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Compositional assignments of methyl methacrylate—vinylidenechloride copolymers by two dimensional NMR spectroscopy

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Abstract

The compositional assignments of methyl methacrylate—vinylidene chloride copolymers prepared by the photopolymerization process was studied by ^{1}H, ^{13}C–NMR, ^{1}H–^{13}C–heteronuclear shift correlation NMR (HSQC) and by double quantum filtered homonuclear shift correlated spectroscopy (DQF–COSY). A ^{13}C distortionless enhancement by polarization transfer (DEPT) spectrum was used to differentiate between the resonance signals of methoxy and the methylene units. Assignments to the methylene regions have been done up to the tetrad levels using 2D HSQC experiments. The geminal couplings in the methylene proton region is evident from the 2D-COSY experiments. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

2D heteronuclear NMR spectroscopy is being frequently used for the study of many homopolymers [1–4] and copolymers [5–8]. The chemical shift variation observed in polymethyl methacrylate (PMMA) due to the tacticity was reported by Koinuma et al. [9]. Further, the stereochemical configurational studies on PMMA have been done both by 1D [10, 11] and 2D experiments [12]. Pham et al. have reported the composition [13] and the reactivity ratios [14] of the methyl methacrylate/vinylidene chloride copolymer. Pham et al. [14] have also made assignments up to the pentad level using the α-methyl region of the ^{1}H–NMR spectrum. In this paper we report the compositional and configurational assignments in methyl methacrylate–vinylidene chloride (M/V) copolymers using 2D NMR spectroscopy. The methylene region has been completely analysed using 2D HSQC and COSY spectra. The complex ^{1}H–NMR spectrum was assigned with the help of a HSQC spectrum. The overlap of methoxy carbon with the methylene carbon was distinguished using DEPT carbon 135 NMR spectrum.

2. Experimental

2.1. Materials

Copolymers of various compositions of methyl methacrylate and vinylidene chloride were prepared by a photopolymerization process at room temperature using uranyl nitrate as a photoinitiator. Polymerization was stopped by precipation in methanol and were recrystallized from chloroform. The conversion was kept below 10%. A determination of the molecular weight by gel permeation chromatography in tetrahydrofuran at 35°C indicated the $\bar{M}_n$ to be 1.9×10^4 and

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the $\bar{M}_w/\bar{M}_n$ to be 2.09 for the composition of $F_V = 0.43$ vinylidene chloride in the copolymer.

2.2. NMR measurements

^1H, $^{13}C\{^1H\}$–NMR spectra were recorded on a Bruker FX-300 spectrometer under standard conditions in $CDCl_3$ at room temperature at a frequency of 300.13 and 75.5 MHz, respectively. Distortionless enhancement by polarization transfer (DEPT) measurements were carried out in $CDCl_3$ using the standard pulse sequence with a J modulation time of 3.7 ms ($J_{CH} = 135$ Hz) with 2 s delay time. Two dimensional proton detected ^1H–^{13}C heteronuclear chemical shift correlation spectra were recorded in $CDCl_3$ using the standard pulse sequence [15]. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 t_1 experiments. The double quantum filtered homonuclear shift correlated spectroscopy (DQF–COSY) experiment, with 32 scans being collected for each t_1 value, was carried out in $CDCl_3$. A total of 512 spectra, each containing the 1 K data points, were accumulated.

3. Results and discussion

The complete $^{13}C\{^1H\}$–NMR spectrum of the methyl methacrylate/vinylidene chloride (M/V) copolymer ($F_V = 0.43$) recorded in $CDCl_3$ is shown in Fig. 1. The carbonyl carbon region of methyl methacrylate appears most downfield at δ 175.8–178.1 ppm, whereas the α-methyl region appears the most upfield from δ 15.1–21.5 ppm. The resonating signals of the region δ 83.0–89.0 ppm and δ 44.0–48.0 ppm are assigned as the quaternary carbons of V- and M-centered triads [16, 12], respectively. The region of δ 51.9–67.0 ppm is assigned to the methylene and methoxy carbons. This was clearly distinguished by DEPT carbon-135 recorded in $CDCl_3$ (Fig. 2), which shows that methoxy carbon resonances at δ 51.9–52.6 ppm and methylene carbon resonances at δ 52.6–67.0 ppm.

