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Compositional Assignments and Sequence Distribution of Vinylidene Chloride−Methyl Acrylate Copolymers Using One- and Two-Dimensional NMR Spectroscopy

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ABSTRACT: The microstructure of vinylidene chloride−methyl acrylate copolymers prepared by a photopolymerization process using uranyl ion as photosensitizer is analyzed by one- and two-dimensional NMR spectroscopy. Sequence distribution was calculated from $^{13}C\{^1H\}$ NMR spectra of the copolymers. A ^{13}C distortionless enhancement by polarization transfer spectrum was used to differentiate between the resonance signals of methoxy and methylene units in the copolymer. Comonomer reactivity ratios were determined using Kelen−Tudos and the nonlinear error in variables methods. The sequence distribution of vinylidene chloride- and methyl acrylate-centered triads determined from $^{13}C\{^1H\}$ NMR spectra of copolymers is in good agreement with triad concentrations calculated from statistical model and Monte Carlo simulation methods. 2D heteronuclear single quantum correlation and correlated spectroscopy spectrum was used to analyze the complex ^1H NMR spectrum.

Introduction

Vinylidene chloride−vinyl chloride, vinylidene chloride−acrylonitrile, and vinylidene chloride−alkyl acrylate copolymers are commercially important copolymers.[1,2] These can be molded into filaments or films; fabricated into fibers which are used as staple yarn, and used in coating the many films required in the packaging industry; in coating the interiors of ship tanks, fuel storage tanks, etc., and used as a binder in magnetic tapes.

^{13}C NMR spectroscopy is the most powerful experimental technique to characterize the compositional and configurational distribution of vinyl copolymers.[3] For configurational analysis, resolved lines in the NMR spectrum have to be assigned to various stereochemical sequences in the copolymer. Kamide et al.[4] made the assignments of the ^{13}C NMR spectrum of acrylonitrile−vinylidene chloride copolymer and reported its sequence distribution. Cais et al.[5] investigated the microstructure of vinylidene halide and vinyl halide copolymers, whereas the microdynamical study of vinylidene chloride−vinyl chloride copolymer was undertaken by Menge et al.[6] The physical aspects like shear degradation,[7] crystallization kinetics,[8] structure, morphology,[9] and thermal behavior of vinylidene chloride−methyl acrylate have been studied.[10]

Two-dimensional (2D) NMR experiments[11,12] have been used as the most reliable method for determining the conformational[15] and configurational[16] microstructure of the copolymers. The characterizations of the stereochemical structure of poly(cyclohexyl acrylate)[13] and poly(*tert*-butyl acrylate)[14] using two-dimensional ^{13}C-^1H spectroscopy have been reported. In our earlier publications, we have reported the microstructure of acrylonitrile,[17] alkyl methacrylate,[18] and alkyl acrylate[19] copolymers. To the best of our knowledge, detailed microstructure studies of vinylidene chloride−methyl acrylate have not been reported. In this work, an attempt has been made to investigate the stereochemical structure and sequence distribution of vinylidene chloride−methyl acrylate (V−M) copolymers, by one- and two-dimensional NMR spectroscopy. The ^1H NMR spectrum of the copolymers is a complex one and has been interpreted with the use of 2D heteronuclear single quantum correlation (HSQC) NMR spectrum. The assignments in the ^1H NMR spectrum are then used to confirm the interactions within the copolymer using homonuclear 2D correlated spectroscopy (COSY) NMR spectrum. The reactivity ratios of the comonomers have been calculated using Kelen−Tudos (KT) and the nonlinear error in variable (EVM) methods.[20] The V- and M-centred triad sequence distribution obtained from $^{13}C\{^1H\}$ NMR are compared with those calculated from the first-order Markov model using reactivity ratios determined from the EVM program and the values obtained from the Monte Carlo (MC) simulation method.[21]

Experimental Section

Reagents. Methyl acrylate (CDH) and vinylidene chloride (Fluka) were distilled under reduced pressure to purify them and to remove the inhibitor. These were then stored below 5 °C.

Synthesis and Composition Determination. The V−M copolymers were prepared by photopolymerization at room temperature.[22] Uranyl nitrate (0.5%) dissolved in acetone was mixed with the comonomers at different molar feed ratios, and the polymerization was carried out by irradiation at a wavelength of ~435 nm. The percent conversion was kept below 10% by precipitating the copolymers in methanol. The copolymers were further dissolved in chloroform and reprecipitated in methanol.

