_2$ (3.12)	$^2\text{CH}_2$ (2.15)
12	$\beta\text{-CH}_2$ of V (1.45)	$\beta\text{-CH}_2$ of M (1.99)

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