The ^1H–NMR spectrum of the M/V copolymer (Fig. 3) is broad and overlapping, whoose assignments are done with the help of 2D ^1H–^{13}C–heteronuclear single quantum correlation spectrum ($F_V = 0.43$) shown in Fig. 4. The methoxy carbon at δ 51.9–52.6 ppm is correlated to methoxy protons at δ 3.6–3.7 ppm. For the α-methyl region, it is observed that there is compositional overlap of triads in the $^{13}C\{^1H\}$–

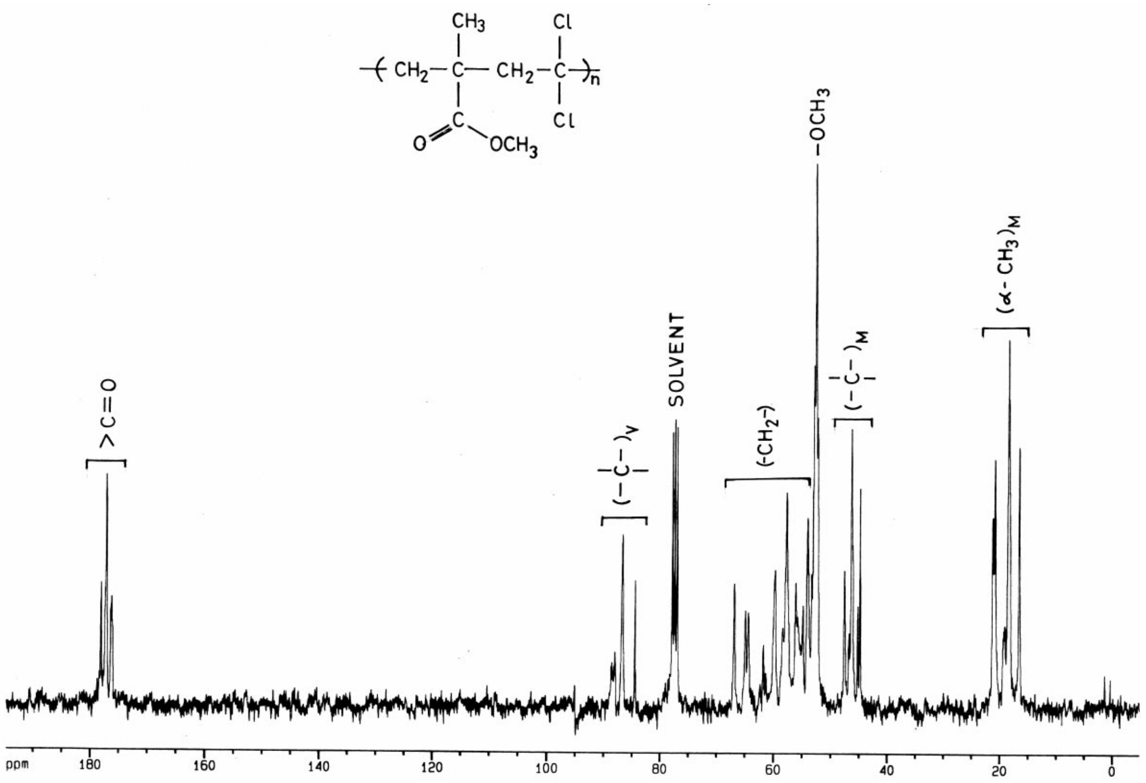

Fig. 1. 75 MHz $^{13}C\{^1H\}$–NMR spectrum of methyl methacrylate/vinylidene chloride (M/V) copolymer in $CDCl_3$. ($F_V = 0.43$).