The copolymer composition was determined by estimation of chlorine content in the copolymers using the Schoneger technique.[23,24]

NMR Measurements. ^1H and $^{13}C\{^1H\}$ NMR and ^{13}C-DEPT (distortionless enhancement by polarization transfer-135) NMR spectra of V−M copolymers were recorded under standard conditions at 25 °C in deuterated chloroform on a JEOL 300 MHz spectrometer, operating at 300 and 75.5 MHz, respectively. The two-dimensional proton-detected ^1H-^{13}C HSQC spectrum was recorded under using the standard HSQC pulse sequence, whereas the homonuclear ^1H-^1H COSY experiment was carried out on a Bruker 300 MHz spectrometer, using the standard pulse sequence. The details of the lorentzian shape curve fitting have been described in our earlier publication.[25] All regressions converged to $\chi^2 < 1$.

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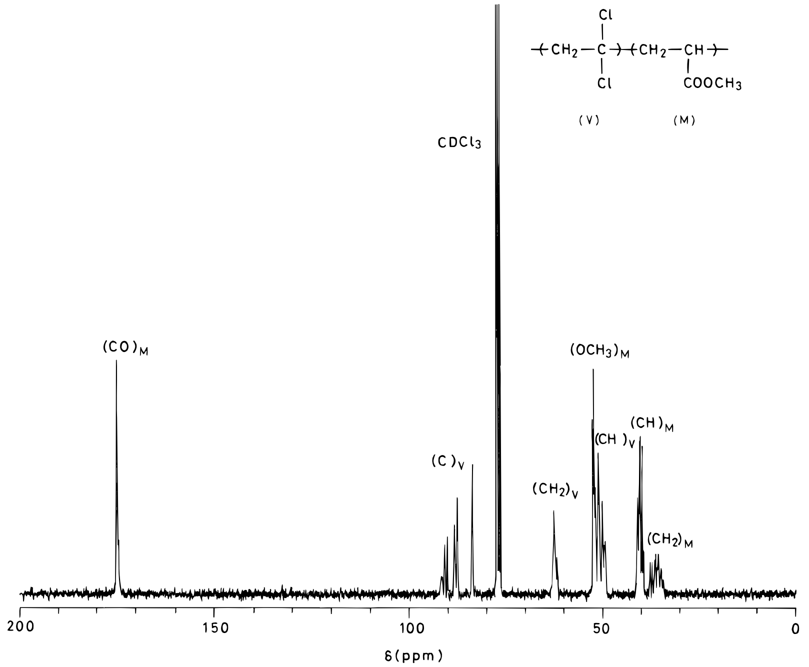


Figure 1. 75 MHz $^{13}C\{^1H\}$ NMR spectrum of the V−M copolymer (F_v = 0.5).

Table 1. Copolymer Composition for Vinylidene Chloride−Methyl Acrylate Copolymers

sample no.	feed mole fraction f_v	feed mole fraction f_M	% chlorine	copolymer composition (mole fraction) F_v	copolymer composition (mole fraction) F_M
1	0.2	0.8	16.73	0.21	0.79
2	0.3	0.7	25.48	0.32	0.68
3	0.4	0.6	31.51	0.40	0.60
4	0.5	0.5	39.74	0.50	0.50
5	0.6	0.4	48.41	0.60	0.40
6	0.7	0.3	53.91	0.71	0.29
7	0.8	0.2	59.94	0.80	0.20

Results and Discussion

Reactivity Ratio Determination. The composition of the V−M copolymer was estimated by the percent chlorine content of the copolymers using the oxygen flask combustion method. Table 1 shows the comonomer mole fractions in the feed and copolymer and the percentage of chlorine in the copolymer. The copolymer composition data were used to estimate the reactivity ratio by the KT method, and the values obtained are r_v = 0.98 ± 0.08 for vinylidene chloride and r_M = 0.92 ± 0.08 for methyl acrylate. A better estimate of the reactivity ratios was made by the EVM program using the reactivity ratios obtained from the KT method and the copolymer composition data. The values of the reactivity ratios obtained from the EVM program are r_v = 0.95 ± 0.13 and r_M = 0.90 ± 0.08, which are in agreement with the values reported in the literature.[1] The percentage error values in determining the monomer composition in the feed and copolymer were estimated to be 1% and 5%, respectively.

Carbon-13 NMR Studies. The $^{13}C\{^1H\}$ NMR spectrum of the V−M copolymer [F_v (mole fraction of vinylidene chloride in the copolymer) = 0.5] recorded in $CDCl_3$ at room temperature, with all assignments, is shown in Figure 1. The methine carbon of the monomeric M unit appears in the region from δ 39.5 to 41.5 ppm as a multiplet and is configurationally as well as compositionally sensitive. As the concentration of methyl acrylate increases, the resonance signals around δ 40.6−41.5 ppm increase, the upfield signal around δ 39.5−40.0 ppm decreases, and the signal around δ 40−40.6 ppm increases, goes through a maximum, and then decreases as the M unit in the copolymer is increased. These signals are thus assigned as MMM, MMV, VMV triad sequences from low to high field on the basis of variation in the composition of the copolymers. These triad fractions show further splitting, which was assigned to pentad sequences (Figure 2). Similar assignments have been reported for acrylonitrile−vinylidene chloride copolymers.[4] A multiplet is also obtained for the carbonyl carbon of M monomeric units that is not completely resolved and hence cannot be used for the triad sequence determination.

