

Microstructure Analysis of Poly(styrene-co-vinylidene chloride) Copolymers by NMR Spectroscopy

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ABSTRACT: Poly(styrene-co-vinylidene chloride) (S/V) copolymers were prepared by free-radical photopolymerization using uranyl nitrate as an initiator. The microstructure of the copolymer S/V was investigated by ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR, ^1H - ^{13}C -heteronuclear shift quantum correlation (HSQC) NMR, and homonuclear total correlated spectroscopy (TOCSY). The ^1H -NMR spectra of the copolymers is complex due to overlapping resonance signals of the various triad configurations. Assignments were made up to the triad and tetrad levels for the methylene and methine regions using two-dimensional HSQC experiments. A ^{13}C -distortionless enhancement by polarization transfer (DEPT) spectrum was used to differentiate between the carbon resonance signals of methine and the methylene units. The geminal couplings in the methylene protons and vicinal coupling between the methine and methylene protons were detected from the TOCSY spectra. Monte Carlo simulations were used to investigate the effect of the degree of polymerization on the triad fractions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 544–554, 2001

Key words: styrene-vinylidene chloride copolymers; 2D NMR; microstructure

INTRODUCTION

It is well established that the difference in the monomer sequence distribution within synthetic copolymers can result in a difference in the properties of the copolymers. Consequently, knowledge of the chemical microstructure can be important in understanding the macroscopic properties of polymers.¹

Two-dimensional (2D) NMR spectroscopy has been demonstrated to be a useful technique for the both comonomer and stereosequence assignments for synthetic polymers.^{2–5} 2D-heteronuclear NMR spectroscopy is being frequently used for the study of many homopolymers^{6–9} and copolymers.^{10–12}

Kamide et al.¹³ studied the sequence distribution of acrylonitrile-vinylidene chloride copolymers by ^{13}C -NMR spectroscopy. Bailey and Henrichus¹⁴ reported the relationship of sequence distribution determined by ^{13}C -NMR to both the copolymer property, T_g , and copolymerization theory for acrylonitrile-vinylidene chloride copolymers. Fischer et al.¹⁵ and Johnson¹⁶ reported the assignments for methylene proton resonance for vinylidene chloride-isobutylene and vinyl chloride copolymers. Pham et al. reported the composition and the reactivity ratios¹⁷ of a methyl methacrylate/vinylidene chloride copolymer and also made assignments up to the pentad level using α -methyl resonance signals of the ^1H -NMR spectrum. Ito and Yamashita¹⁸ studied the microstructure of vinylidene chloride-styrene copolymers up to the dyad level by NMR spectroscopy. Earlier, Brar and Malhotra¹⁹ reported the compositional assignments and microstructure of vinylidene chloride-alkyl acrylate copolymers using 2D-NMR spectroscopy.

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Table I Feed Mol Fraction and Copolymer Composition Data of the Copolymer S/V

Sample No.	Feed Mol Fraction		Copolymer Composition	
	f_s	f_v	F_s	F_v
1	0.75	0.25	0.82	0.18
2	0.60	0.40	0.75	0.25
3	0.50	0.50	0.70	0.30
4	0.40	0.60	0.60	0.40
5	0.30	0.70	0.55	0.45
6	0.25	0.75	0.51	0.49
7	0.10	0.90	0.35	0.65

In this communication, we report the reactivity ratios of the comonomers calculated by the non-linear error-in-variables (EVM) method. The microstructure in terms of triad sequence distribution was obtained from the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the copolymers and compared with those calculated from the first-order Markov model using reactivity ratios determined from the EVM program and from the Monte Carlo (MC) simulation method. The complex ^1H -NMR spectrum was as-

signed using 2D heteronuclear shift quantum correlation (HSQC) and homonuclear total correlated spectroscopy (TOCSY) spectra. Monte Carlo (MC) simulation²⁰ was used to study the variation of the triad fractions as a function of the degree of polymerization.

EXPERIMENTAL

Materials

Copolymers of various compositions of styrene and vinylidene chloride were prepared by a photopolymerization process at room temperature using uranyl nitrate as a photoinitiator. Polymerization was stopped by precipitating in methanol and reprecipitating from chloroform. The conversion was kept below 10%. Molecular weight was determined by gel permeation chromatography in tetrahydrofuran at 35°C.

NMR Measurements

^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded on a Bruker DPX-300 spectrometer under standard conditions in CDCl_3 at room temperature at a