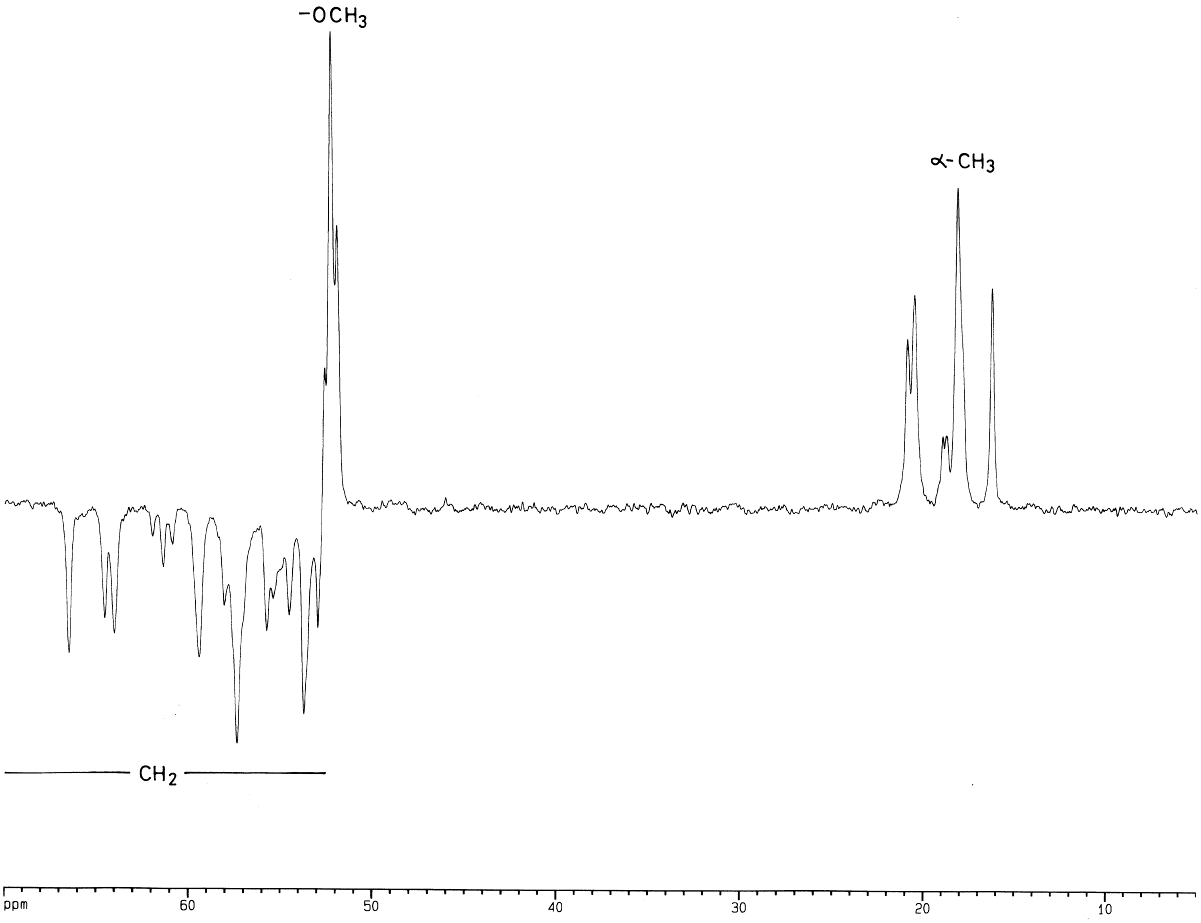

Fig. 2. 75 MHz ^{13}C DEPT NMR spectrum of M/V copolymer. (F_V = 0.43).

NMR spectrum as implied from the poly(methyl methacrylate) spectrum. In order to assign the ^{1}H–NMR spectrum of this region, the heteronuclear shift correlation (HSQC) NMR experiments were recorded for various compositions (F_V = 0.2–0.8). From the variation in the intensity of the contours observed on the HSQC spectrum with varying composition, the ^{1}H–NMR of this region is assigned as δ 0.80–1.25 ppm for MMM triad; δ 1.25–1.60 ppm for MMV triad and δ 1.60–1.80 ppm for the VMV triad. Further, splitting within these triads may be because of the higher compositional or configurational sequencing.

