Compositional and Configurational Sequence Determination of Methacrylonitrile–Vinylidene Chloride Copolymers by Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: Methacrylonitrile–vinylidene chloride (M/V) copolymers of different composition were prepared by bulk polymerization using benzoyl peroxide as an initiator under nitrogen atmosphere in a sealed tube. The copolymer composition was determined from quantitative $^{13}C[^{1}H]$ NMR spectra. The reactivity ratios for M/V copolymers obtained from a linear Kelen–Tudos method and nonlinear error-in-variables method are $r_M = 2.47 \pm 0.14$, $r_V = 0.40 \pm 0.02$, and $r_M = 2.43$, $r_V = 0.39$, respectively. The complete spectral assignment in term of compositional and conformational sequences of these copolymers were done with the help of distortionless enhancement by polarization transfer, two-dimensional heteronuclear single-quantum coherence spectroscopy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1865–1874, 2005

Key words: copolymers; NMR; spectroscopy

INTRODUCTION

High-resolution NMR spectroscopy[1–5] is the most versatile, reliable, and generally acceptable technique for the determination of microstructure of polymers. Vinylidene chloride copolymers provide an important class of polymers that are widely used in several applications. They form the innermost barrier layer in the rigid containers for food packaging, capable of protecting oxygen-sensitive foods at ambient temperature. The excellent chemical resistance and good adhesion results in long-term performance of coating. The microstructure of copolymers of methacrylonitrile[6,7] and vinylidene chloride[8,9] with some vinyl monomers has been reported earlier. To the best of our knowledge, the microstructure of methacrylonitrile–vinylidene chloride (M/V) copolymers has not been reported so far. Kamide and colleagues[10] have determined the sequences of acrylonitrile–vinylidene chloride copolymers from $^{13}C[^{1}H]$ NMR spectra. Bailey et al.[11] have reported the copolymerization theory and relationship of sequence distribution with T_g for acrylonitrile–vinylidene chloride copolymers. In this paper, we report the microstructure of methacrylonitrile–vinylidene chloride copolymers. The reactivity ratios of the comonomers were calculated using a linear Kelen–Tudos (KT) method[12] and nonlinear least-square error-in-variables method.[13] The complete ^{1}H and $^{13}C[^{1}H]$ NMR spectral assignments of methacrylonitrile–vinylidene chloride copolymers were done with the help of distortionless enhancement by polarization transfer (DEPT) and 2D heteronuclear single-quantum coherence (HSQC) NMR experiments.

EXPERIMENTAL PROCEDURES

Methacrylonitrile and vinylidene chloride monomers were distilled under reduced pressure and stored below 5°C. A series of M/V copolymers of different composition was prepared by bulk polymerization using benzoyl peroxide as an initiator at 60°C under nitrogen atmosphere in a sealed tube. The percentage conversion was kept below 10% by precipitating the copolymer in methanol. The copolymers were further purified from dimethyl sulfoxide/methanol system. The conditions for recording of all spectra have been described elsewhere.[14]

RESULTS AND DISCUSSION

The composition of M/V copolymers was determined from quantitative ^{13}C $[^{1}H]$ NMR spectra using standard pulse program with repetition time 10 s. Table I

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TABLE I
Copolymer Composition and Molecular Weight Averages of Methacrylonitrile/Vinylidene Chloride (M/V) Copolymers

Sample No.	f_M	F_M	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_z \times 10^{-5}$	$\bar{M}_{z+1} \times 10^{-5}$	P
MV1	0.10	0.22	1.13	2.31	4.35	5.12	2.04
MV2	0.20	0.38	1.08	2.09	3.78	4.72	1.94
MV3	0.30	0.52	1.12	2.12	3.25	4.25	1.89
MV4	0.40	0.62	1.06	1.88	2.77	3.54	1.77
MV5	0.50	0.79	1.11	1.92	2.76	3.48	1.73

f_M is the mole fraction of M comonomer in feed and F_M is the mole fraction of M comonomer in copolymer. M_w, M_n, M_z, and M_{z+1} are the weight average, number average, Z-average, and (Z + 1) average molecular weights of the copolymers, respectively. P, polydispersity.

shows the comonomer mole fractions in the feed and in the copolymer. According to the KT method, the terminal model reactivity ratios were calculated using the copolymer composition data. The reactivity ratios from error-in-variable method (EVM) were calculated using the reactivity ratio values obtained from KT method along with copolymer composition data. The values of reactivity ratios obtained from KT[12] and nonlinear EVM[13] are $r_M = 2.47 \pm 0.14$, $r_V = 0.40 \pm 0.02$ and $r_M = 2.43$, $r_V = 0.39$, respectively. Table I shows the molecular weight averages of M/V copolymers obtained from the GPC technique.

^{13}C [^{1}H] NMR studies

The ^{13}C[^{1}H] NMR spectrum of M/V ($F_M = 0.52$) copolymer in DMSO-d_6 at 80°C is shown in Figure 1. The signals around $\delta24.0$–27.4 ppm are due to α-CH$_3$ carbon resonances of the methacrylonitrile unit in the copolymer. The β-methylene carbon of both methacrylonitrile and vinylidene chloride units resonate around $\delta45.0$–65.0 ppm. The quaternary carbon signals of methacrylonitrile unit of M/V copolymer are assigned around $\delta31.6$–34.0 ppm, whereas the signals around $\delta83.4$–87.8 ppm are assigned to the quaternary carbon resonances of V-unit. The nitrile carbon signals are assigned around $\delta121.6$–123.4 ppm.

