

Investigation of Microstructure of 4-Vinyl Pyridine–Methacrylonitrile Copolymers by NMR Spectroscopy

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ABSTRACT: 4-Vinyl pyridine–methacrylonitrile (V/M) copolymers of different composition were prepared by bulk polymerization using benzoyl peroxide as an initiator. The copolymer composition was determined from quantitative ¹³C{¹H}-NMR spectra. The reactivity ratios for V/M copolymer obtained from a linear Kelen-Tudos method (KT) and nonlinear error-in-variables method (EVM) are $r_V = 0.79 \pm 0.12$, $r_M = 0.38 \pm 0.09$ and $r_V = 0.79 \pm 0.13$, $r_M = 0.38 \pm 0.07$, respectively. The complete spectral assignment in term of compositional and configurational sequences of

these copolymers were done with the help of distortionless enhancement by polarization transfer (DEPT), two-dimensional heteronuclear single quantum coherence spectroscopy (HSQC). Total correlated spectroscopy (TOCSY) experiment was used to assign the various three-bond ¹H-¹H couplings in the V/M copolymer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3232–3238, 2003

Key words: microstructure; NMR; 4-vinyl pyridine–methacrylonitrile copolymers

INTRODUCTION

NMR spectroscopy has become an important technique for the investigation of microstructure of the polymers.^{1–3} DEPT is used extensively for the analysis of overlapping carbons resonance in ¹³C-NMR spectra.^{4,5} Poly (methacrylonitrile) and random copolymers of methacrylonitrile with other acrylic monomers such as methacrylic acid seem to have potential uses as photoresistant materials.⁶ The microstructure of methacrylonitrile copolymers with some vinyl monomers has been reported earlier,^{7,8} but to the best of our knowledge, the microstructure of the 4-vinyl pyridine–methacrylonitrile (V/M) copolymer has not been reported so far. The microstructure of 4-vinyl pyridine copolymers have been studied earlier by us.^{9,10} In the continuation of our earlier work, in this communication, we report the microstructure of V/M copolymer. The reactivity ratios of the comonomers were calculated using a linear Kelen-Tudos (KT) method¹¹ and nonlinear least-square error-in-variables method using the RREVM program.¹² The highly complex and overlapped ¹H- and ¹³C{¹H}-NMR spectra of these copolymers have been assigned completely with the help of DEPT-135, HSQC, and TOCSY

(low mixing time) experiments. The α -methyl region overlapped with the methine and methylene region in ¹H-NMR spectra, which can be resolved with the help of 2D-HSQC spectra. The α -methyl, methylene, and methine carbon signals of V/M copolymers were sensitive to compositional and configurational sequences. The 2D TOCSY spectra of V/M copolymers show excellent splitting in the aromatic region, which indicate their sensitivity toward various compositional and configurational sequences.

EXPERIMENTAL

Methacrylonitrile (Merck), 4-vinyl pyridine (Merck) were distilled under reduced pressure and stored below 5°C. A series of V/M copolymers of different composition were prepared by bulk polymerization using benzoyl peroxide as an initiator at 60°C. The percent conversion was kept below 10% by precipitating the copolymer in benzene. The copolymers were further purified from the dimethyl sulphoxide/benzene system. The condition for recording of all spectra have been described elsewhere.¹⁰

RESULTS AND DISCUSSION

Determination of copolymer composition and reactivity ratios

The quantitative ¹³C{¹H}-NMR spectrum of the 4-vinyl pyridine–methacrylonitrile (V/M) copolymer is used for the determination of copolymer composition (Fig.

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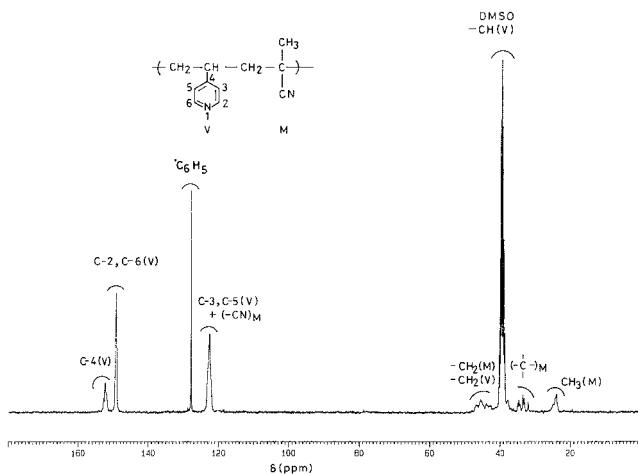


Figure 1 The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the 4-vinyl pyridine-methacrylonitrile (V/M) copolymer ($F_M = 0.45$ mol fraction in the copolymer) in $\text{DMSO}-d_6$ at 80°C .