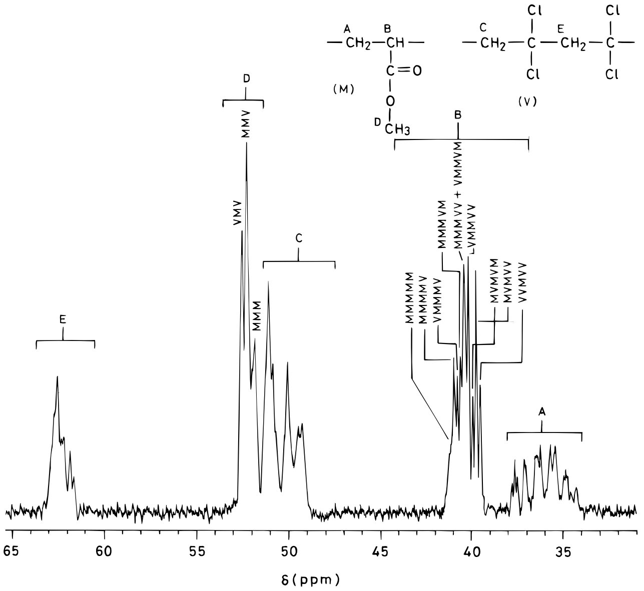


Figure 2. Methine and methoxy carbon resonances of M monomeric units and methylene carbon resonance signals for both V and M monomeric units of the $^{13}C\{^1H\}$ NMR spectrum of the V−M copolymer.

A multiplet resonance signal appears in the region from δ 49.0 to 53.0 ppm due to the methoxy carbon of the M monomeric units and the methylene carbon of the V monomeric units. These resonance signals were

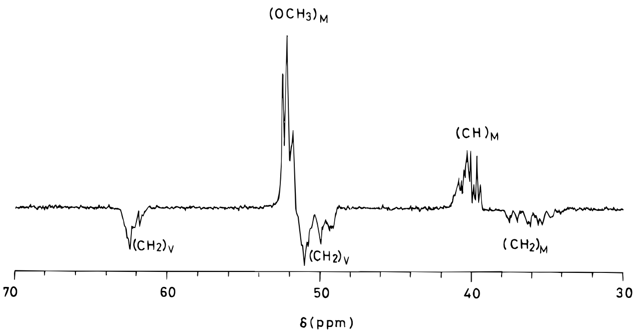
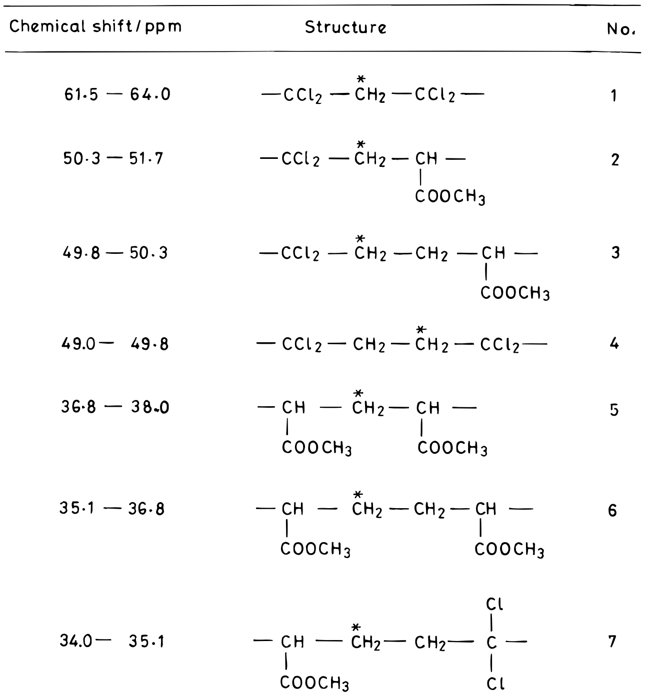


Figure 3. 75 MHz ^{13}C-DEPT NMR spectrum of V$-$M copolymer ($F_v = 0.5$).