The expanded nitrile carbon region of M-unit of the copolymers along with poly(methacrylonitrile) are shown in Figure 2a–e. The multiplet in the nitrile carbon region of the M-unit of the copolymer is assigned to compositional triad sequences. The assignments to various signals are done with the help of the spectrum of poly(methacrylonitrile) and by observing
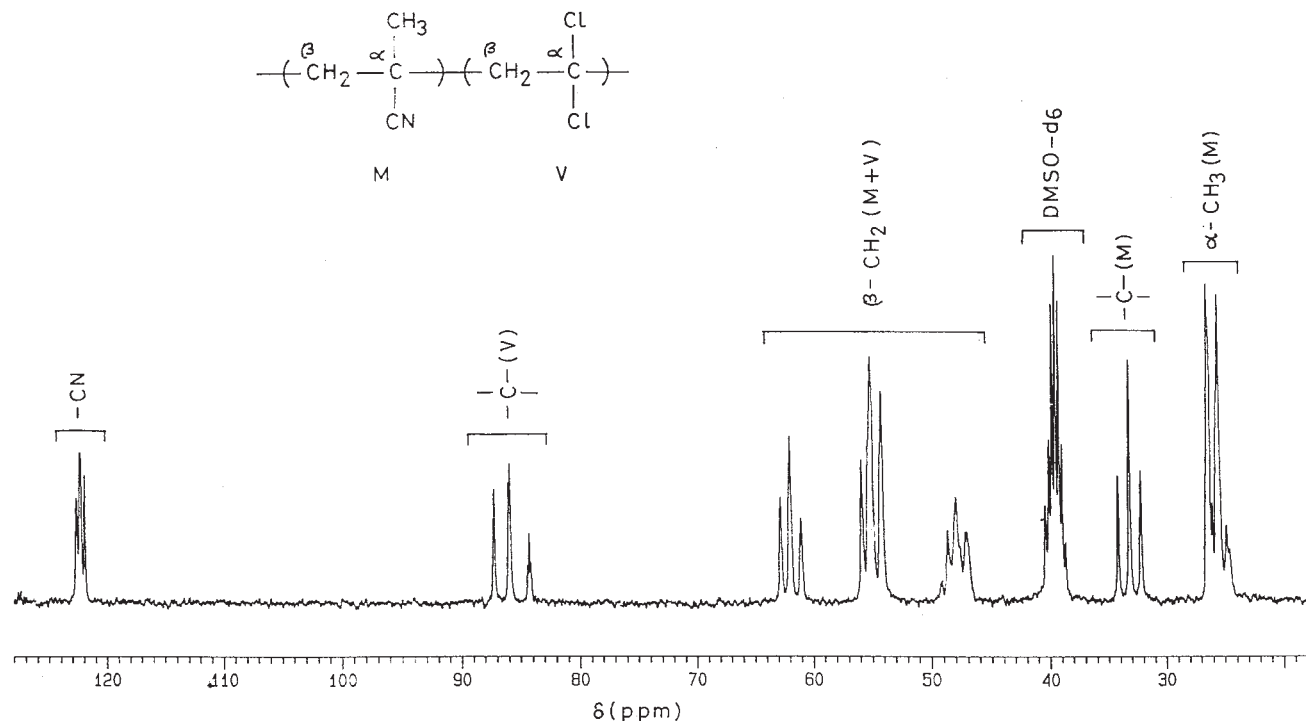

Figure 1 The ^{13}C[^{1}H] NMR spectrum of methacrylonitrile–vinylidene chloride (M/V) copolymer ($F_M = 0.52$) in DMSO-d_6 at 80°C.
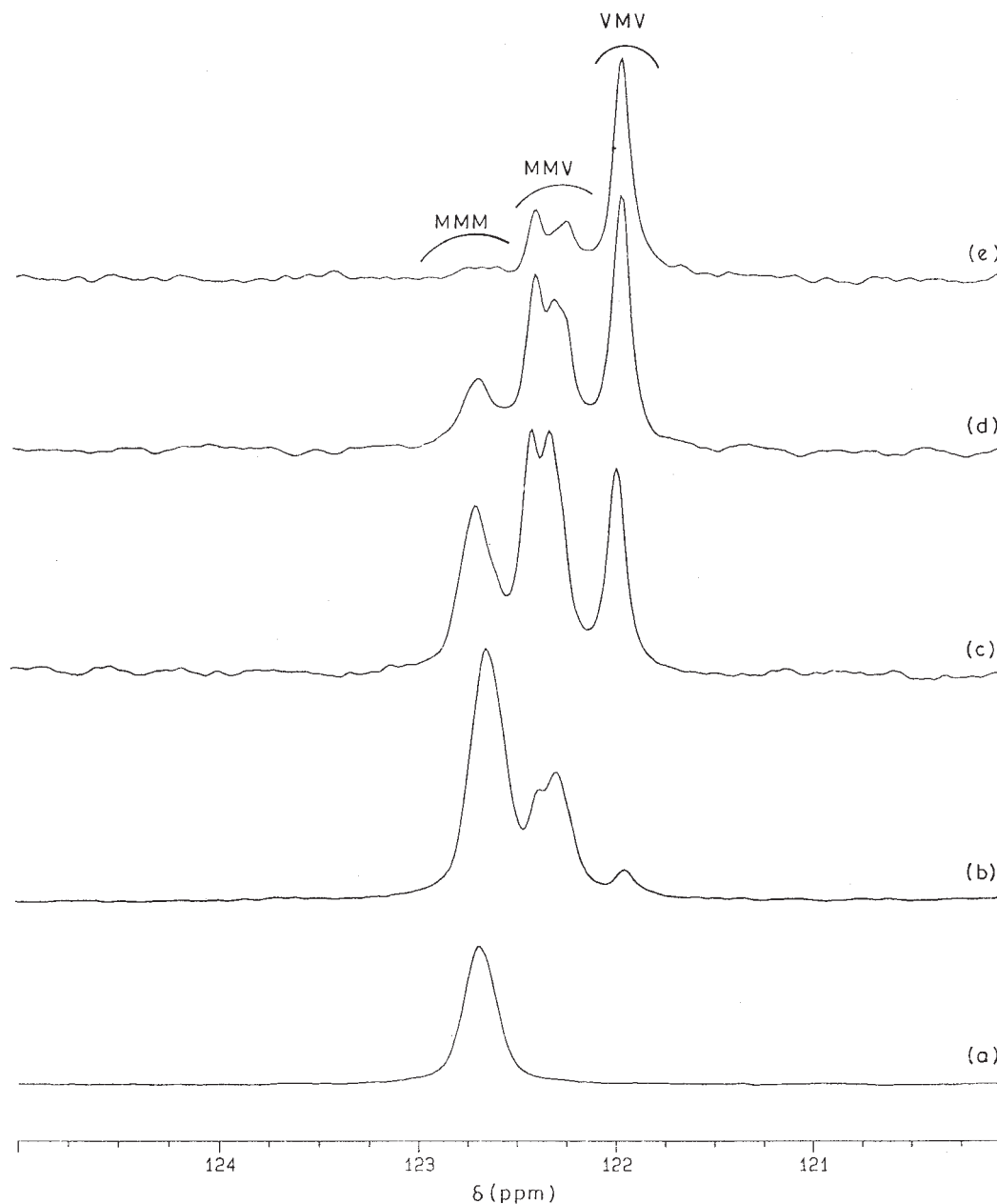
Figure 2 The expanded nitrile carbon regions of (a) PMAN and methacrylonitrile–vinylidene chloride (M/V) copolymers with compositions (F_M =): b) 0.79, c) 0.52, d) 0.38, and e) 0.22.

the change in intensity of signals with the change in composition of copolymers. The signals at δ122.5–123.3 ppm are assigned to the MMM triad by comparison with the homopolymer. The other signals at δ122.2–122.5 and δ121.8–122.5 ppm, which show increased in intensity of the signals with increase in V-content and decrease in M-content, are assigned to MMV and VMV triads, respectively.