1). The copolymer composition was calculated from the relative intensities of aromatic carbon signal (C-4)

of V-unit and quaternary carbon signal $\left(\text{---}\overset{\text{---}}{\underset{\text{---}}{\text{C}}}\text{---}\right)$ of the M-unit in quantitative $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra using the following expression:

$$F_M = \frac{I\left(\text{---}\overset{\text{---}}{\underset{\text{---}}{\text{C}}}\text{---}\right)_M}{I(\text{C-4})_V + I\left(\text{---}\overset{\text{---}}{\underset{\text{---}}{\text{C}}}\text{---}\right)_M} \quad (1)$$

where $I\left(\text{---}\overset{\text{---}}{\underset{\text{---}}{\text{C}}}\text{---}\right)_M$ is the area under the resonance signal of quaternary carbon of the M-unit and $I(\text{C-4})_V$ is the area under the resonance signal of aromatic carbon (C-4) of the V-unit.

F_M is the mol fraction of the M-unit in the copolymers. Table I shows the copolymer composition of

TABLE I
The Feed in Mole Fraction and Copolymer Composition Data for the V/M Copolymer

Sample	Feed in mol fractions		Mol fraction in copolymer	
	f_V	f_M	F_V	F_M
VM2	0.80	0.20	0.79	0.21
VM4	0.60	0.40	0.65	0.35
VM5	0.50	0.50	0.55	0.45
VM6	0.40	0.60	0.42	0.58
VM8	0.20	0.80	0.32	0.68

f 's—mol fractions in feed.

F 's—mol fractions in copolymer.

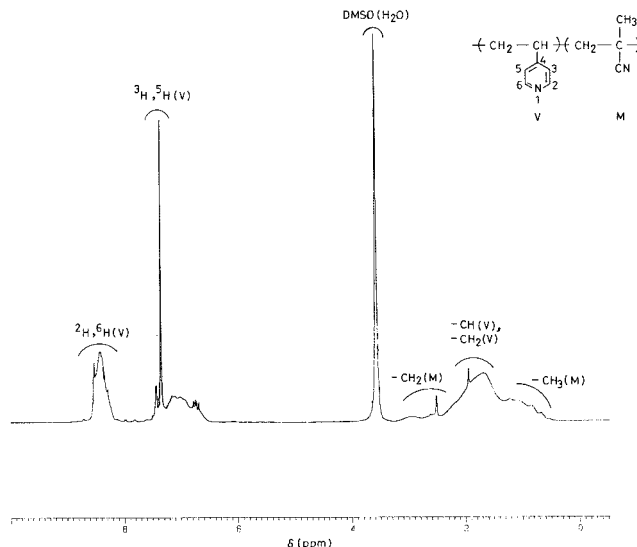


Figure 2 The ^1H -NMR spectrum of the V/M copolymer ($F_M = 0.45$ mol fraction in the copolymer) in $\text{DMSO}-d_6$ at 80°C .

various V/M copolymers along with feed in the composition. The copolymer composition data was used to calculate the terminal model reactivity ratios by the KT method. The reactivity ratios calculated from the KT method are $r_V = 0.79 \pm 0.12$ and $r_M = 0.38 \pm 0.09$. These reactivity ratios, along with feed in composition, were used as the initial estimates for the calculation of reactivity ratios from nonlinear EVM using the RREVM program. The reactivity ratios obtained from EVM are $r_V = 0.79 \pm 0.13$ and $r_M = 0.38 \pm 0.07$. The reactivity ratios of comonomers in the V/M copolymer are not reported in literature.

