Comprehensive Assignments of ^{1}H and ^{13}C NMR Signals for the Vinylidene Chloride–Butyl Acrylate Copolymers Using 2D NMR Spectroscopy

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ABSTRACT: Vinylidene chloride–butyl acrylate copolymers were prepared by photopolymerization at room temperature. The molecular weight of these copolymers have been determined using Gel Permeation Chromatography and the copolymer composition estimated using Schoneger technique. 2D NMR techniques such as ^{1}H–^{13}C heteronuclear single quantum correlation (HSQC) was used for the compositional and configurational assignments of ^{1}H and ^{13}C\{^{1}H\} NMR spectra for various resonating signals. 2D ^{1}H homonuclear double quantum filter-correlated spectroscopy (DQF-COSY) is used to get better insight for the copolymer structure.

KEY WORDS Photopolymerization / Gel Permeation Chromatography / Composition / Heteronuclear Single Quantum Correlation / Correlated Spectroscopy / Vinylidene Chloride / Butyl Acetylate / Copolymer /

Two dimensional homonuclear and heteronuclear NMR spectroscopy have been used extensively for the structure elucidation of polymers. The microstructure of homopolymers[1] such as poly(methacrylonitrile),[2] poly-(vinyl chloride),[3] polyisobutylene,[4] poly(*tert*-butyl acrylate)[5] and poly(cyclohexyl acrylate)[6] have reports by 2D NMR spectroscopy. 2D NMR has also been used for the characterization of the copolymers.[7,8]

In our earlier publications on vinylidene chloride–methyl acrylate copolymers,[9] we have determined their microstructure and reported the detailed assignment of the ^{13}C\{^{1}H\} NMR signals. In this the methine and methylene signals were assigned upto triad and diad levels respectively on the ^{1}H NMR using heteronuclear single quantum correlation (HSQC) experiments. Further splittings on the HSQC for these resonating regions were attempted in the vinylidene chloride–ethyl acrylate[10] where the methine and methylene signals were assigned upto pentad and tetrad levels, respectively. But 2D-COSY spectrum was not discussed in detail. In the continuation of our work, we report the 2D studies of commercially important[11] vinylidene chloride–butyl acrylate (V-B) copolymer by using one dimensional (^{1}H and ^{13}C) and two dimensional NMR spectroscopy. The 2D-COSY spectrum shows all the 1, 2 bond geminal couplings feasible for the methylene protons along with the 1, 3 bond coupling of the methine with the methylene protons.

EXPERIMENTAL

Vinylidene chloride (Fluka) and butyl acrylate were freed from inhibitor by distilling under reduced pressure prior to use. The copolymers are prepared by photo-polymerization[12,13] using uranyl nitrate as photo-sensitizer.[14] The molecular weights of the copolymers were determined by gel permeation chromatography (GPC) using polystyrene as narrow standard (Waters, 410). Tetrahydrofuran was used as solvent.

The composition was determined using Schoneger technique.[15,16] The 1D NMR spectra and the 2D HSQC spectra of the copolymers were recorded on a JEOL 300 MHz spectrometer, whereas 2D DQF-COSY spectra was recorded on the Bruker-DPX 300 MHz spectrom-eter. Experimental details are mentioned in our earlier publication.[9]

RESULTS AND DISCUSSION

Schoneger technique is used for the estimation of chlorine content of the V-B copolymers. This is used to obtain the copolymer compositions. The copolymer composition, the percent chlorine and the molecular weight averages, determined from the GPC of these copolymers are shown in Table I.