Figure 3a–f shows the expanded quaternary carbon region of the M-unit of the copolymers along with poly-(methacrylonitrile). By following the compositional trends in the series of spectra, the various groups of peaks were assigned to three M-centered triads. The signals at δ31.8–32.7 ppm are assigned to MMM triad by comparison with the quaternary carbon region of poly-(methacrylonitrile). The VMV triad is assigned to δ33.8–34.6 ppm, the intensity of which increases with the increase in V-content and decrease in M-content. Finally, the intermediate region around δ32.8–33.6 ppm is assigned to the MMV triad, due to the fact that the intensity of signal first increases and then decreases with the variation in copolymer composition.
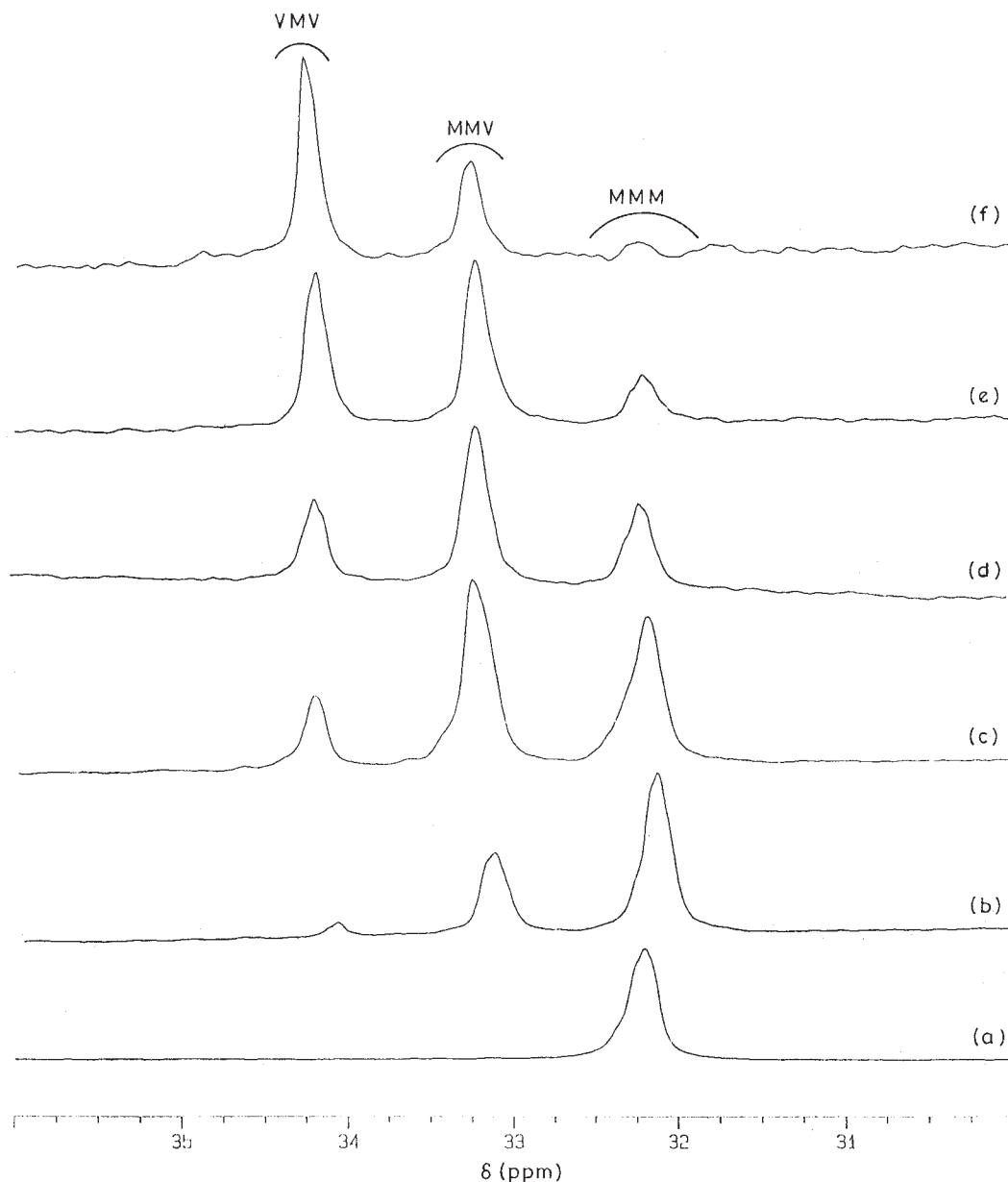
Figure 3 The expanded quaternary carbon regions of a) PMAN and methacrylonitrile - vinylidene chloride (M/V) copolymers with compositions (F_M =) : b) 0.79, c) 0.62, d) 0.52 e) 0.38, and f) 0.22.

The expanded quaternary carbon region of the V-unit of M/V copolymers is sensitive to the compositional sequences as shown in Figure 4a–e. All assignments were done on the basis of the variation in intensity of the signals with variation in copolymer composition. The signals around $\delta 83.8–84.7$ ppm are assigned to the VVV triad, which shows the decrease in intensity of signals with decrease in V-content. Further, the region around $\delta 86.8–87.8$ ppm is assigned to the MVM triad, whose intensity increases with the increase in M-content. Similarly, the MVV triad is assigned to $\delta 85.5–86.6$ ppm. The high chemical shift

value of MVM triad is due to the increased deshielding by the nitrile (-CN) group of the M-unit.