The methylene resonance signal in the ^{13}C{^{1}H}–NMR spectrum has a wide range from δ 52.5–67.0 ppm due to the fact that the V-unit, which has two highly electronegative chlorine atoms, increases the chemical shift. This can be divided into three regions viz δ 52.5–55.5 ppm, δ 55.5–61.0 ppm and δ 61.0–67.0 ppm corresponding to the MM, MV and VV dyads, respectively. This is so because the chlorine atoms produce a deshielding affect for the carbon at α and β position whereas the shielding affect for the carbon is at the γ position. Further splitting of these signals in the ^{13}C{^{1}H}–NMR spectrum are assigned to the tetrad level as shown in the expanded methylene region in Fig. 5. The labelling of these tetrads are based on the variation of resonance signal intensities with the varying compositions of the monomer in the copolymer. These assignments have been confirmed by curve fitting of the resonance signals and the values obtained for the intensities of each of the tetrads are found to be in good agreement with the values from the first order Markov model as given in the Table 1.

The assignment of the tetrads for methylene carbons from 2D heteronuclear single quantum correlation spectrum (Fig. 4) helps to assign the methylene protons on the ^{1}H–NMR spectrum. The VV dyad region at δ

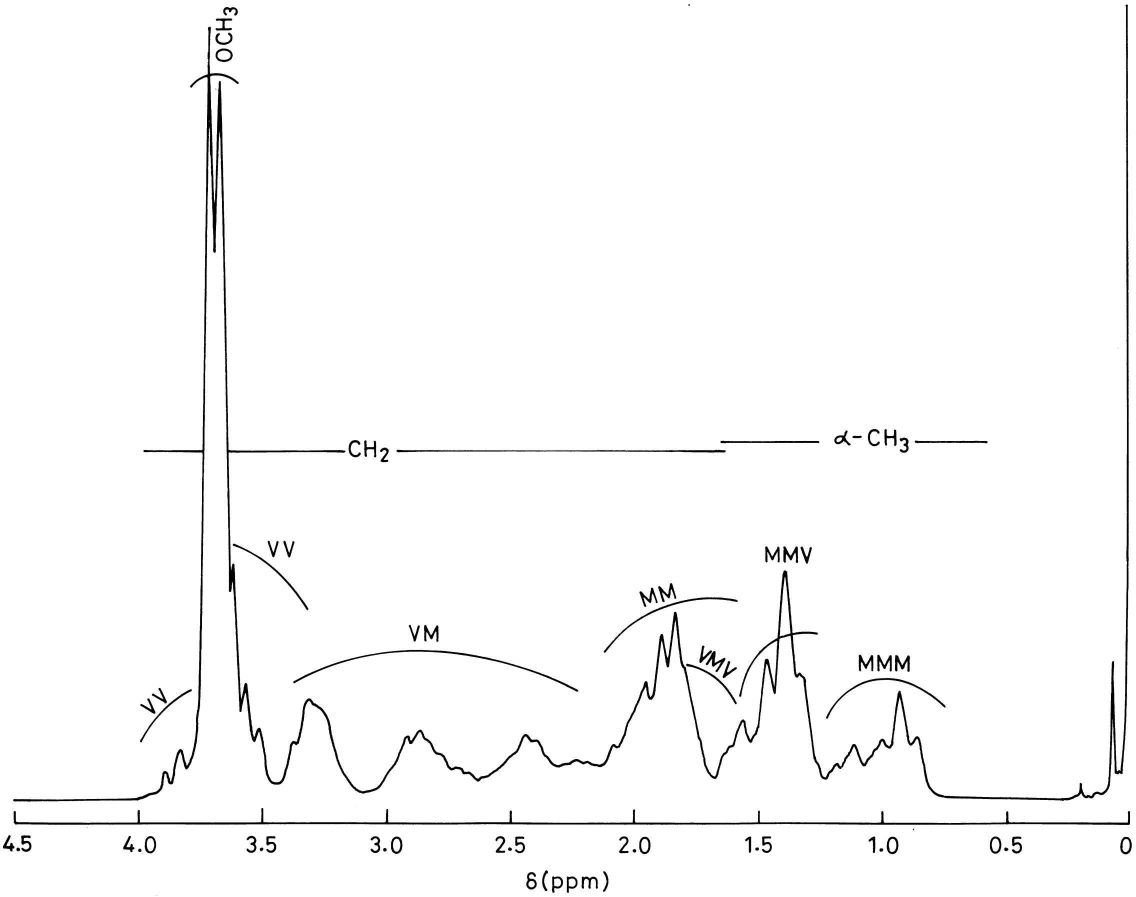

Fig. 3. 300 MHz 1D ^{1}H–MR spectrum of the M/V copolymer (F_V = 0.43).