^1H -NMR studies

The ^1H -NMR spectrum of the V/M copolymer ($F_M = 0.45$ mol fraction in copolymer) is shown in Figure 2. The broad resonance signal around δ 0.45–3.15 ppm is assigned to aliphatic protons present in the V/M copolymer. This broad resonance signal is due to the overlap of several resonance signals so it is very difficult to obtain any type of information from ^1H -NMR spectrum alone. The assignment of ^1H -NMR spectrum was done with the help of 2D hetero nuclear proton-carbon correlation spectroscopy. The 2D-HSQC spectrum of the V/M copolymer is shown in Figure 3. It is seen that α -methyl carbon around δ 23.10–25.80 ppm is correlated to protons from δ 0.60–1.70 ppm and the methine carbon in the region around δ 38.00–40.00 ppm is correlated to the protons at the δ 2.95, δ 2.45, and δ 1.65 ppm region. The region at δ 2.95, δ 2.45, and δ 1.65 ppm are assigned to the proton of the $-\text{CH}$ group in MVM, MVV, and VVV triads. The methylene carbon of the V- and M-unit in the region around δ 40.50–44.10 and δ 45.85–48.00 ppm is correlated to

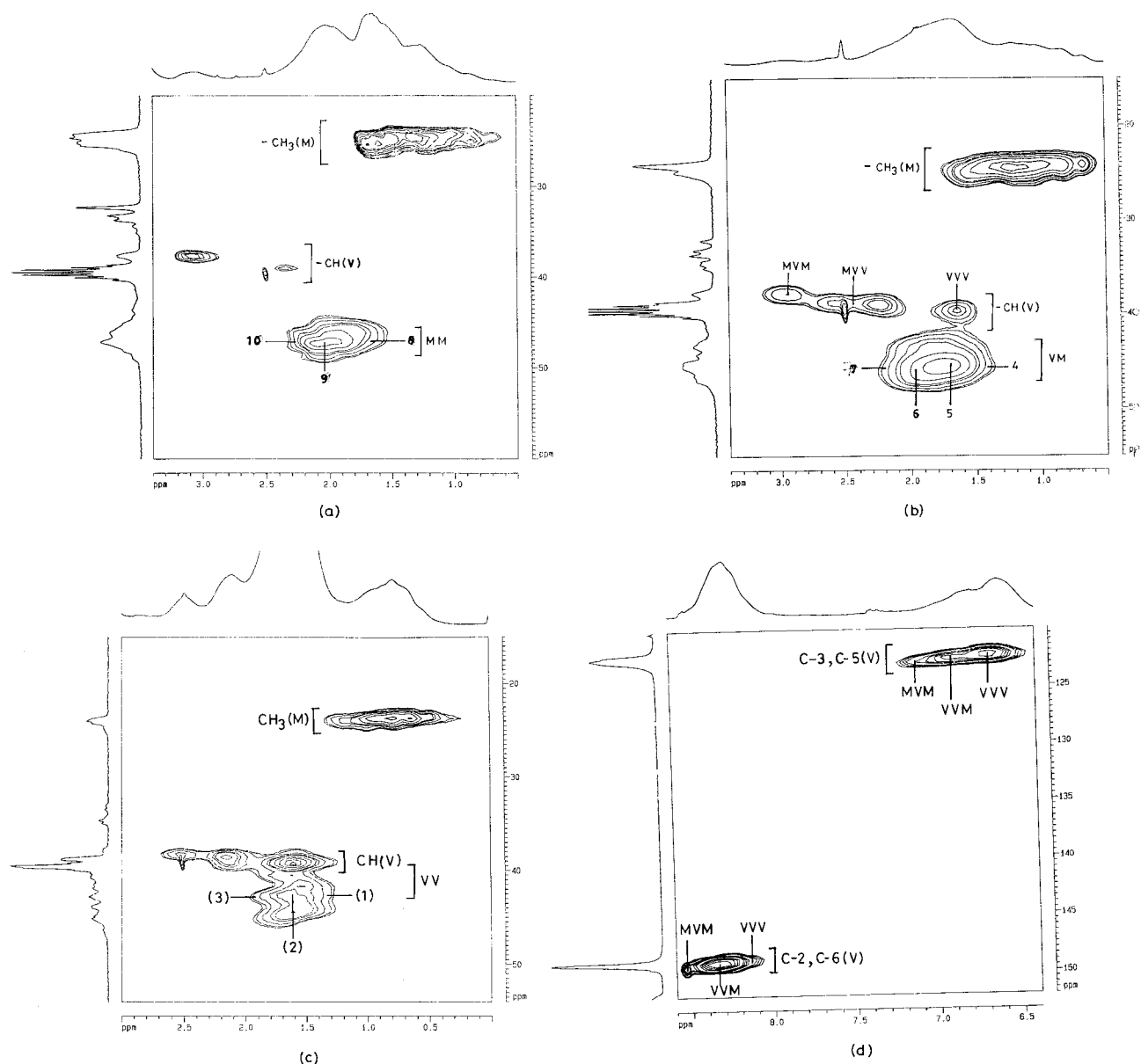


Figure 3 The 2D HSQC spectrum of the V/M copolymer with an expanded aliphatic region ($F_M = 0.68$) (a), with $F_M = 0.45$ (b), with $F_M = 0.21$ (c), expanded aromatic region ($F_M = 0.21$) (d).