The expanded β-methylene carbon regions of the M- and V- units of M/V copolymers are sensitive to the distribution of dyad as well as tetrad compositional and configurational sequences. Figure 5a–e shows the expanded methylene carbon regions of M- and V-monomeric units of the copolymers along with the methylene carbon region of poly(methacrylonitrile). There are three broad envelopes in the methylene carbon regions around $\delta 46.0–50.0$, $\delta 53.5–57.2$, and $\delta 60.5–63.5$ ppm, which are assigned to MM, MV, and
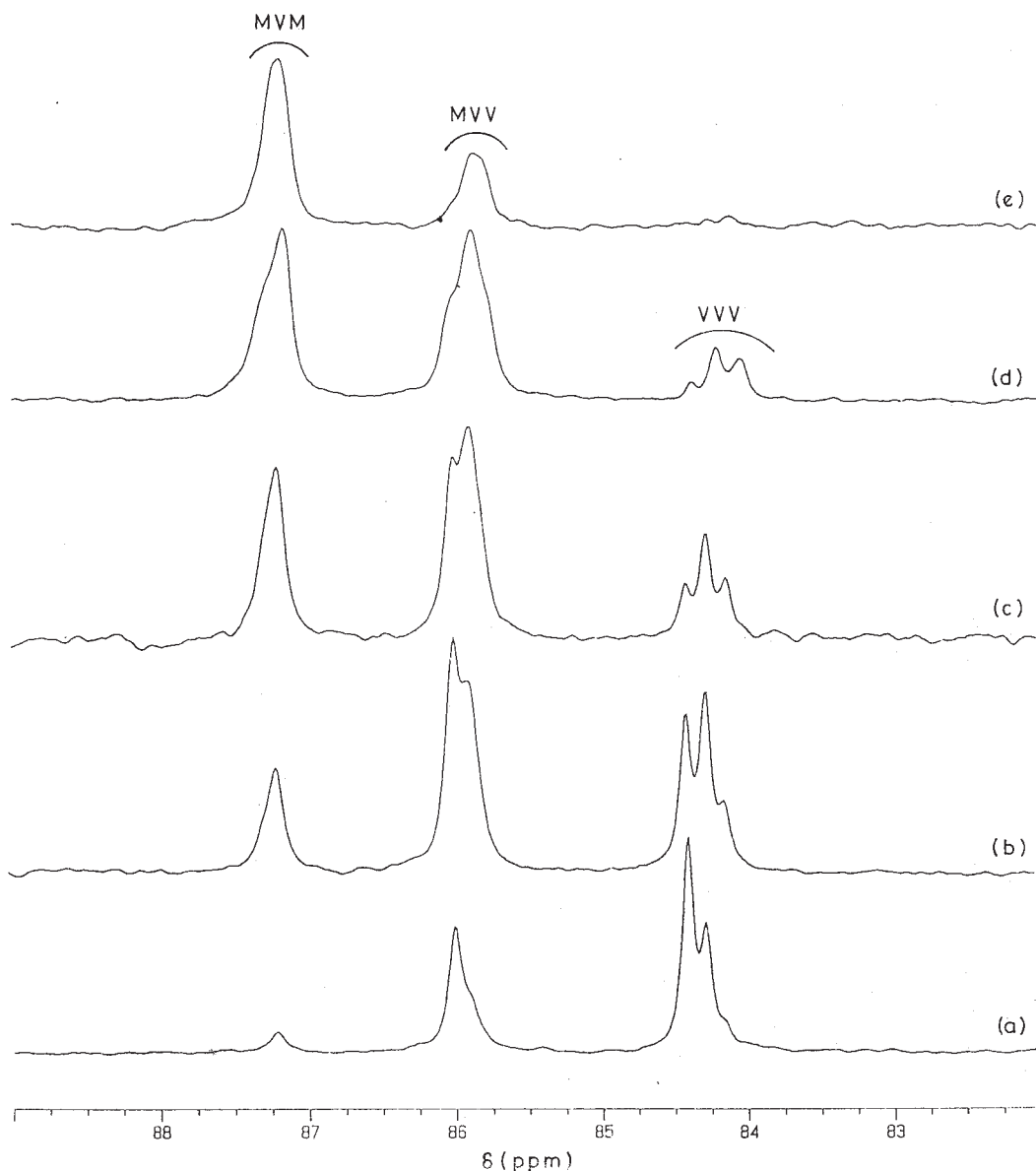
Figure 4 The expanded quaternary carbon regions of V- unit of methacrylonitrile - vinylidene chloride (M/V) copolymers with compositions (F_M =) : a) 0.22, b) 0.38, c) 0.52, d) 0.62, and e) 0.79.

VV dyads, respectively, on the basis of change in intensity of signals with the copolymer composition. Further splitting within the dyad regions can be assigned to tetrad compositional sequences. In the VV dyad region, the signals around $\delta 60.5$–61.5^1 ppm are assigned to the VVVV tetrad, which shows the increase in intensity of signals with the increase in V-content and decrease in M-content. Similarly, the other two signals around $\delta 61.5$–62.7^2 and $\delta 62.7$–63.5^3 ppm are assigned to the VVVM and MVVM tetrads, respectively. In the MV dyad region, the signal around $\delta 53.5$–54.6^4 ppm, the intensity of which increases with the increase in V-content, is assigned to the VMVV tetrad. The other signals around $\delta 54.6$–55.7^5 and

$\delta 55.7$–56.7^6 ppm are assigned to the MMVV (VMVM) and MMVM tetrads, which show the decrease in intensity of signals with the decrease in M-content. The signals around $\delta 46.0$–$47.0,^7$ $\delta 47.0$–$47.8,^8$ $\delta 47.8$–$48.8,^9$ and $\delta 48.8$–49.8^{10} ppm are assigned to mrm, mrr + mmm, rrr + mmr, and rmr configurational sequences, respectively, by comparison with poly(methacrylonitrile). In the MM dyad region of the copolymer, the compositional sequences are overlapped with the configurational sequences and difficult to assign. All assignments (Fig. 6.5) are shown in Table II.