66.5; δ 64.0 and δ 61.5 ppm on ^{13}C–NMR spectrum shows three contours on the 2D HSQC spectrum appearing at δ 3.30; δ 3.55 and δ 3.82 ppm which is because of the MVVM, VVVM and VVVV tetrads, respectively. Further, fine splittings may be due for higher compositional sequences and tactic reasons. Thus, the region δ 3.3–3.9 ppm is because of the methylene protons of the VV region. In the VM dyad region, it is observed that each of the four tetrads MVMM, VVMM , MVMV and VVMV tetrads split into two each on the ^{1}H–NMR spectrum. Thus, the MVMM tetrad at δ 59.5 ppm on the ^{13}C{^{1}H}–NMR is correlated to the protons at δ 2.22 and δ 2.83 ppm; the MVMV tetrad at δ 57.5 ppm on ^{13}C is correlated to protons at δ 2.42 and δ 2.92 ppm; then the VVMM tetrad at δ 57.0 ppm on the ^{13}C spectrum is correlated to protons at δ 2.42 and δ 3.22 ppm and the VVMV tetrad at δ 55.2 ppm on ^{13}C is correlated to protons at δ 2.7 and δ 3.32 ppm. This may be because the methylene protons of the VM dyads are magnetically non equivalent.

The methylene protons of the MM dyad region appear in two groups. The first group consists of equivalent protons connected to the same carbon, such as methylene protons in a symmetrical racemic dyad for which a single contour is observed at δ 1.8–2.1 ppm covering the MMrMM, MMrMV and VMrMV tetrads. The corresponding signal on ^{13}C{^{1}H} appears at δ 53.5 ppm. The second group is methylene protons connected to the same carbon but which are inequivalent such as methylene protons in a meso dyad. Thus, for the tetrads in the meso dyad viz MMmMM, MMmMV and VMmMV, whose percentage though less appears at δ 1.55 and δ 1.80–2.1 ppm on the ^{1}H–NMR corresponding to δ 53.5 ppm on the ^{13}C spectrum. In these cases the protons will be coupled to each other (geminal coupling) as observed in the previous work on methacrylates, acrylates and