protons in the region δ 1.55–1.80 and δ 2.00–2.30 ppm, respectively. The aromatic protons appeared as a set of two separate signals, one centered around δ 8.42 ppm and another at δ 7.10 ppm. The broad signal around δ 8.42 ppm is assigned to 2, 6 protons while at δ 7.10 ppm is assigned to 3, 5 protons of the aromatic ring.

$^{13}\text{C}\{^1\text{H}\}$ -NMR studies

The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the V/M copolymer ($F_M = 0.45$ mol fraction in the copolymer) along with assignment of various resonance signals is shown in Figure 1. The assignment of various resonance signals is done by comparing the spectra of the copolymer

with that of the homopolymers, i.e., poly(4-vinyl pyridine) and poly(methacrylonitrile).¹³ The resonance signal around δ 122.00–123.00 ppm is assigned to the overlap of aromatic carbons (C-3 and C-5, *meta* position) of the V-unit and cyanide carbon of the M-unit. The aromatic carbons {C-2 and C-6, *ortho* position) and quaternary carbon (C-4, *para* position) appeared around δ 149.00–150.00 and δ 152.00–153.2 ppm, respectively. The resonance signal around δ 127.81 ppm is assigned to the phenyl radical (C_6H_5) produced from a benzoyl peroxide initiator. The α - CH_3 of the M-unit appeared as a multiplet around δ 23.10–25.80 ppm. The spectral region around δ 37.25–47.50 ppm is quite complex and overlapped, and can be assigned to aliphatic carbons in the main chain of the copolymer.

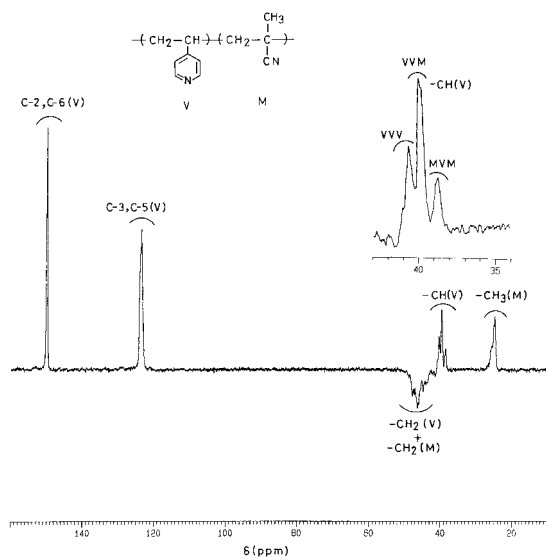


Figure 4 The DEPT-135 spectrum of the V/M copolymer ($F_M = 0.45$ mol fraction in the copolymer) in $\text{DMSO-}d_6$ at 80°C (a), expanded methine region of the V-unit.

The extent of overlapping of various carbon signals cannot be ascertained from $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum alone. The overlapped carbon regions can be resolved by employing the DEPT-135 spectrum as shown in Figure 4. In this experiment, the methylene carbon signal appeared as a negative phase, while methine and the methyl carbon signal appeared as a positive phase. The multiplet around $\delta 40.50$ – 48.00 ppm can be assigned to the methylene carbons of the M- and V-unit. The multiplet around $\delta 40.50$ – 44.10 ppm and around $\delta 45.85$ – 47.50 ppm are assigned to methylene carbon of the V- and M-unit, respectively. The resonance signal around $\delta 38.00$ – 40.50 ppm is assigned to the methine carbon of the V-unit [Fig. 4(a)]. The peak centered around $\delta 40.33$ ppm increases in intensity with an increase in the concentration of the V-unit, can be assigned to the VVV triad. On a similar basis, the peak centered around $\delta 39.60$ and $\delta 38.47$ ppm can be assigned to the VVM and MVM triads, respectively. The HSQC spectrum [Fig. 3(b)] shows that the methine region of the V-unit appeared as multiplet around $\delta 38.00$ – $40.00/3.18$ – 1.50 ppm. On the basis of the variation in the intensity of crosspeaks with copolymer composition, the crosspeaks around $\delta 38.50/2.95$, $\delta 39.35/2.45$, and $\delta 39.60/1.65$ ($^{13}\text{C}/^1\text{H}$) ppm are assigned to MVM, VVM, and VVV triads, respectively.