The ^{1}H NMR spectrum of the V-B copolymers ($F_V = 0.5$) in CDCl$_3$ at room temperature is shown in Figure 1. In the V-B copolymer, the side chain methyl (^{4}CH$_3$) protons are assigned at δ 0.88—0.96 ppm. The alkyl side chain methylene protons (^{3}CH$_2$) and (^{2}CH$_2$) resonate around δ 1.38 and δ 1.61 ppm, respectively. The oxy-methylene protons (O^{1}CH$_2$) appear the most downfield at δ 4.08 ppm. All these assignments are confirmed by 2D HSQC NMR experiment. The 2D-COSY NMR spectrum further shows 1, 3 bond coupling of the oxy-methylene–methylene, methylene–methylene, and methy-lene–methyl protons at δ 4.07/1.59 ppm, δ 1.59/1.36 ppm and δ 1.38/0.9 ppm (Figure 6, X, Y, Z). The region extending from δ 1.6—3.9 ppm is enveloped by the methine and methylene protons of the main chain. These are clearly distinguished using ^{13}C NMR assignments and the 2D HSQC NMR experiment.
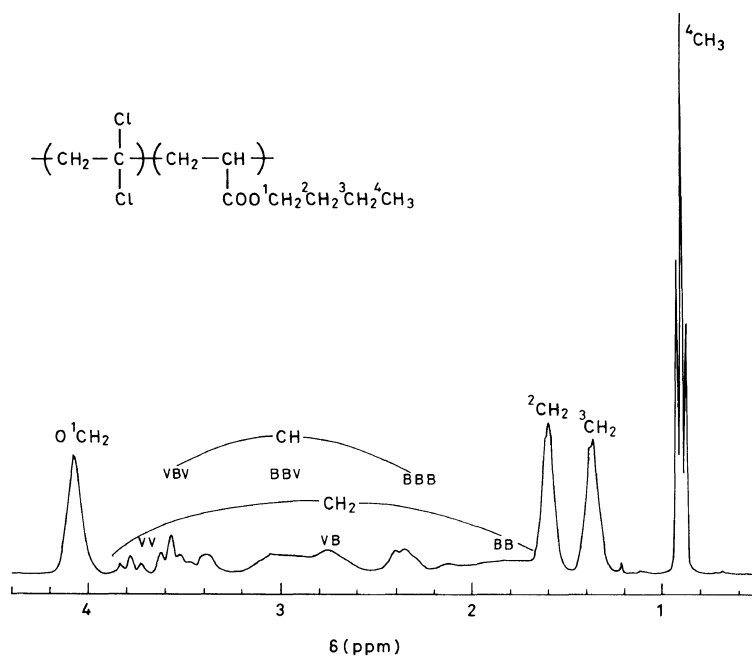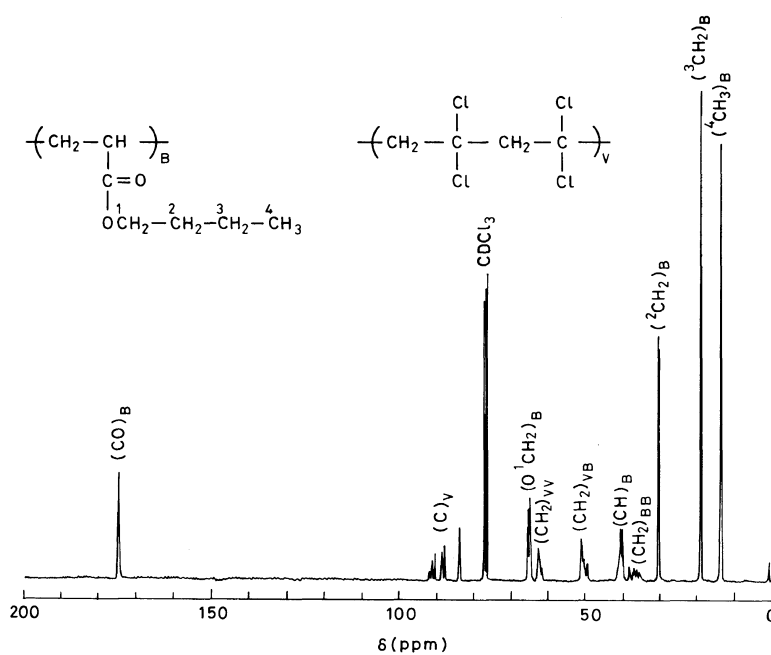
The ^{13}C\{^{1}H\} NMR spectrum of the V-B copolymer ($F_V = 0.5$) in CDCl$_3$ is shown in Figure 2. The methyl carbon (^{4}CH$_3$) of the alkyl side chain resonances at δ 13.64 ppm. The methylene carbons of the alkyl side chain, resonances at δ 19.08 (^{3}CH$_2$) and δ 30.5 ppm (^{2}CH$_2$). The oxymethylene carbon of the alkyl side chain and the carbonyl carbon of the B unit show multiplets at δ 64.6—65.5 and δ 174.0—176.0 ppm respectively