The splitting pattern of α-CH$_3$ carbon resonances seems to be well separated but spread over a wide range of chemical shifts due to tacticity effects in the spectrum
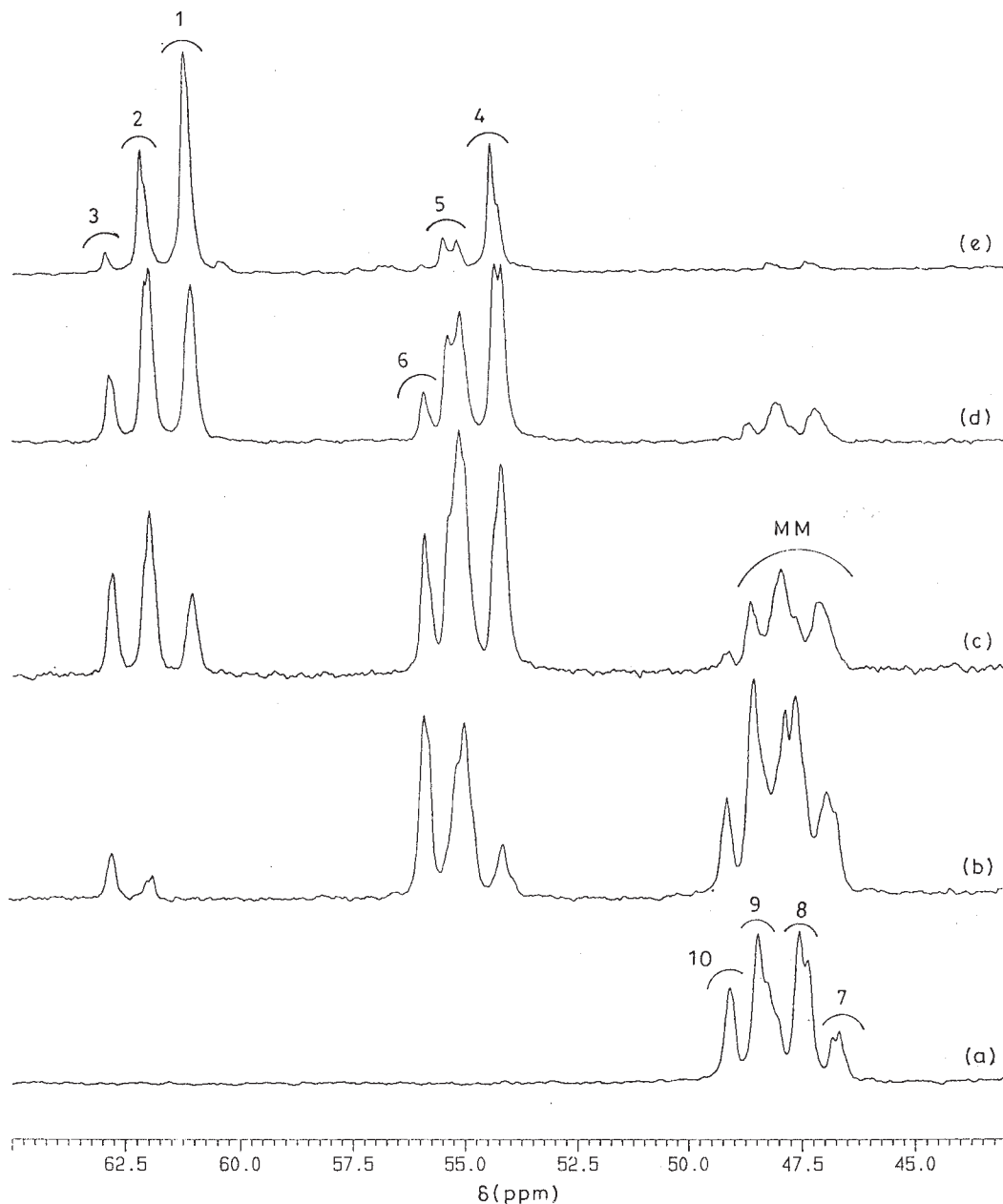
Figure 5 The expanded β-methylene regions of a) PMAN and methacrylonitrile- vinylidene chloride copolymers (M/V) copolymers with compositions (F_M =) : (b) 0.79, (c) 0.52, (d) 0.38, and (e) 0.22.

of poly(methacrylonitrile). Figure 6a–d shows the expanded α-methyl carbon resonance signals of M/V copolymers along with poly(methacrylonitrile). The MrMrM triad appears the most upfield at δ24.10–25.0 ppm, whereas MmMrM and MmMmM triads are assigned at δ25.0–25.8 and δ25.8–26.4 ppm, respectively (Fig. 6). The MrMrM and MmMrM triads appear predominantly in the M/V copolymer, because the MmMmM triad sequence is very low. In the M/V copolymer, the resonance signal around δ24.2–25.0 ppm is assigned to MrMrM triads. The resonance signals around δ25.0–25.8[4] ppm is assigned to the overlap of

MMV and MrMmM triads, on the basis of the change in intensity of signals with the copolymer composition and by comparison with the homopolymer. Similarly, the resonance signal around δ25.8–27.0[5] ppm is assigned to the overlap of VMV and MmMmM triads, which also shows the increase in intensity with increase in V-content and decrease in M-content.

¹H and 2D HSQC NMR studies

The ¹H-NMR spectrum of the M/V copolymer is broad and overlapping, and these assignments are
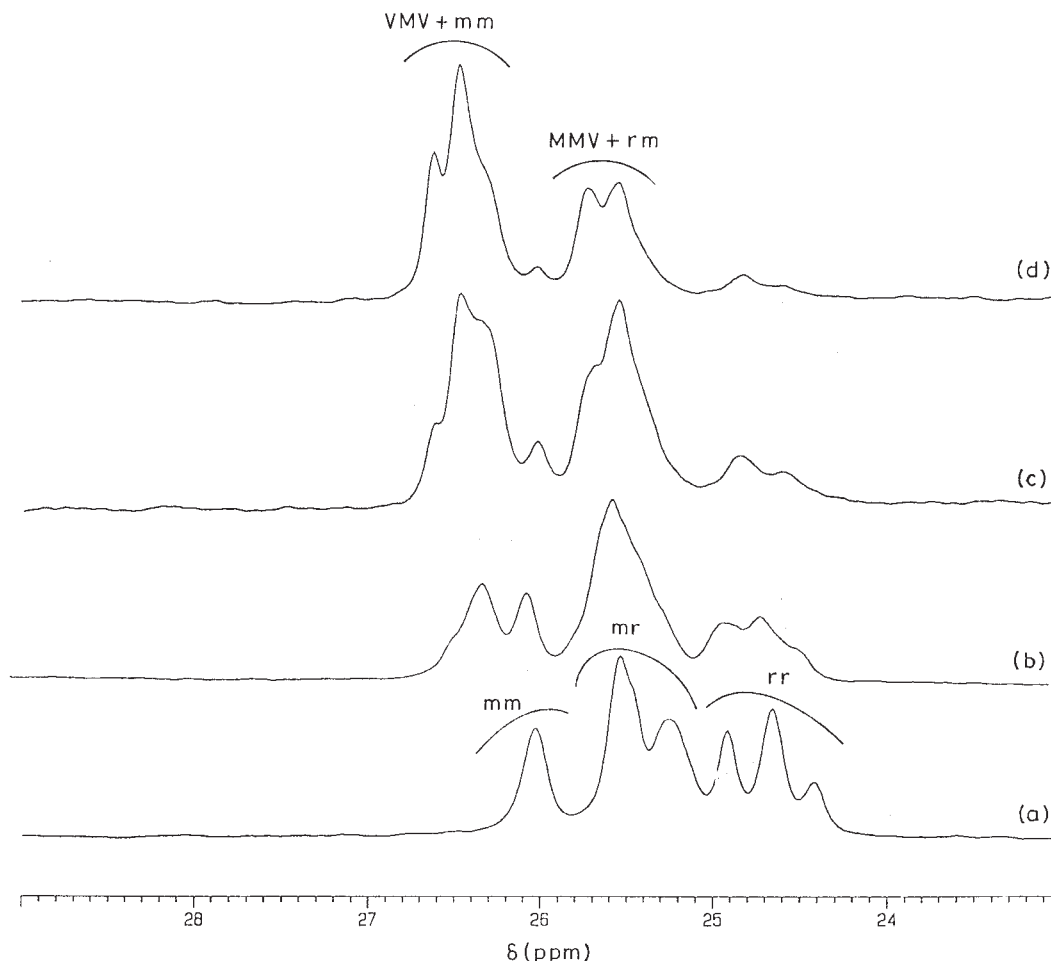
Figure 6 The expanded α-methyl regions of (a) PMAN and methacrylonitrile–vinylidene chloride (M/V) copolymers with compositions (F_M =): (b) 0.79, (c) 0.52, and (d) 0.38.