The quaternary carbon of the M-unit appeared as a multiplet around $\delta 31.80$ – 35.10 ppm [Fig. 5(a)]. The multiplet can be divided into three regions, i.e., around $\delta 31.80$ – 32.50 , $\delta 32.50$ – 33.80 , and $\delta 33.80$ – 35.10 ppm. On the basis of variation in intensity of these resonance signals with copolymer composition, the resonance signal around $\delta 31.80$ – 32.50 , $\delta 32.50$ – 33.80 , and $\delta 33.80$ – 35.10 ppm are assigned to MMM, MMV,

and VMV triads, respectively. The quaternary carbon in poly (methacrylonitrile)¹³ appeared as a singlet around $\delta 32.38$ ppm, indicating its insensitivity to configurational sequences. So further splitting within these triads are assigned to higher order compositional sequences. The resonance signal around $\delta 31.99$ (1) ppm is assigned to MMMMM pentad while three resonance signals in VMM triad region, i.e., around $\delta 32.90$ (2), $\delta 33.14$ (3), and $\delta 33.54$ (4) ppm are assigned to MVMMM, VVMMM, or MVMMV and VVMMV pentad sequences, respectively. Similarly, three resonance signals in VMV triad, i.e., around $\delta 34.15$ (5), $\delta 34.61$ (6), and $\delta 34.95$ (7) ppm are assigned to MVMVM, VVMVM, or MVMVV and VVMVV pentads, respectively. The assignment of various resonance signals in $\left(\begin{array}{c} | \\ -\text{C}- \\ | \end{array}\right)_M$

region is given in Table II.

The α -methyl carbon of the M-unit appeared as a multiplet around $\delta 23.75$ – 26.50 ppm as shown in Figure 5(b), indicating its sensitivity towards various

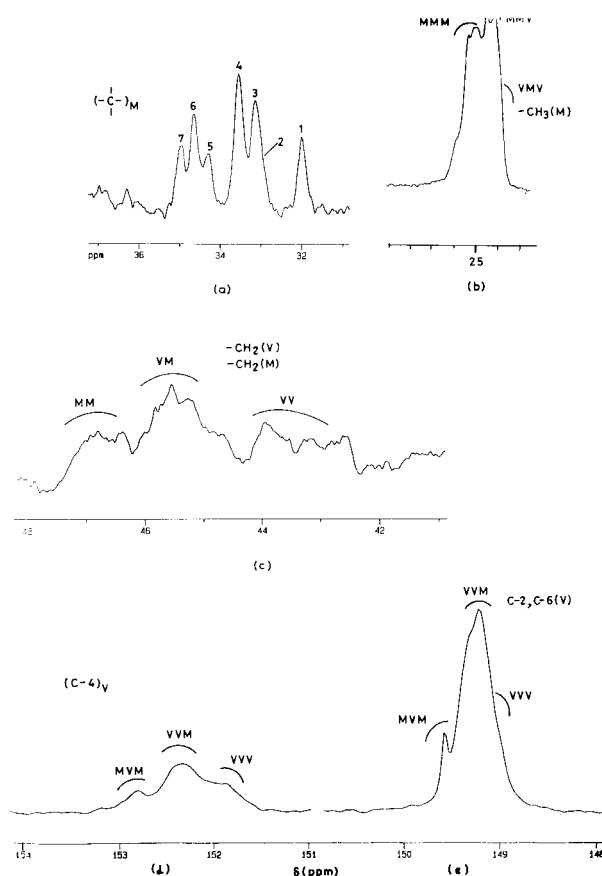


Figure 5 Expanded $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum showing quaternary carbon $\left(\begin{array}{c} | \\ -\text{C}- \\ | \end{array}\right)$ ($F_M = 0.45$) (a), α - CH_3 ($F_M = 0.68$) (b) of the M-unit, and $-\text{CH}_2$ carbon region of the M- and V-unit (c), C-4 carbon of ring of the V-unit (d), C-2 and C-6 carbons of the aromatic ring with $F_M = 0.45$ (e).