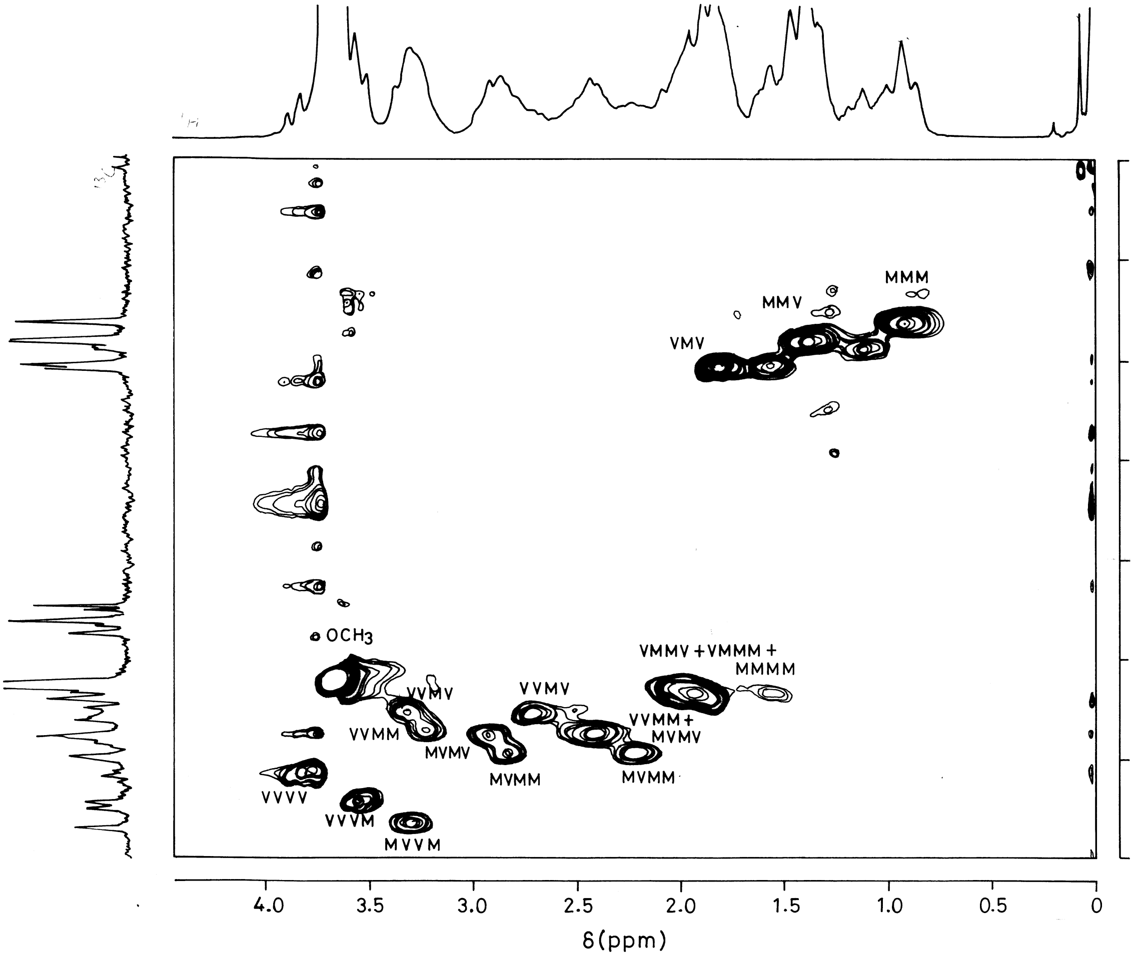

Fig. 4. 75 MHz 2D ^1H–^{13}C heteronuclear NMR specstroscopy of methyl methacrylate/vinylidene chloride copolymer (F_V = 0.43).

methacrylonitrile [12, 17, 18]. Table 2 shows the complete information obtainable from HSQC and COSY spectrum with assignments.

It is evident from the 2D HSQC spectrum, that for the methylene chemical shifts at the tetrad level, the signals having higher chemical shifts for $^{13}C\{^1H\}$–NMR correspond to the lower chemical shifts for ^1H and vice versa. A DQF–COSY spectrum is shown in Fig. 6 (F_V = 0.43). The COSY spectrum generally shows the 1,3 bond coupling, since here no such coupling is expected, hence, the cross peaks observed are assigned to the 1,2 bond geminal coupling. The cross peaks observed are in the MM and VM dyad of the methylene region and no cross peaks in the VV dyad methylene region. This predicts that the observed cross peaks are due to the inequivalence of the methylene protons in VM and

Table 1
Comparison of the theoretical and experimental (NMR) tetrad fractions of M/V copolymer (F_V = 0.43)

Tetrad	Tetrad fractions Theoretical	Experimental $^{13}C\{^1H\}$[a]
VVVV	0.02	0.05
VVVM	0.08	0.10
MVVM	0.06	0.06
VVMV	0.09	0.10
VVMM	0.25	0.20
MVMM	0.18	0.16
VMMV	0.06	0.04
VMMM	0.16	0.20
MMMM	0.10	0.09

[a] Methylene resonance signals used for tetrad fractions determination

Table 2
Methylene assignments from 2D HSQC and DQF–COSY spectrum

Assignments	HSQC ^{13}C (ppm)	^{1}H (ppm)	DQF–COSY (geminal coupling)
VVVV	61.5	3.88, 3.82, 3.76	—
VVVM	64.0	3.55, 3.52	—
MVVM	66.5	3.30	—
VVMV	55.2	3.32, 2.7	3.2, 3.3, 3.35/2.6, 2.68, 2.75
VVMM	57.0	3.22, 2.42	3.2, 3.26, 3.4/2.36, 2.43, 2.53
MVMV	57.5	2.92, 2.42	2.8, 2.85, 2.86, 2.94, 2.95/2.42, 2.45, 2.48, 2.52, 2.57
MVMM	59.5	2.83, 2.22	2.77, 2.76, 2.81, 2.88, 2.89/2.12, 2.18, 2.22, 2.23, 2.32
VMrMV + VMrMM + MMrMM	53.2	1.80–2.10	—
VMmMV VMmMM MMmMM	53.2	1.55, 1.8–2.1	1.45, 1.6, 1.7/1.98, 2.08, 2.1

MM dyad regions as for the VV dyad region, the methylene protons are both chemically and magnetically equivalent.