Table I. Copolymer composition and molecular weight averages of vinylidene chloride–butyl acrylate (V-B) copolymers

S. no.	Monomer feed content (mole fraction)		Copolymer composition (mole fraction)		% Cl	$\bar{M}_n \times 10^{-4}$ g mol^{-1}	$\bar{M}_w \times 10^{-4}$ g mol^{-1}
	f_V	f_B	F_V	F_B			
1	0.2	0.8	0.21	0.79	12.26	13	26
2	0.3	0.7	0.31	0.69	18.58	10	22
3	0.4	0.6	0.41	0.59	25.23	7	18
4	0.5	0.5	0.50	0.50	31.54	5	14
5	0.6	0.4	0.60	0.40	38.93	4	10
6	0.7	0.3	0.69	0.31	45.94	4	10

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

Figure 1. 300 MHz ^{1}H NMR spectrum of vinylidene chloride–butyl acrylate copolymer ($F_V = 0.5$).

Figure 2. 75 MHz ^{13}C{^{1}H} NMR spectrum of the V-B copolymer ($F_V = 0.5$).

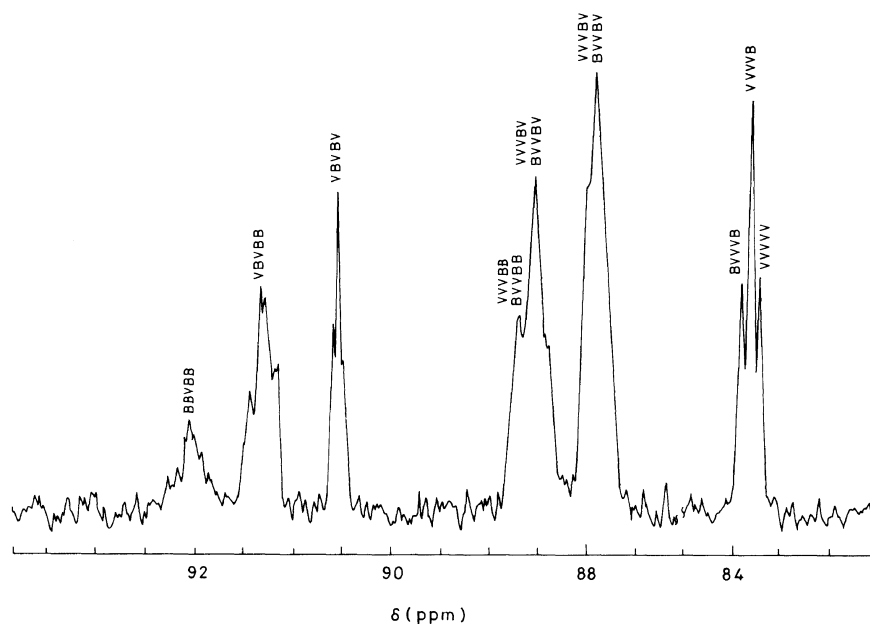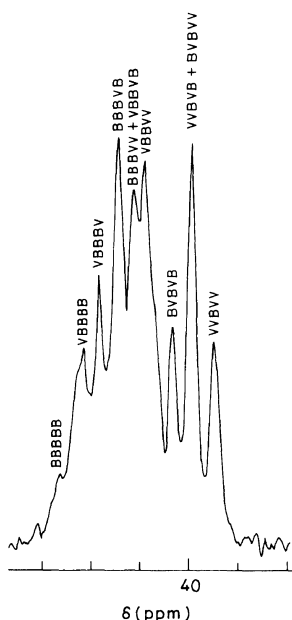**Figure 3.** $^{13}C\{^1H\}$ NMR spectrum showing the expanded quaternary carbon resonances of the V-monomeric unit.

**Figure 4.** $^{13}C\{^1H\}$ NMR spectrum showing the expanded methine carbon resonances of the B-monomeric unit.

which is due to the compositional sensitivity.