done with the help of 2D ^{1}H-^{13}C heteronuclear single quantum correlation spectra of the copolymers. The expanded α-CH$_3$ regions of 2D ^{13}C-^{1}H HSQC NMR spectra of M/V copolymer are shown in Figure 7 [(Fig.

TABLE II
Compositional and Configurational Assignments of the β-Methylene Carbon Regions of the Methacrylonitrile/ Vinylidene Chloride (M/V) Copolymers

Peak No.	Chemical shifts (δ, ppm)	Assignments
1	60.5–61.5	VVVV
2	61.5–62.7	VVVM
3	62.7–63.5	MVVM
4	53.5–54.6	VMVV
5	54.6–55.7	MMVV (VMVM)
6	55.7–56.7	MMVM
7	46.0–47.0	MmMrMmM
8	47.8–48.8	MmMrMrM + MmMmMmM
9	47.8–48.8	MrMrMrM + MmMmMrM
10	48.8–49.8	MrMmMrM

7a) F_M = 0.79;(Fig. 7b) F_M = 0.52; and (Fig. 7c) F_M = 0.22]. The α-CH$_3$ region of the M-monomeric unit in the copolymer shows compositional sensitivity. The crosspeaks at δ24.4/1.79,[1] δ25.5/1.77,[2] and δ26.2/1.74[3] ppm are assigned to MrMrM, MmMrM, and MmMmM triads (Fig. 7a), respectively, by comparison with the HSQC spectrum of poly(methacrylonitrile). Similarly, the MMV triad is assigned at δ25.8/1.80– 1.86[4] ppm, the intensity of which decreases as the concentration of the M-unit decreases. The crosspeak at δ26.3/1.86–1.94[5] ppm is assigned to the VMV triad, which shows the increase in intensity of signals with the increase in V-content and decrease in M-content (Fig. 7c).

The methylene regions of the M/V copolymer show the compositional dyad, tetrad, etc., due to its symmetry. The expanded methylene carbon region of M/V copolymer (F_M = 0.53) is shown in Figure 8. The crosspeak region around δ45.1–50.0/2.0–2.60 ppm is assigned to the MM dyad on the basis of variation of intensity of signals with copolymer composition and
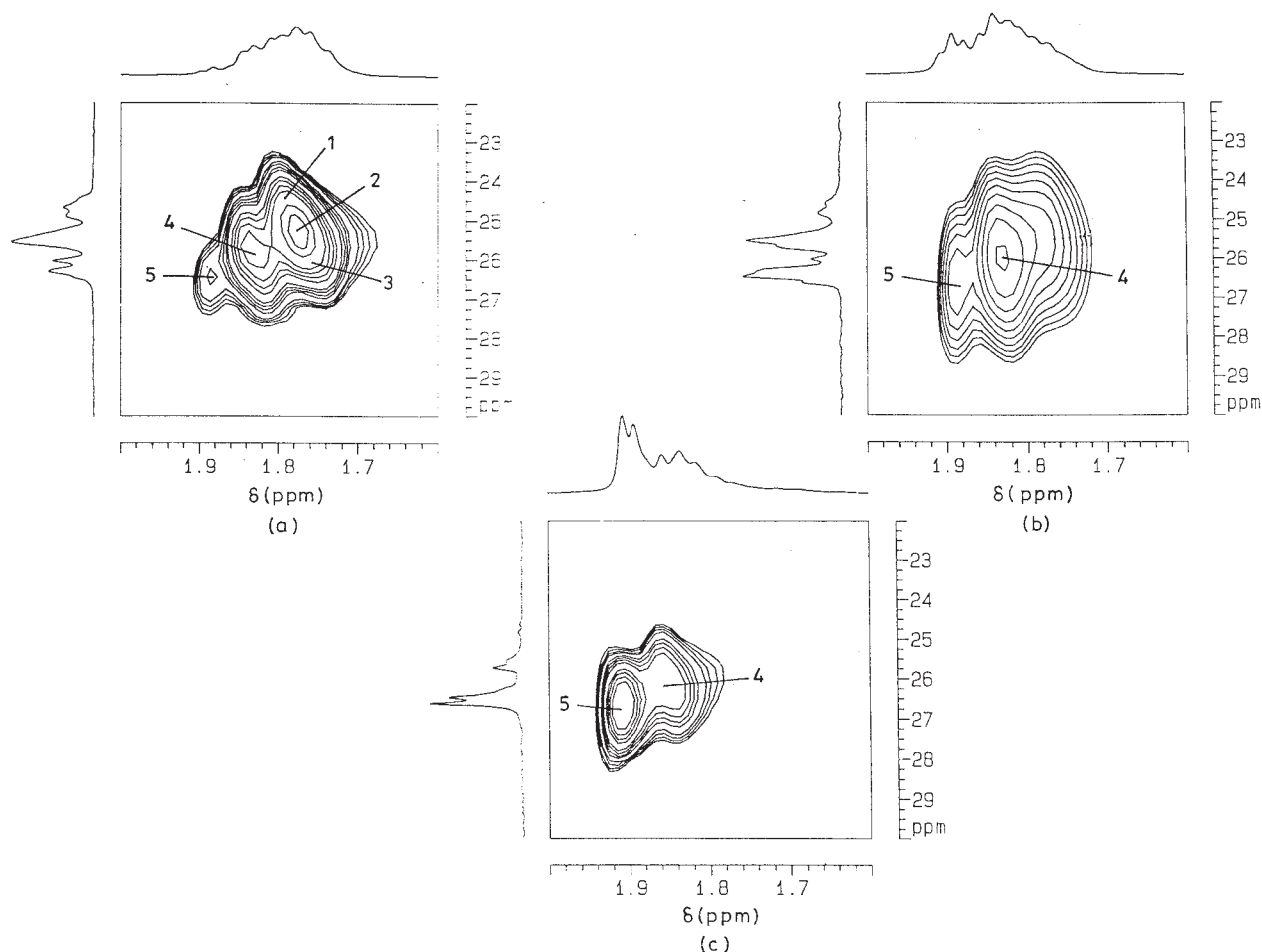
Figure 7 The expanded α methyl carbon regions of 2D HSQC spectra of methacrylonitrile–vinylidene chloride (M/V) copolymers with compositions ($F_M =$): (a) 0.79, (b) 0.52, (c) 0.22.