In the VM methylene dyad region, the cross peaks observed are the 1,2 geminal couplings viz- δ 2.12–2.32/2.77–2.89; δ 2.42–2.57/2.80–2.95; δ 2.36–2.53/3.20–3.40 and δ 2.60–2.75/3.20–3.35 ppm which are because of the inequivalence of the methylene protons in the copolymer sequence of MVMM, MVMV, VVMM and VVMV tetrad, respectively. This confirms the splitting observed in the 2D HSQC spectrum.

In the MM methylene dyad region, since the major part is because of the racemic variety of the three tetrads, and since, in these, the methylene protons are equivalent, no cross peaks are expected. However, a small percentage of the meso variety of the tetrads is also present due to which a cross peak is observed from δ 1.4–1.7/1.9–2.1 ppm corresponding to the

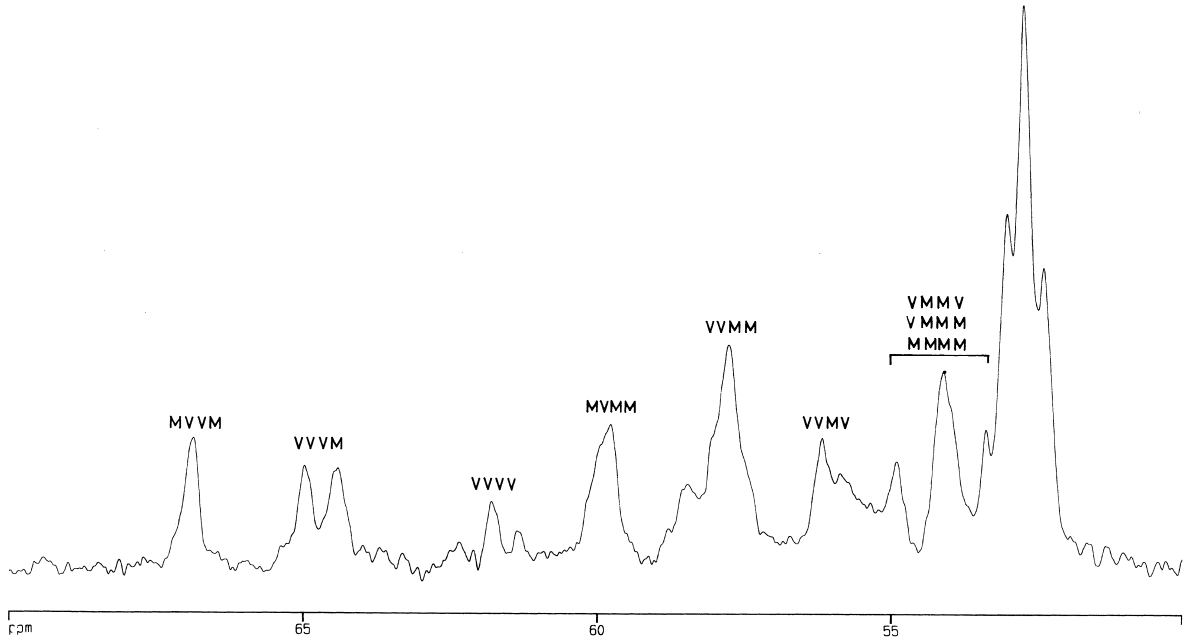

Fig. 5. Expanded methylene carbon resonance signals of the ^{13}C{^{1}H}–NMR spectrum of the M/V copolymer.