The quaternary carbon of the V-unit shows sharp and well separated signals in the region δ 83.7—92.1 ppm indicating that it is compositional sensitive. These have been assigned upto the pentad level, the expanded region is shown in Figure 3. The triads are labeled as VVV (δ 83.74—83.94), VVB (δ 87.89—88.68) and BVB (δ 90.5—92.1 ppm) which are based on the variation in the resonating intensities with respect to the variation in the composition and are also found to be in agreement with assignments reported in the literature.[17]

The methine carbon of the B unit of the V-B copolymer which appears at δ 39.74—41.30 ppm is shown in Figure 4. The resonance signals are assigned as BBB (δ 40.91—41.30), BBV (δ 40.45—40.71) and VBV (δ 39.74—40.17) triads based on the variation of the intensity of the signal

with the composition. The fine splittings further observed is due to pentad sequencing.[9,18] A 2D proton detected HSQC NMR spectrum has been recorded (Figure 5), which shows the direct proton to carbon correlations. Three contours are observed for the methine protons viz.: δ 3.4—3.6 ppm for VBV, δ 2.8—3.1 ppm for BBV, and δ 2.25—2.45 ppm for BBB triads in the HSQC spectrum. It is observed that the resonating signal at higher chemical shifts for ^{13}C corresponds to lower chemical shifts for ^1H in the methine region.

The methine proton in the different triads (VBV, VBB, BBB) will couple with each of the nearby methylene protons having different environments due to the unsymmetrical butyl acrylate unit. All these 1, 3 interactions between methine and methylene protons are clearly seen in the 2D-COSY spectrum (Figure 6). These structures are shown below:
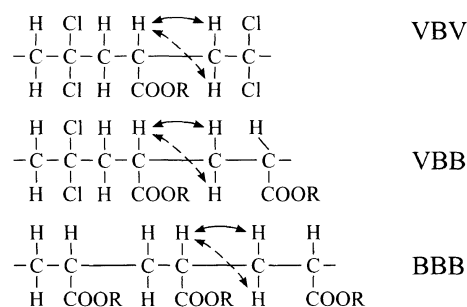
The VBV methine triads at δ 3.45 ppm couples with methylene protons of the VB region at δ 3.05 ppm and δ 2.76 ppm (Figure 6, I and II). Then BBV methine triad at δ 2.92 ppm couples with methylene protons of BB region at δ 1.92 and δ 1.7 ppm (Figure 6, III and IV) and the methine protons of BBB triad at δ 2.3 ppm couples to methylene protons of BB region at δ 1.8 ppm and δ 1.65 ppm (Figure 6, V and VI).