Chemical shift/ppm	Structure	No.
61.5 — 64.0	$-\mathrm{CCl_2}-\overset{*}{\mathrm{C}}\mathrm{H_2}-\mathrm{CCl_2}-$	1
50.3 — 51.7	$-\mathrm{CCl_2}-\overset{*}{\mathrm{C}}\mathrm{H_2}-\underset{\mathrm{COOCH_3}}{\mathrm{CH}}-$	2
49.8 — 50.3	$-\mathrm{CCl_2}-\overset{*}{\mathrm{C}}\mathrm{H_2}-\mathrm{CH_2}-\underset{\mathrm{COOCH_3}}{\mathrm{CH}}-$	3
49.0— 49.8	$-\mathrm{CCl_2}-\mathrm{CH_2}-\overset{*}{\mathrm{C}}\mathrm{H_2}-\mathrm{CCl_2}-$	4
36.8 — 38.0	$-\underset{\mathrm{COOCH_3}}{\mathrm{CH}}-\overset{*}{\mathrm{C}}\mathrm{H_2}-\underset{\mathrm{COOCH_3}}{\mathrm{CH}}-$	5
35.1 — 36.8	$-\underset{\mathrm{COOCH_3}}{\mathrm{CH}}-\overset{*}{\mathrm{C}}\mathrm{H_2}-\mathrm{CH_2}-\underset{\mathrm{COOCH_3}}{\mathrm{CH}}-$	6
34.0— 35.1	$-\underset{\mathrm{COOCH_3}}{\mathrm{CH}}-\overset{*}{\mathrm{C}}\mathrm{H_2}-\mathrm{CH_2}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-$	7

Figure 4. Predicted structures for the observed chemical shifts of the methylene carbons.

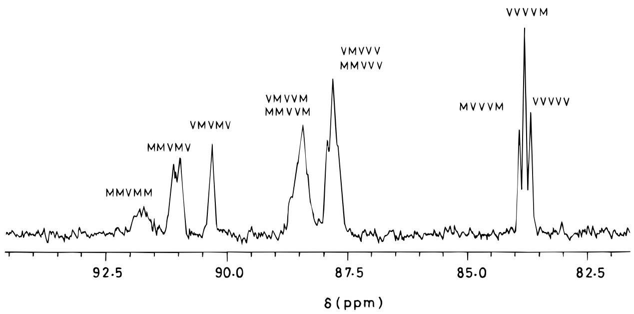


Figure 5. Quaternary carbon resonance region of the ^{13}C-{^{1}H} NMR spectrum of V$-$M copolymer.

distinguished using the ^{13}C-DEPT NMR spectrum (Figure 3). It is clear from ^{13}C-DEPT that the signals in the region δ 49.0$-$51.7 ppm are due to the methylene carbon of the V monomeric units and the signals in the region δ 51.7$-$53.0 ppm are due to the methoxy carbon of the M monomeric units. The methoxy carbon region further shows a triplet which is assigned to MMM, MMV, and VMV from high to low field on the basis of the change in intensity of the resonance signals with the change in copolymer composition. This region can thus be used for calculation of the M-centered compositional triad sequences.

Table 2. Triad Fractions Calculated from NMR Spectra, Harwood's Terminal Model, and Monte Carlo Simulations in Vinylidene Chloride$-$Methyl Acrylate Copolymers

sample no.	f_v	triads	triad fractions[c]			
			expt (NMR)		theoritical[d]	
			a	*b*	Harwood's terminal	Monte Carlo
1	0.2	VVV	0.06	–	0.04	0.02
		VVM	0.33	–	0.31	0.20
		MVM	0.61	–	0.65	0.78
		MMM	0.58	0.77	0.61	0.73
		MMV	0.35	0.21	0.34	0.25
		VMV	0.07	0.02	0.05	0.02
2	0.3	VVV	0.11	–	0.08	0.04
		VVM	0.41	–	0.41	0.33
		MVM	0.48	–	0.51	0.63
		MMM	0.45	0.44	0.46	0.57
		MMV	0.44	0.49	0.44	0.37
		VMV	0.11	0.07	0.10	0.06
3	0.4	VVV	0.15	–	0.15	0.10
		VVM	0.44	–	0.47	0.44
		MVM	0.41	–	0.38	0.46
		MMM	0.32	0.38	0.33	0.40
		MMV	0.51	0.44	0.49	0.46
		VMV	0.17	0.18	0.18	0.14
4	0.5	VVV	0.23	–	0.24	0.22
		VVM	0.48	–	0.50	0.50
		MVM	0.29	–	0.26	0.28
		MMM	0.23	0.27	0.22	0.20
		MMV	0.49	0.45	0.50	0.50
		VMV	0.28	0.28	0.28	0.30
5	0.6	VVV	0.37	–	0.35	0.42
		VVM	0.49	–	0.48	0.45
		MVM	0.14	–	0.17	0.13
		MMM	0.13	0.15	0.14	0.09
		MMV	0.47	0.44	0.47	0.42
		VMV	0.40	0.41	0.39	0.49
6	0.7	VVV	0.49	–	0.47	0.60
		VVM	0.40	–	0.43	0.35
		MVM	0.11	–	0.10	0.05
		MMM	0.10	0.08	0.08	0.04
		MMV	0.32	0.34	0.40	0.31
		VMV	0.58	0.58	0.52	0.65
7	0.8	VVV	0.59	–	0.63	0.76
		VVM	0.36	–	0.33	0.22
		MVM	0.05	–	0.04	0.02
		MMM	0.04	0.07	0.03	0.02
		MMV	0.29	0.28	0.30	0.21
		VMV	0.67	0.65	0.67	0.77