TABLE II
The Assignment of Various Resonance Signals of V/M Copolymer Based on $^{13}\text{C}\{^1\text{H}\}$ -NMR Spectrum

Peak no.	Peak position (ppm)	Peak assignment
	$\left(\begin{array}{c} \\ -\text{C}- \\ \end{array} \right)$ Region of M- unit	
1	31.99	MMMMM
2	32.90	MMMVM
3	33.10	MMMVV
4	33.54	VMMVV
5	34.15	MVMVM
6	34.61	MVMVV
7	34.95	VVMVV
	C-2 and C-6 of V-unit	
8	152.33	VVV
9	152.80	VVM
10	153.00	MVM
	C-4 of V-unit	
11	149.03	VVV
12	149.21	VVM
13	149.57	MVM

compositional and configurational sequences. This multiplet consists of three envelopes. The envelope centered around δ 25.50 ppm increases in intensity as the concentration of the M-unit in the copolymer increases, and can be assigned to the MMM triad. The envelope centered around δ 24.10 ppm decreases in intensity with an increase in concentration of the M-unit, and can be assigned to the VMV triad, while the central envelope around δ 24.66 ppm can be assigned to the MMV triad. The broad crosspeak around δ 23.75–26.50/0.62–1.78 ppm in 2D HSQC spectrum (Fig. 3) is due to the α -methyl group of the M-unit. The broadness may be due to its sensitivity towards higher order compositional and configurational sequences.

The methylene carbon due to its symmetry, is sensitive to the diad, tetrad, hexad, etc., compositional sequences. The methylene region appeared as a multiplet around δ 40.50–48.00 ppm [Fig. 5(c)]. On the basis of variation in intensity of these resonance signals with copolymer composition, the resonance signals around δ 46.15–48.00, δ 44.20–46.15, and δ 40.50–44.20 ppm are assigned to the MM, MV/VM, and VV diads. In the HSQC spectrum (Fig. 3), the methylene resonance signal of the M- and V-unit can be divided into three envelopes of diads, i.e., MM, MV/VM, and VV in the region around δ 48.00–46.00/2.32–1.70, δ 46.05–44.10/2.10–1.55 and δ 44.10–40.50/1.95–1.40 ppm, respectively, on the basis of the change in the intensity of these signals with the copolymer composition. The further splitting within each set of the above cross peaks is assigned to various configurational sequences. All diads show further splitting into three different sets of crosspeaks due to the non-equivalence of the protons in the $-\text{CH}_2$ group of the

V- and M-unit in the meso and racemic configuration. The crosspeaks in the VV diad, i.e., centered around δ 42.75/1.32 (1), δ 42.75/1.83 (3) ppm are assigned to the VmV (H_a) and VmV (H_b) diads, respectively, due to more deshielding of the H_b proton in the meso configuration in comparison to the H_a proton, while both protons in the VrV diad appeared at the same position, i.e., around δ 42.75/1.60 (2) ppm [Fig. 3(c)] due to the presence of both protons in the same magnetic environment. Similarly, in the VM diad, the crosspeaks around δ 45.25/1.41 (4), δ 45.25/2.19 (7), δ 45.75/1.70 (5), and 45.30/1.98 (6) ppm [Fig. 3(b)] are assigned to VmM (H_a), VmM (H_b), VrM (H_a), and VrM (H_b), while the crosspeaks around δ 47.15/1.64 (8), δ 47.15/2.28 (10), δ 47.15/2.03 (9) ppm [Fig. 3(a)] are assigned to the MmM (H_a), MmM (H_b), and MrM (H_a and H_b) protons, respectively. The various other crosspeaks in the $-\text{CH}_2$ region may be due to various higher order compositional and configurational sequences. The assignment of various peaks up to the diad level in $-\text{CH}_2$ region of the V- and M-unit in the V/M copolymer with the help of 2D HSQC spectra is given in Table III.