The β-methylene carbons of both V and B monomeric unit resonances in three well separated regions on the ^{13}C NMR spectrometer viz. δ 35.2—38.3, δ 49.2—51.3,
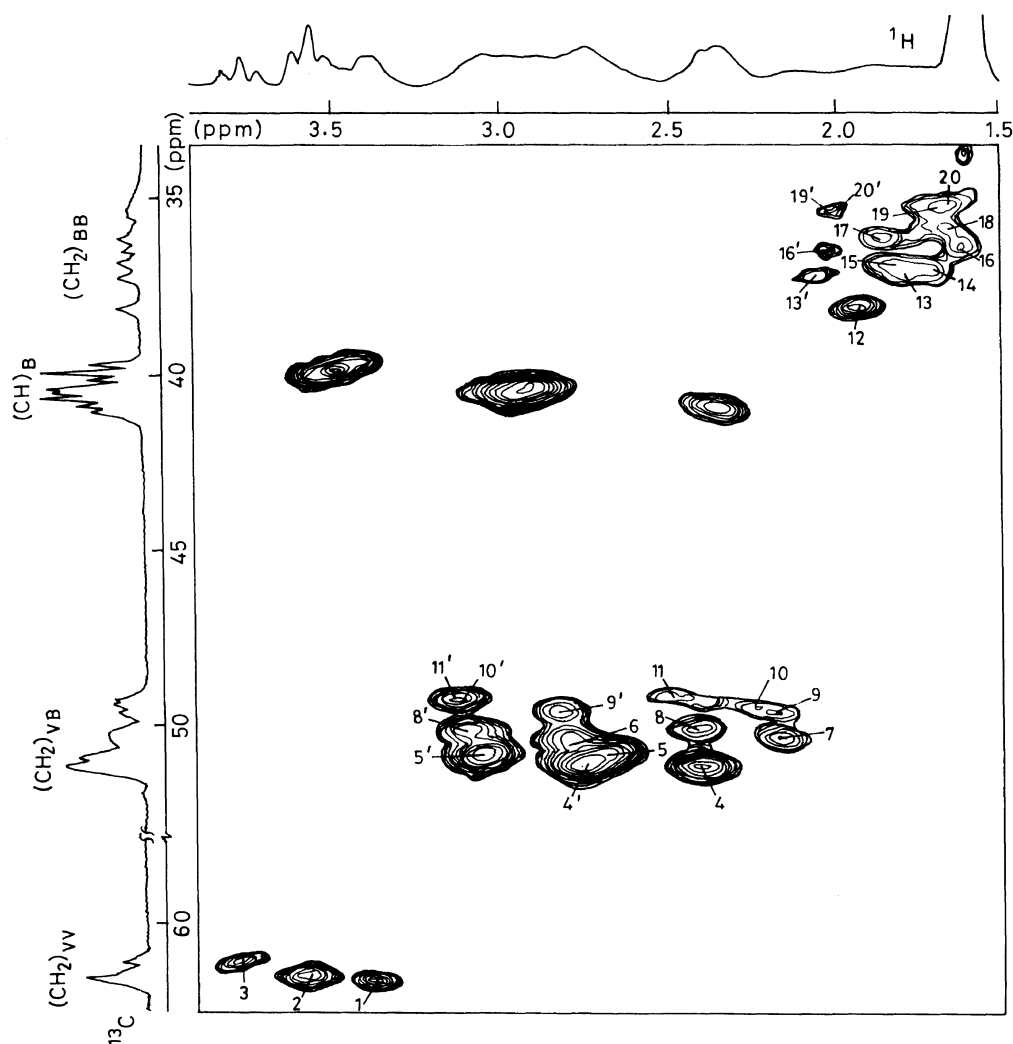
Figure 5. 2D HSQC NMR spectrum showing the methine and methylene resonances of the V-B copolymer.

and δ 61.6—62.8 ppm that are broadly assigned as BB, VB, and VV diads. This is due to the fact that the chlorine group has a strong inductive effect on the chemical shift of the nearby carbons. It produces the deshielding effect for the carbon at the α and β position and has a shielding effect for the carbon at γ position. Similar effect is also produced by the ester group but to the less extent. The corresponding β methylene protons from 2D HSQC spectrum shows that these diads are at δ 1.55—2.1 ppm (BB), δ 2.1—3.2 ppm (VB), and δ 3.32—3.88 ppm (VV) in the ^{1}H NMR spectrum.

Each of these diads further shows multiplets on the ^{13}C NMR which is due to its compositional and configurational sensitivity. These are assigned upto the tetrad level based on the variation in the intensity of the resonance signals with the change in composition. The expanded methylene region is shown in Figure 7. The tetrads of the V.V region are δ 62.6—62.8 ppm (VVVV), δ 62.1—62.6 ppm (VVVB), and δ 61.5—61.8 ppm (BVVB). On the VB diad region, the tetrads are labelled as δ 51.2—51.4 ppm (VVBV), δ 50.1—51.2 ppm (VVBB/BVBV), and δ 49.2—50.0 ppm (BVBB), whereas the tetrads on the BB diad region are labelled as δ 38.0—38.5 ppm (VBBV), δ 36.3—37.5 ppm (VBBB), and δ 35.0—36.3 ppm (BBBB).

It is observed from 2D HSQC spectrum (Figure 5),

that there are fine splittings within these tetrads. These may be assigned to the configurational variation within the tetrad. For the VV dyad region three contours are obtained at δ 62.7/3.4 ppm, δ 62.3/3.6 ppm, and δ 61.8/3.8 ppm corresponding to VVVV, VVVB, and BVVB tetrads (Figures 5, 1—3). Since the two methylene protons in this region are equivalent due to the symmetry of V-monomeric unit, hence no further splittings are seen and also 2D DQF-COSY shows no cross peaks in this region.