[a] Triad fractions were obtained using the quaternary carbon and methine carbon resonance signals for V- and M-centered triads, respectively, of the ^{13}C NMR. [b] Triad fractions were obtained using the methoxy carbon resonance signals of the ^{13}C NMR. [c] V- and M-centered triad fractions add up to unity. [d] Triad fractions were calculated using $r_v = 0.95$ and $r_M = 0.90$.

The methylene carbon resonance signal due to both M and V monomeric units envelope over a large range of the spectrum (δ 34.0$-$64.0 ppm). This is observed in three well-separated groups, which are assigned as MM, MV, and VV diads at δ 34.0$-$38.0, 49.0$-$51.7 and 61.5$-$64.0 ppm, respectively. The large variation in their chemical shifts is due to the fact that the functional group, viz., the chlorine atom or the ester group attached to the carbon chain, has a strong inductive effect on the chemical shift (δ) of nearby carbons.[26] The chlorine atom deshields the carbon at the α- or β-position and has a shielding affect for the carbon at the γ-position. The inductive effect of the ester group is less than that of the chlorine atoms in the vinylidene chloride copolymers. The methylene carbon which is surrounded by two $\mathrm{CCl_2}$ groups is deshielded (δ 61.5$-$64.0 ppm), as is the carbon atom at the position β to the four chlorine atoms (Figure 4, no. 1). The methylene

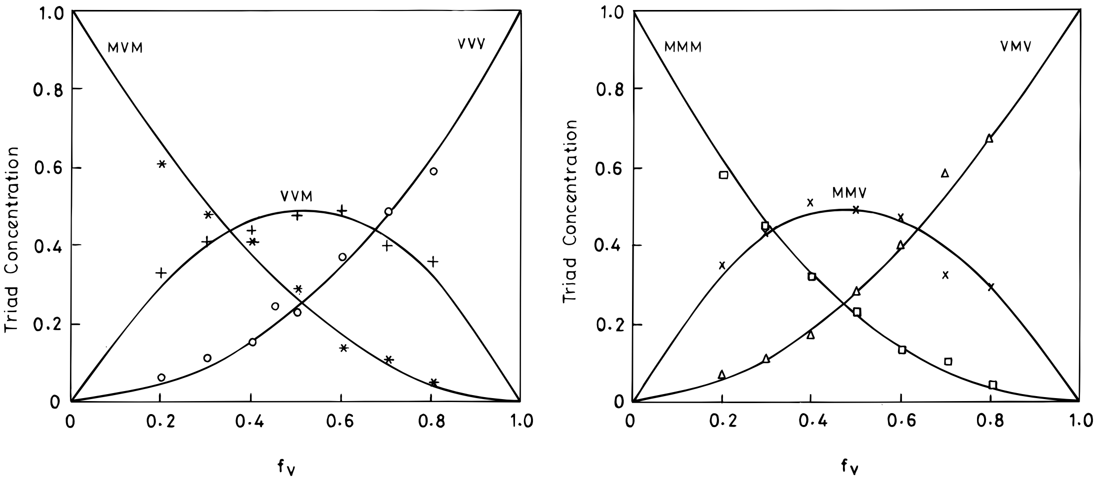


Figure 6. Variation of V- and M-centered triad fractions obtained from theoretical calculation (solid lines) and NMR spectroscopy (symbols) for the V−M copolymer plotted against feed mole fraction (f_v) of vinylidene chloride.

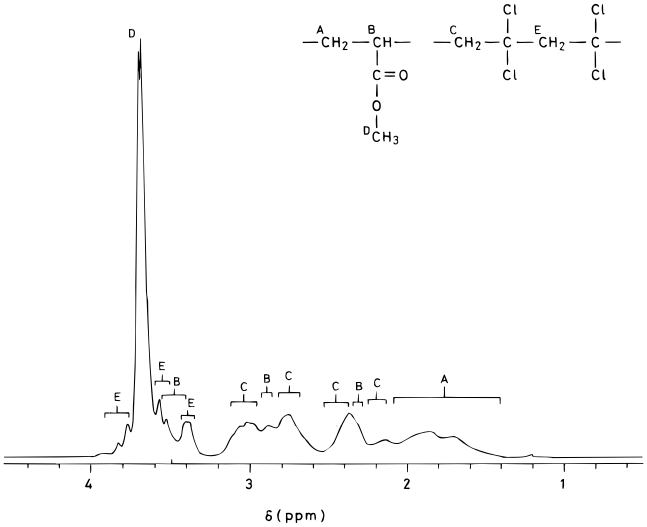


Figure 7. 300 MHz ^{1}H NMR spectrum of the V−M copolymer (F_v = 0.5).