The multiplet around δ 122.00–123.00 ppm is assigned to the overlap of aromatic carbons (C-3, C-5) of the V-unit and the $-\text{CN}$ carbon of the M-unit. The multiplicity in this resonance signal may be due to various compositional sequences in the (C-3, C-5) carbon of the V-unit and the $-\text{CN}$ carbon of the M-unit. The presence of aromatic carbons (C-3, C-5) in triad sequences is confirmed by HSQC spectrum also [Fig. 3(d)]. The crosspeaks around δ 122.25/6.69, δ 123.25/6.95, and δ 123.50/7.12 ppm in the aromatic carbon regions (C-3, C-5) are assigned to VVV, VVM, and MVM triads, respectively, on the basis of variation in intensity of these crosspeaks with copolymer composition. The aromatic carbons (C-2 and C-6) of the V-unit appeared as a multiplet around δ 149.00–150.00 ppm [Fig. 5(d)]. On a similar basis of variation in intensity of resonance signals with copolymer compo-

TABLE III
The Spectral Assignment of $-\text{CH}_2$ Region of M- and V-Unit in the V/M Copolymer Based Upon 2 D-HSQC Spectra

Peak number	Peak assignment	Peak position (ppm)
1	VmV (H_a)	42.75/1.32
2	VrV (H_a and H_b)	42.75/1.60
3	VmV (H_b)	42.75/1.83
4	VmM (H_a)	45.25/1.41
5	VrM (H_a)	45.25/1.70
6	VrM (H_b)	45.30/1.98
7	VmM (H_b)	45.25/2.19
8	MmM (H_a)	47.15/1.64
9	MrM (H_a and H_b)	47.15/2.03
10	MmM (H_b)	47.15/2.28

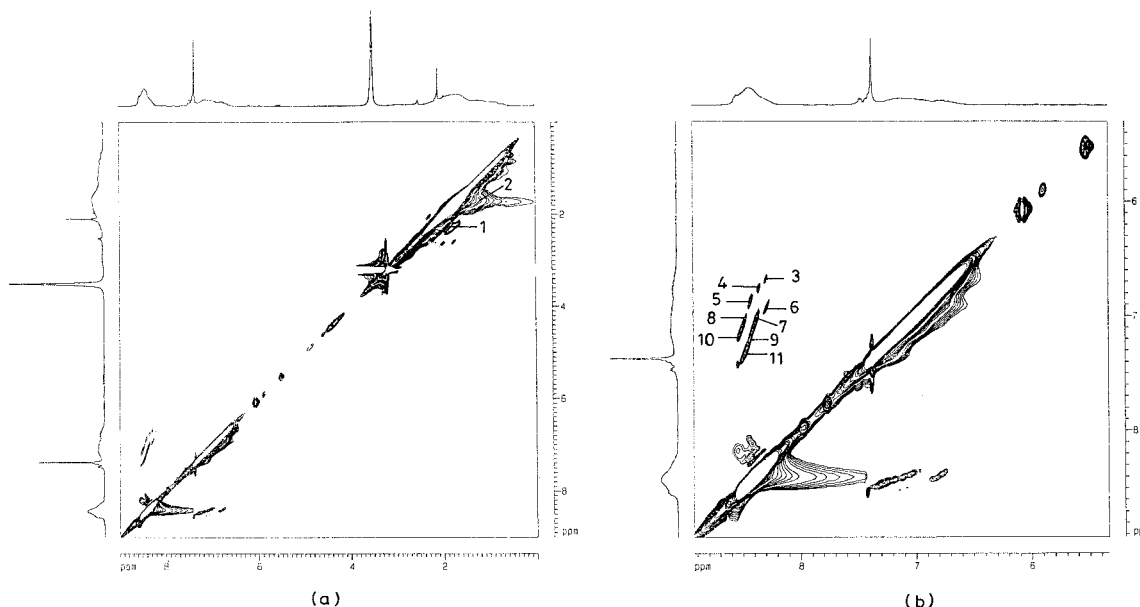


Figure 6 The 2D TOCSY NMR spectrum of the V/M copolymer ($F_M = 0.45$ mol fraction in the copolymer) in $\text{DMSO-}d_6$ at 80°C (a), expanded aromatic region (b).

sition, the signals around δ 149.03, δ 149.21, and δ 149.57 ppm are assigned to the VVV, VVM, and MVM triads, respectively (Table II). In the HSQC spectrum [Fig. 3(d)], the crosspeaks around δ 148.75/8.15, δ 149.00/8.35, and δ 149.25/8.55 ppm are also assigned to the VVV, VVM, and MVM triads, respectively.

The aromatic carbon (C-4) appeared as a multiplet around δ 152.00–153.25 ppm [Fig. 5(e)]. The signal around δ 152.33 ppm increases in intensity with an increase in concentration of the V-unit in the copolymer, and can be assigned to the VVV triad, while the signal around δ 153.00 ppm decreases in intensity with an increase in concentration of the V-unit in the copolymer, and can be assigned to the MVM triad. The central signal around δ 152.80 ppm is assigned to the VVM triad.