by comparison with HSQC spectrum of poly(methacrylonitrile). The crosspeaks region around $\delta 53.5$–$57.0/2.75$–3.45 ppm shows the decrease in intensity of signals with the decrease in M-content and increase in V-content and is assigned to the MV dyad, whereas the crosspeak region around $\delta 59.5$–$65/3.65$–4.0 ppm shows the increase in intensity of signals with the decrease in M-content and increase in V-content and is assigned to the VV dyad. Further splitting within these dyad regions is assigned to tetrad compositional and configurational sequences. In the MM dyad region, the crosspeaks at $\delta 47.5/2.55$,[6] $\delta 47.8/2.45$,[7] $\delta 48.0/2.30$,[8] and $\delta 49.0/2.17$[9] ppm are assigned to MmMrMmM, MmMrMrM + MmMmMmM + MMMV, MrMrMrM + MmMmMrM + VMMV, and MrMmMrM tetrads, respectively. The crosspeaks at $\delta 53.9/3.30$,[10] $\delta 54.4/08$–3.16,[11] and $\delta 55.0/2.88$–2.97[12] ppm of MV dyad region can be assigned to VMVV, VMVM (MMVV), and MMVM tetrads, respectively (Fig. 8). Similarly, the other crosspeaks at $\delta 60.89/3.91$,[13] $\delta 61.96/3.80$,[14] and $\delta 62.8/3.70$[15] ppm are due to

VVVV, VVVM, and MVVM tetrads, respectively. All assignments (Figs. 7 and 8) are shown in Table III.

Figure 9 shows the complete assignment of the ^{1}H-NMR spectrum of M/V copolymer ($F_M = 0.52$) recorded in DMSO-d_6 at 80°C. The α-methyl protons in the copolymer resonate around $\delta 1.70$–1.96 ppm, while the β-methylene protons resonate around $\delta 2.17$–3.98 ppm. The spectral regions $\delta 2.00$–2.65, $\delta 2.65$–3.20, and $\delta 3.50$–3.98 ppm are assigned to MM, MV, and VV dyads of the β-methylene protons in the ^{1}H-NMR spectrum of the copolymer.

CONCLUSIONS

The reactivity ratios of comonomers in M/V copolymers are $r_M = 2.43$ and $r_V = 0.39$. The complex and overlapped ^{1}H and ^{13}C [^{1}H] NMR spectra of the copolymers were resolved with the help of DEPT-135 and 2D-HSQC spectra. The nitrile carbon of th eM-unit and quaternary carbons of the M- and V-units were assigned up to triad compositional sequences in ^{13}C [^{1}H] NMR spectrum.
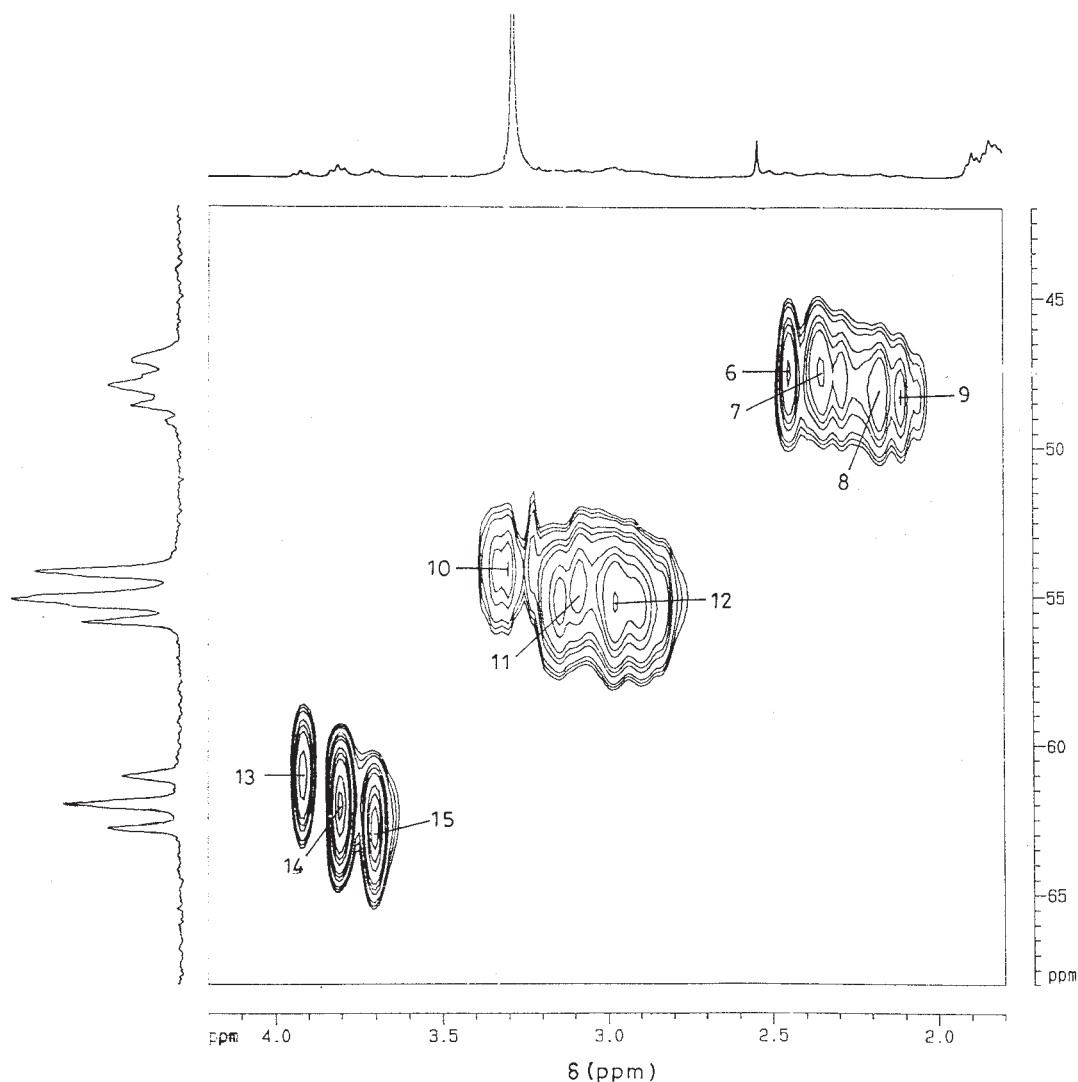
Figure 8 The expanded β-methylene carbon regions of methacrylonitrile–vinylidene chloride (M/V) copolymer ($F_M = 0.52$).