carbon surrounded by CCl_2 on one side and $CHCOOCH_3$ on the other, appearing in the region δ 49.0−51.7 ppm, experiences a β-shift due to two chlorine atoms and one ester group (Figure 4, no. 2). The region from δ 34.0 to 38.0 ppm assigned to the methylene carbon placed in between two $CHCOOCH_3$ groups is thus least deshielded because of the influence of the β-shift due to two ester groups (Figure 4, no. 5). The further splitting in these signals observed in the $^{13}C\{^1H\}$ NMR spectrum (Figure 2) is assigned to the structures in which two methylene groups are enveloped in different environments (Figure 4, nos. 3, 4, 6, and 7). These are also arranged by studying the effective influence on methylene carbons under study due to its environments.

The dichloro-substituted carbons of vinylidene chloride in the copolymer can be easily analyzed in the spectrum (Figure 5), appearing from δ 83.5 to 92.5 ppm and separating very well. The signals around δ 83.5−84.0, 87.5−89.0, and 90.0−92.0 ppm are assigned to VVV, VVM (MVV), and MVM, respectively, on the basis of trends observed in the series of spectra with different copolymer compositions. The spectra indicate that a M monomer unit adjacent to the V-centered triad gives considerably higher chemical shift (about 3.4−3.8 ppm) for the CCl_2 carbon. This means that the electron density on the CCl_2 carbon becomes low, due to the donation of the lone pair electron from the chlorine atom to the M monomer. The lowering in electron density on CCl_2 is obviously greater for the MVM triad than that for the MVV triad. Similar observation is also reported by Bailey and Henrichs.[27] Further splitting of these signals results from different pentad structures; for example, the VVV region is made up of three pentads, VVVVV, VVVVM, and MVVVM. For the MVV region, two signals are observed, each of which is an overlap of two pentads, viz. XMVVV (X = M and V) and XMVVM (X = M and V). The MVV triad region shows three clear distinct regions which can be assigned to VMVMV, MMVMV, and MMVMM. Moreover, tacticity effects are observed here, giving further splitting whenever two methyl acrylate units appear together in a sequence.

As the quaternary carbon resonance signals of V monomeric units, the methoxy and the methine carbon signals of M monomeric units appear as multiplets and are compositionally sensitive; hence, these are used for the estimation of V- and M-centered triad concentrations. The triad fractions estimated from NMR by measuring the normalized areas under various resonance signals were compared with the triad values obtained using reactivity ratios $r_v = 0.95 \pm 0.13$ and $r_M = 0.90 \pm 0.08$ in Harwood's statistical model. This assumes that the Alfrey Mayo model (first-order Markov terminal model) is valid at any moment of the polymerization at low conversions. These values are in excellent agreement with each other, as is evident from Table 2 and shown graphically in Figure 6. Figure 6 shows the variation of V- and M-centered triad fractions against the mole fraction of vinylidene chloride, where symbols represent the experimentally determined (NMR) triad fractions and the solid lines represent the theoretically calculated (AlfreyMayo) triad fractions. The correlation coefficient for NMR−Alfrey Mayo data is $R = 0.99$. Figure 6 shows a constant increase in the VVV triad sequence and a constant decrease in the MVM triad, whereas VVM triad fraction first increases, reaches a maximum at 0.51 feed mole fraction of V, and then decreases with the increase in mole fraction of vinylidene chloride. A similar trend is observed for the M-centered triads, with a maximum observed for MMV triad at 0.48 feed mole fraction of V.

Another potential tool for the microstructure determination is the Monte Carlo (MC) simulation method. The MC simulation method is used to monitor the changes in copolymer sequence behavior during the