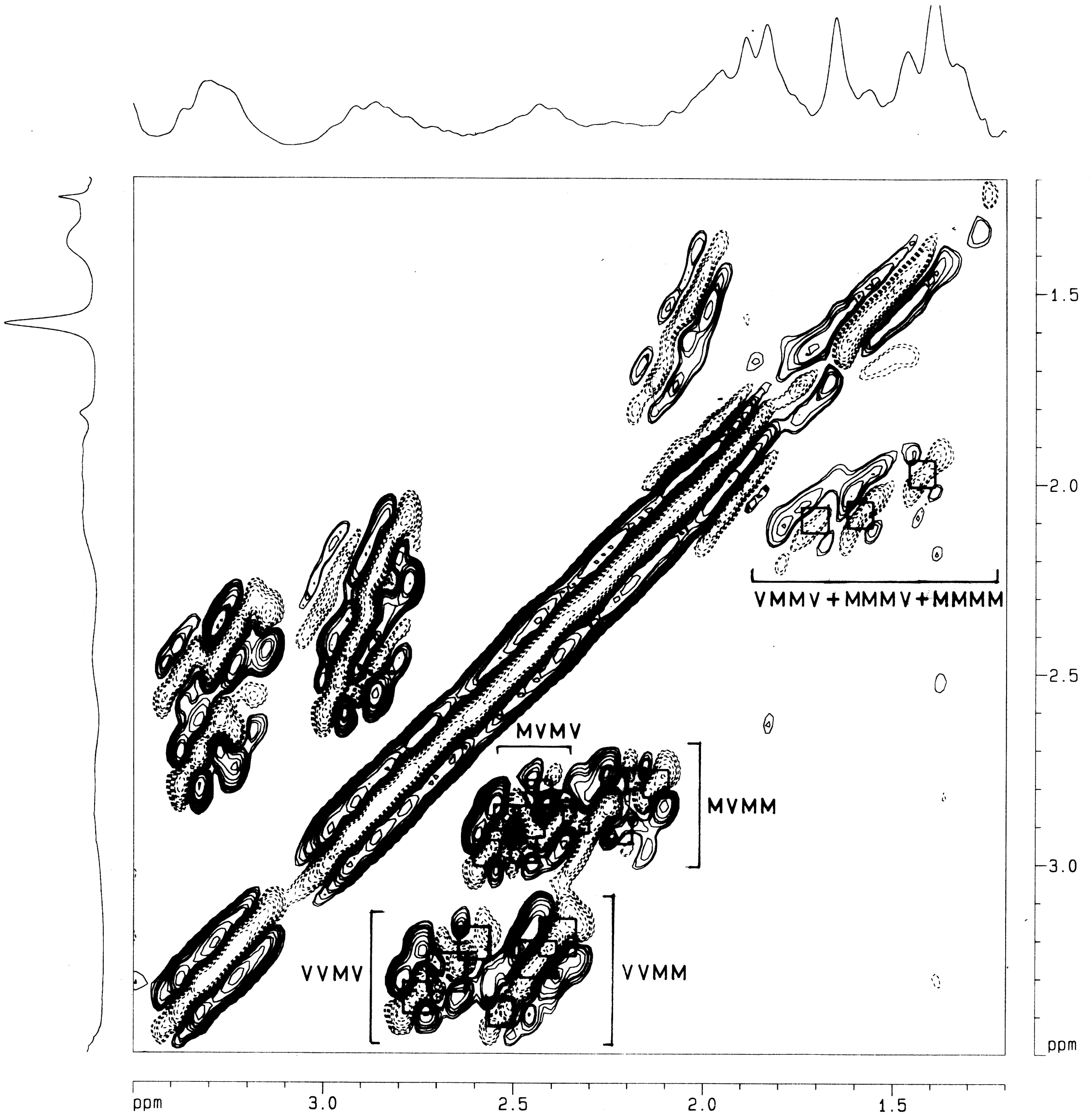

Fig. 6. 2D DQF–COSY NMR spectrum of the M/V copolymer ($F_V = 0.43$). Assignments have been marked on the figure.

geminal couplings of the MMmMM, MMmMV and VMmMV tetrads.

4. Conclusion

By means of DQF–COSY and proton detected ^1H–^{13}C–heteronuclear shift correlation NMR, the compositional and configurational assignments have been done for methyl methacrylate/vinylidene chloride copolymers. The broad and complex ^1H–NMR spectrum has been assigned. The HSQC spectrum predicted the possibilities of the inequivalent protons and was confirmed by the geminal couplings observed in the DQF–COSY spectrum.

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