For the VB diad region, a multiplet is observed in the HSQC spectrum, which is because of the configurational splitting. The methylene protons in the VVBV tetrad becomes inequivalent because of different magnetic environment and this tetrad which appears at δ 51.1 ppm on ^{13}C spectrum shall appear at δ 2.4 and δ 2.77 ppm on the ^{1}H NMR spectrum. Then for VVBB tetrad the tacticity between the two B units, make the ^{13}C signals to appear at δ 50.9 and δ 50.6 ppm due to VVBmB and VVBrB tetrads respectively. Further in the VVBmB tetrad since two methylene protons are magnetically different therefore appear at δ 2.68 and δ 3.08 ppm on the ^{1}H spectrum whereas for VVBrB tetrad the methylene protons appear at δ 2.8 ppm on the ^{1}H spectrum. Similarly, for BVBV tetrad the BrVBV tetrad at δ 50.4 ppm on ^{13}C spectrum, is at δ 2.15 ppm on ^{1}H NMR and
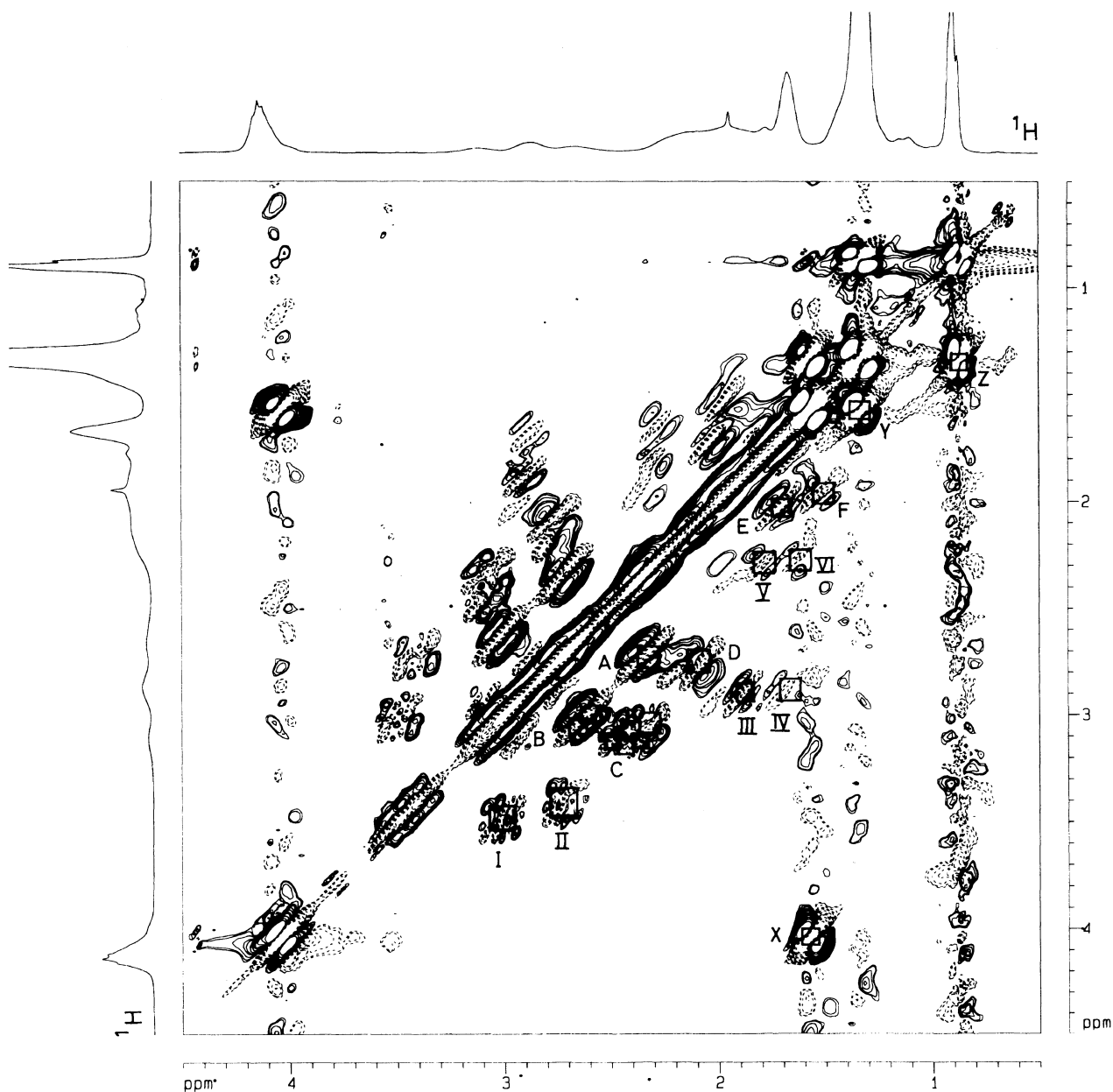
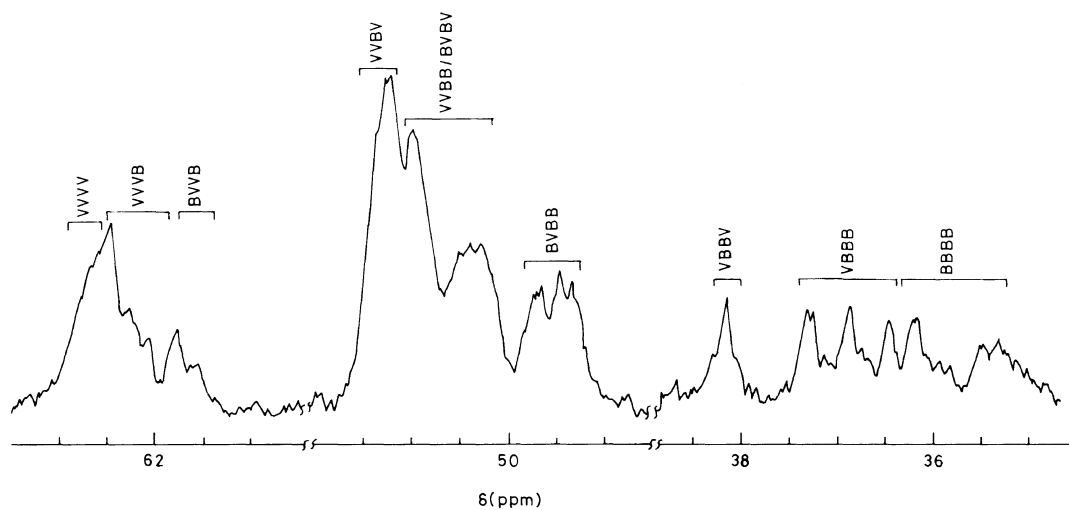**Figure 6.** 2D DQF-COSY NMR spectrum of the V-B copolymer ($F_V = 0.5$).