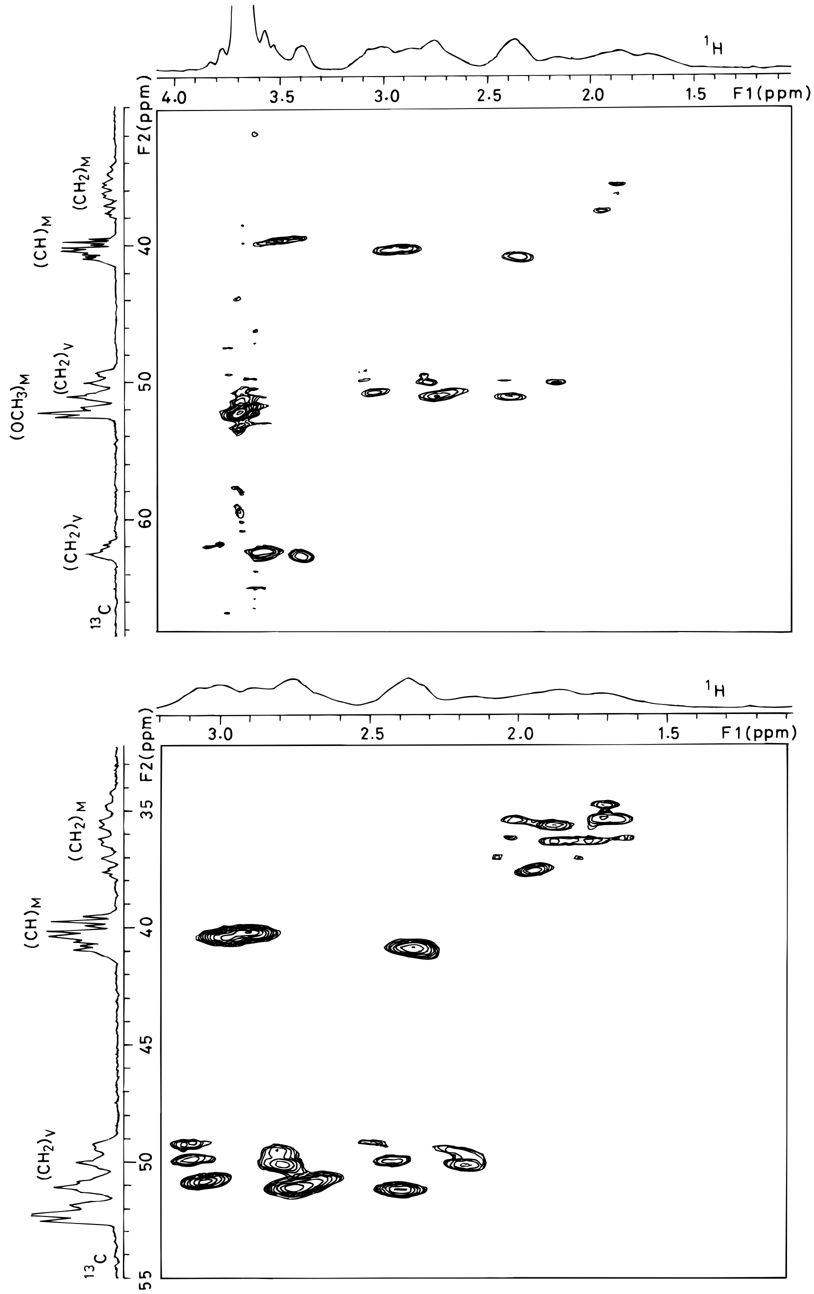


Figure 8. (a) 75 MHz 2D HSQC NMR spectrum of the V–M copolymer (F_v = 0.5). (b) Expanded region of the 2D HSQC NMR spectrum.

course of the polymerization. Triad concentrations obtained from the MC method were compared with the ones obtained from NMR and theoretical models. The good agreement between these values is evident from Table 2. The correlation coefficient between the simulated data (MC) and the experimental data (NMR) is 0.96.

^{1}H NMR and 2D NMR Studies. The ^{1}H NMR spectrum of the V–M copolymer (F_v = 0.5) recorded in $CDCl_3$ at room temperature is shown in Figure 7. The broad signals observed in the ^{1}H spectrum shows the overlap of several resonance signals so as such it cannot be used to obtain good information. Interpretation of ^{1}H NMR was done with the help of 2D heteronuclear spectroscopy by means of single bond proton–carbon correlations. This technique makes it possible to correlate the directly bonded proton and carbon atoms. The 2D ^{13}C-^{1}H HSQC NMR spectrum of V–M copolymer (F_v = 0.5) is shown in Figure 8a. It can be observed that the methoxy carbons from δ 51.7 to 53.0 ppm are correlated to protons at δ 3.6–3.8 ppm and that the methine carbon extending in the region δ 39.5–41.5 ppm is correlated to protons at δ 2.3–2.4, 2.9–3.0, and 3.4–3.6 ppm. Thus δ 3.6–3.8 ppm corresponds to methoxy protons (labeled as D) and the regions δ 2.3–2.4, 2.9–3.0, and 3.4–3.6 ppm correspond to the protons of the methine carbon of MMM, MMV, and VMV triads (labeled as B), respectively, in the ^{1}H NMR spectrum (Figure 7) of V–M copolymer. Thus, methine protons which are distinguished up to the triad level in the ^{1}H NMR were assigned up to the pentad level in the ^{13}C-{^{1}H} NMR spectrum.