2D-TOCSY spectra studies

To understand the connectivity and confirm the various couplings in the polymer chain, the TOCSY spectrum was recorded. The three bond coupling between the protons of different directly coupled groups in the V/M copolymer can be clearly seen in the TOCSY experiment in a short mixing time (4 ms). The crosspeak at δ 1.75/2.31 ppm (1) is due to the coupling between the protons of the methylene group of the M-unit and the methine group of the V-unit of the main chain while the crosspeak around δ 1.75/1.28 ppm (2) is due to the coupling between methylene protons of the M- and V-unit [Fig. 6(a)]. The various geminal coupling between the protons of $-\text{CH}_2$ (M), $\alpha\text{-CH}_3$ (M), $-\text{CH}_2$ (V), and $-\text{CH}$ (V) groups are also

possible, which are difficult to distinguished due to the low value of the coupling constants. The coupling within the aromatic protons ($^2\text{H-}^3\text{H}$ and $^5\text{H-}^6\text{H}$) of the V-unit is also possible, as shown in Figure 6(b). It appeared as a multiplet around δ 8.18–8.55/6.55–6.95 ppm. This multiplet may be assigned to the coupling of aromatic protons in different configurational and compositional sequences. The assignment of various couplings in this region is carried out on the basis of variation in intensity of these signals with copolymer composition. The crosspeaks around δ 8.20–8.40/6.55–6.95 ppm are assigned to the coupling of aromatic protons in the VVV triad. The further splitting within this triad can be assigned to various configurational sequences on comparison with the TOCSY spectrum of poly(4-vinyl pyridine). The crosspeaks

TABLE IV
TOCSY $^1\text{H-}^1\text{H}$ Shift Correlation for the V/M Copolymer

Peak number	Type of proton (ppm)	Coupled to (ppm)
1	CH_2 (M) (1.75)	CH (V) (2.31)
2	CH_2 (M) (1.75)	CH_2 (V) (1.28)
	Aromatic ^2H and ^6H in	Aromatic ^3H & ^5H in
3	VrVrV (8.25)	VrVrV (6.62)
4	VrVmV (8.31)	VrVmV (6.71)
5	VmVmV (8.37)	VmVmV (6.85)
6	VVVMV (8.25)	VVVMV (6.92)
7	VVVMM (8.32)	VVVMM (7.01)
8	MVVMM (8.42)	MVVMM (7.09)
9	VMVMV (8.45)	VMVMV (7.18)
10	VMVMM (8.52)	VMVMM (7.25)
11	MMVMM (8.48)	MMVMM (7.31)

around δ 8.25/6.62 (3), δ 8.31/6.71 (4), and δ 8.37/6.85 (5) ppm are assigned to the coupling in the VrVrV, VrVmV, and VmVmV sequences, respectively. The multiplet around δ 8.21–8.51/6.88–7.15 ppm and δ 8.55–8.40/7.10–7.36 ppm are assigned to the coupling in the VVM and MVM triads, respectively. The further splitting within these triads are assigned to higher order compositional sequences, on the basis of variation in intensity of these crosspeaks with the copolymer composition. The crosspeaks around δ 8.25/6.92 (6), δ 8.32/7.01 (7), and δ 8.42/7.09 (8) are assigned to the couplings in VVVMV, VVVMM, and MVVMM pentads while the crosspeaks around δ 8.41/7.18 (9), δ 8.52/7.25 (10), and δ 8.48/7.31 (11) ppm are assigned to the coupling in VMVMV, VMVMM, and MMVMM pentads, respectively. These possible couplings are shown in Table IV.

CONCLUSIONS

The reactivity ratios of comonomers in the V/M copolymer are $r_V = 0.79$ and $r_M = 0.38$. The overlapped and complex proton and carbon-13 spectra are well resolved with the help of DEPT-135 and 2D HSQC spectra. The α -methyl and quaternary carbon of the M-unit are assigned up to pentad sequences. The

methylene carbon of the M- and V-unit are assigned up to the diad and tetrad levels with the help of the HSQC spectra. The aromatic carbon signals are assigned up to the triad levels. The various types of couplings between different groups in the V/M copolymer are assigned by TOCSY experiments with a mixing time of 4 ms.

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