Figure 7. $^{13}C\{^1H\}$ NMR spectrum showing the expanded methylene carbon resonances of the V- and B-monomeric unit.

Table II. Complete assignments of the methylene signals using 2D HSQC and 2D DQF = COSY spectrum for the vinylidene chloride–butyl acrylate copolymer

$^{13}C\{^1H\}$ ppm	^1H ppm	Label on HSQC spectrum	Label on COSY with coupling protons	Assignments
62.7	3.4	1	—	VVVV
62.3	3.6	2	—	VVVB
61.8	3.8	3	—	BVVB
51.1	2.4, 2.77	4, 4′	A (2.39/2.75)	VVBV
50.9	2.68, 3.08	5, 5′	B (2.65/3.02) (2.7/3.09)	VVBmB
50.6	2.8	6	—	VVBrB
50.4	2.15	7	—	BrVBV
50.3	2.41, 3.1	8, 8′	C (2.45/3.1) (2.45/3.18)	BmVBV
49.7	2.18, 2.82	9, 9′	D (2.13/2.80)	BmVBrB
49.6	2.22, 3.1	10, 10′	C (2.3/3.05)	BrVBrB
49.5	2.5, 3.12	11, 11′	C (2.40/3.15) (2.52/3.15)	BmVBmB
38.2	1.92	12	—	VBBV
37.4	1.8, 2.08	13, 13′	E (1.72/2.05)	VBmBrB
37.3	1.7	14	—	VBrBrB
36.8	1.85	15	—	VBrBmB
36.5	1.62, 2.02	16, 16′	F (1.60/1.98)	VBmBmB
36.1	1.86	17	—	BrBrBrB
35.8	1.65	18	—	BmBrBmB + BmBrBrB
35.5	1.65, 2.0	19, 19′	F (1.60/1.98)	BrBmBrB + BmBmBrB
35.3	1.65, 2.0	20, 20′	F (1.60/1.98)	BmBmBmB

the BmVBV at δ 50.3 ppm on ^{13}C splits into two on ^1H spectrum again due to non-equivalent environment of methylene protons at δ 2.41 and δ 3.1 ppm. Then for BVBB tetrad, the BmVBrB tetrad which resonances at δ 49.7 ppm on ^{13}C appears at δ 2.18 and δ 2.82 ppm on ^1H NMR; the BrVBrB tetrad shows cross peaks at δ 49.6/2.22 and δ 49.6/3.1 ppm. The *meso* variety of this tetrad BmVBmB appears at δ 49.5 ppm on ^{13}C and δ 2.5 and δ 3.12 ppm on ^1H NMR spectrum. All these assignments are mentioned in Table II and Figure 5(4—11). For all the above tetrads, wherever inequivalent protons are seen on the HSQC experiment there is a corresponding 1, 2 bond geminal coupling cross peak observed on the 2D DQF-COSY spectrum which have been labelled from A to D (Figure 6).

For the BB diad region, since the splittings seen on 2D HSQC is due to the tacticity splittings at the tetrad level. The VBBV tetrad, which is a symmetrical compositional tetrad shows only one contour at δ 38.2/1.92 ppm. For the VBBB tetrad, the VBmBrB tetrad which is at δ 37.4 ppm on ^{13}C splits in two on ^1H at δ 1.8 and δ 2.08 ppm; the VBrBrB and VBrBmB show cross peaks at δ 37.3/1.7 and δ 36.8/1.85 ppm, respectively. Then VBmBmB tetrad which appears at δ 36.5 ppm on ^{13}C is

split into two at δ 1.62 and δ 2.02 ppm on ^1H NMR spectrum. For the BBBB tetrads, it is expected that *rrr*, *mrm* have equivalent protons whereas *mmm*, *rmr* have nonequivalent protons and the expected splittings are observed in 2D HSQC spectrum. The BrBrBrB shows a contour at δ 36.1/1.86 ppm. The BmBrBmB (which has magnetically equivalent protons) and the BmBrBrB shows one contour at δ 35.8/1.65 ppm. Then the tetrads having inequivalent methylene protons *viz*. BrBmBrB and BmBmBrB show cross peaks at δ 35.5/1.65 ppm and δ 35.5/2.0 ppm. Then BmBmBmB which also has inequivalent methylene protons appears at δ 35.3 ppm on ^{13}C and on ^1H appears at δ 1.65 ppm and δ 2.0 ppm. These assignments are shown in Table II and Figure 5(12—20). The cross peaks observed on the 2D DQF-COSY spectrum corresponding to the 1, 2 bond geminal coupling of the inequivalent methylene protons of the BB diad region are labeled as E and F on Figure 6.

CONCLUSIONS

The structural assignments of the vinylidene chloride–butyl acrylate copolymers were done by using 2D-experiments. The methine and quaternary carbon resonances have been assigned upto the pentad level whereas the methylene carbon resonances have been assigned upto the tetrad configurational level. The 2D HSQC experiment separated the overlap in the ^1H NMR of methine and methylene protons and also helped in the detailed assignments of complicated multiplets seen in the V-B copolymer of the methylene region in ^1H NMR. The 2D DQF-COSY further confirms the possible connectivities between the methine and methylene protons and predicts the geminal coupling of the methylene protons in different environments.

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