The methylene carbons in three different environments which appear at different chemical shifts in ^{13}C-{^{1}H} NMR spectrum are correlated to three different regions of the ^{1}H NMR spectrum, viz., δ 1.6–2.1 ppm, corresponding to protons of the methylene carbon incorporated between $CHCOOCH_3$ on both sides (la-

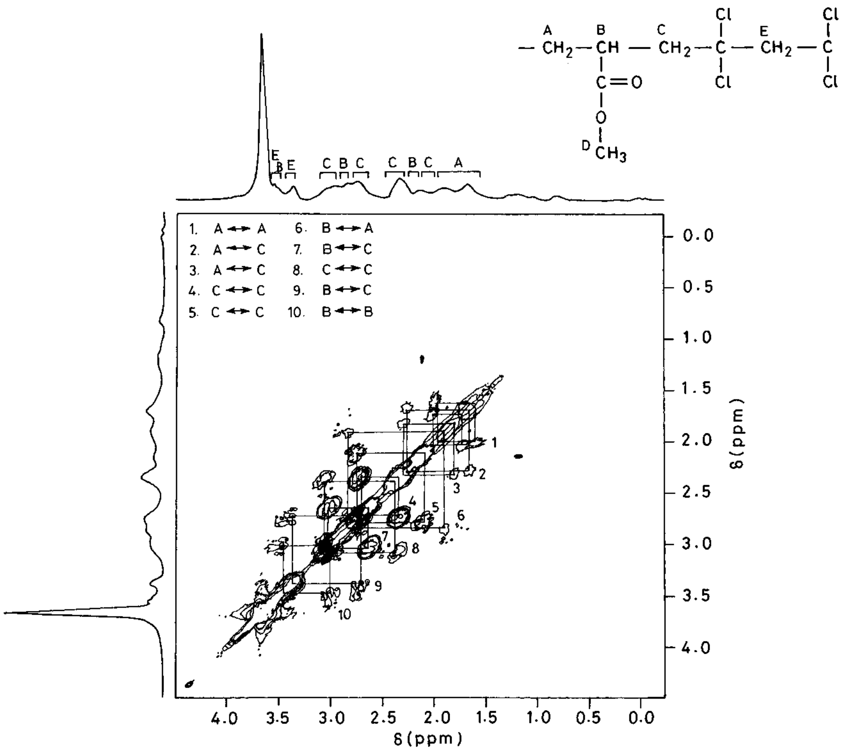


Figure 9. 2D COSY NMR spectrum of the V−M copolymer (F_v = 0.4).

beled A); δ 2.1−3.18 ppm, corresponding to protons of the methylene carbon in between $CHCOOCH_3$ on one side and CCl_2 on the other (labeled C), and the region δ 3.35−3.85 ppm, corresponding to the protons of the methylene carbon resting between CCl_2 on both sides (labeled E) in the ^1H NMR spectrum (Figure 7).

It is very well evident from the 2D-HSQC spectrum (Figure 8a,b) that ^1H NMR is more sensitive for methylene region as compared to $^{13}C\{^1H\}$ NMR. The methylene carbon extending in the region δ 61.5−64.0 ppm (Figure 4, no. 1) corresponds to three bands in the ^1H NMR spectrum attributed to different configurational affects on the triads. Similarly, the other methylene regions extending in the range δ 49.0−51.7 ppm (Figure 4, nos. 2−4) and δ 34.0−38.0 ppm (Figure 4, nos. 5−7) of the $^{13}C\{^1H\}$ NMR spectrum correspond to multiplets in the ^1H NMR spectrum. These again may be attributed to different compositionally and configurationally sensitive triads.

The 300 MHz COSY NMR spectrum for V−M copolymer is shown in Figure 9. The cross peaks observed in this spectrum show all the 1,3 interactions possible between the protons. These are labeled from 1 to 10, corresponding to six different possible interactions, viz., interactions between methylene groups of the M unit, methine groups of the M unit, methylene groups of the V unit, the methylene group of the M unit with the methylene group of the V unit, the methylene and methine group of the M unit, and the methylene group of the V unit with the methine group of the M unit. Thus the spectrum predicts the feasibility of various structures in a polymer sequence.

Conclusions

The stereochemical structure of vinylidene chloride−methyl acrylate copolymer was analyzed by 1D and 2D NMR techniques. It has helped us to characterize methoxy resonances up to the triad level and methine and quaternary resonances up to the pentad level in $^{13}C\{^1H\}$ NMR spectra. Triad fractions obtained from NMR spectra were compared to those calculated from theoretical models and MC simulation and found to be in excellent agreement. The heteronuclear $^1H-^{13}C$ 2D NMR spectra gave the correct assignments of the ^1H NMR spectrum of V−M copolymer and the homonuclear 2D(1H−1H) COSY NMR spectrum suggested various structural arrangements of the polymer chain. ^1H NMR spectroscopy was observed to be more sensitive for the methylene region as compared to $^{13}C\{^1H\}$ NMR spectroscopy, compositionally and configurationally different methylene protons appear at different chemical shifts in the ^1H NMR spectrum.

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