TABLE III
Compositional and Configurational Assignments of α-Methyl and β-Methylene Resonances from 2D HSQC Spectra of Methacrylonitrile/Vinylidene (M/V) Chloride Copolymers

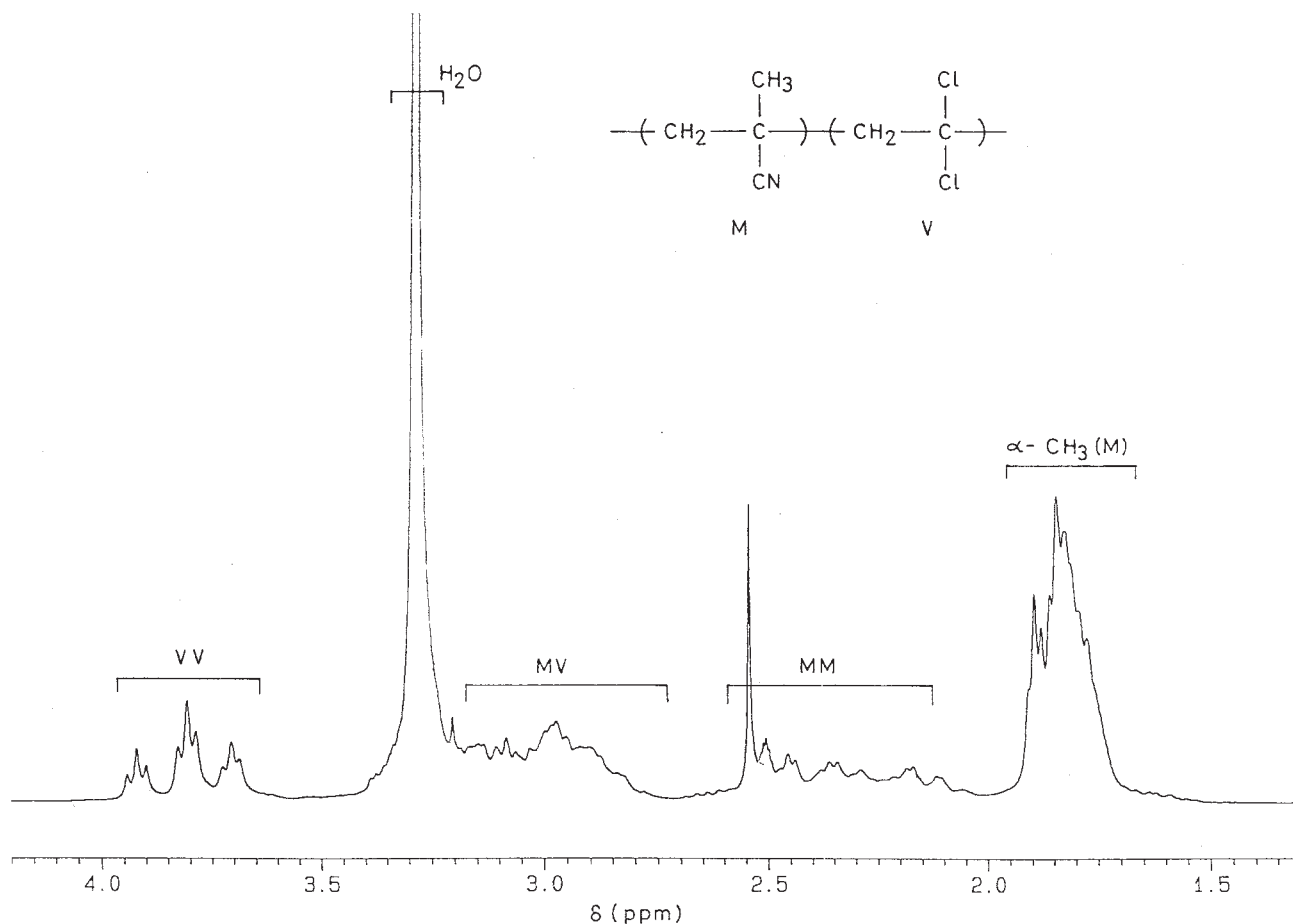| Peak No.	^{13}C(ppm)	^1H(ppm)	Assignments
α-CH$_3$			
1	24.4	1.79	MrMrM
2	25.5	1.77	MmMrM
3	26.2	1.74	MmMmM
4	25.8	1.80	MMV
5	26.3	1.86	VMV
β-CH$_2$			
6	47.5	2.55	MmMrMmM
7	47.8	2.45	MmMrMrM + MmMmMmM + MMMV
8	48.0	2.30	MrMrMrM + MmMmMrM + VMMV
9	49.0	2.17	MrMmMrM
10	53.9	3.30	VMVV
11	54.4	3.08–3.16	VMVM (MMVV)
12	55.0	2.88–2.97	MMVM
13	60.89	3.91	VVVV
14	61.96	3.80	VVVM
15	62.8	3.70	MVVM

Figure 9 The proton NMR spectrum of methacrylonitrile–vinylidene chloride (M/V) copolymer ($F_M = 0.52$) in DMSO-d_6 at 80°C.

The α-CH$_3$ carbon signals were assigned up to triad compositional and configurational sequences, whereas β-methylene carbon resonances were assigned up to tetrad compositional sequences.

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