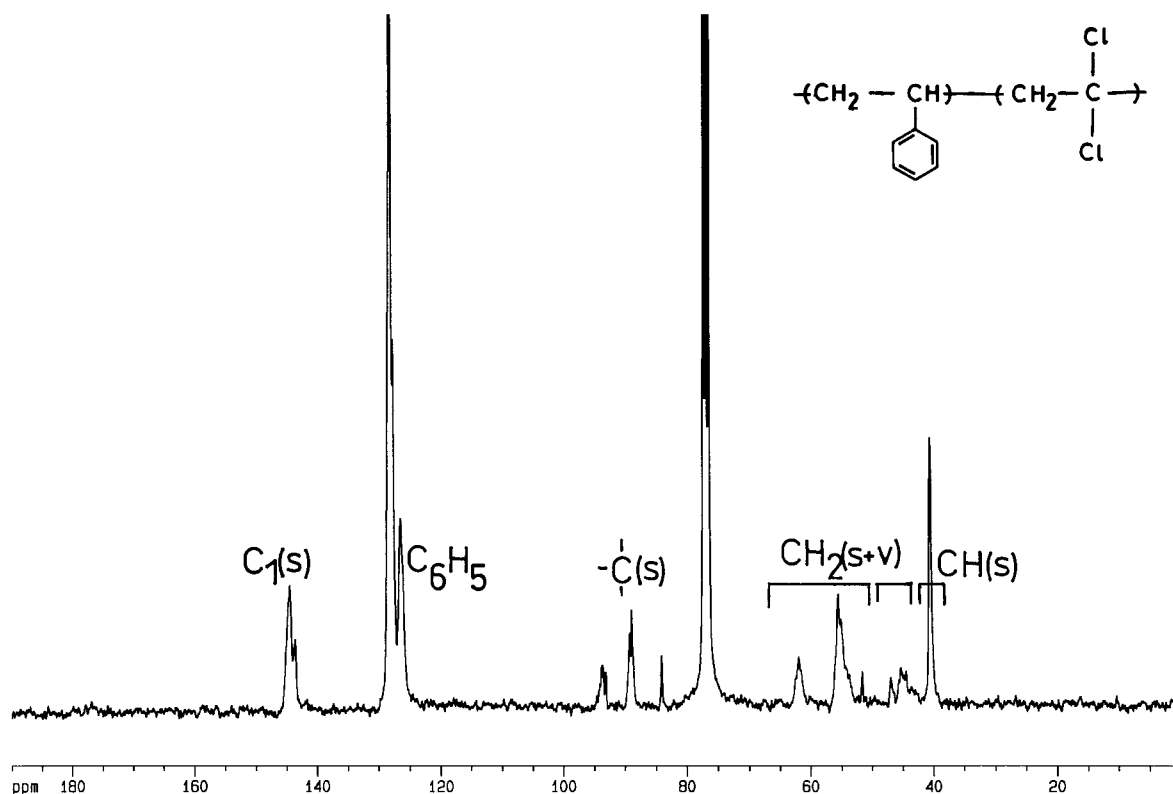


Figure 1 75-MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of S/V copolymer in CDCl_3 ($F_s = 0.51$).

Table II Triad Compositions Calculated from the NMR Spectra, Harwood Model, and MC Simulations in S/V Copolymers

Sample No.	Copolymer Composition F_S	Triads	Triad Compositions		
			$^{13}\text{C}\{^1\text{H}\}$ -NMR	Harwood Model	MC
1	0.82	SSS	0.62	0.65	0.60
		SSV	0.30	0.31	0.32
		VSV	0.08	0.04	0.08
		VVV	0.00	0.00	0.02
		VVS	0.05	0.08	0.10
		SVS	0.95	0.92	0.88
2	0.75	SSS	0.47	0.46	0.44
		SSV	0.48	0.44	0.51
		VSV	0.05	0.10	0.05
		VVV	0.05	0.01	0.05
		VVS	0.15	0.14	0.12
		SVS	0.80	0.85	0.83
3	0.60	SSS	0.28	0.23	0.19
		SSV	0.50	0.50	0.48
		VSV	0.22	0.27	0.33
		VVV	0.08	0.03	0.02
		VVS	0.22	0.27	0.20
		SVS	0.70	0.70	0.78
4	0.55	SSS	0.09	0.14	0.08
		SSV	0.50	0.47	0.41
		VSV	0.41	0.39	0.51
		VVV	0.05	0.05	0.03
		VVS	0.38	0.35	0.27
		SVS	0.57	0.60	0.70
5	0.51	SSS	0.10	0.10	0.05
		SSV	0.45	0.43	0.34
		VSV	0.45	0.47	0.61
		VVV	0.11	0.08	0.05
		VVS	0.39	0.40	0.35
		SVS	0.50	0.52	0.60
6	0.35	SSS	0.00	0.02	0.03
		SSV	0.25	0.23	0.17
		VSV	0.75	0.75	0.80
		VVV	0.30	0.29	0.43
		VVS	0.45	0.50	0.45
		SVS	0.25	0.21	0.12

frequency of 300.13 and 75.5 MHz, respectively. ^{13}C -Distortionless enhancement by polarization transfer (DEPT) measurements were carried in CDCl_3 using the standard pulse sequence with a J modulation time of 3.7 ms ($J_{\text{CH}} = 135$ Hz) with a 2-s delay time. 2D proton-detected HSQC spectra were recorded in CDCl_3 using the standard pulse sequence.²¹ A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 t_1 experiments. The 2D TOCSY experiment with 32 scans collected for each t_1 value was

carried out in CDCl_3 using standard pulse sequences.²² A total of 512 spectra, each containing 1K data points, were accumulated. Details of the Lorentzian shape curve fitting were described elsewhere.²³ All regression converged to $x^2 < 1$.

RESULTS AND DISCUSSION

The compositions of styrene/vinylidene chloride (S/V) copolymers were determined from the quan-

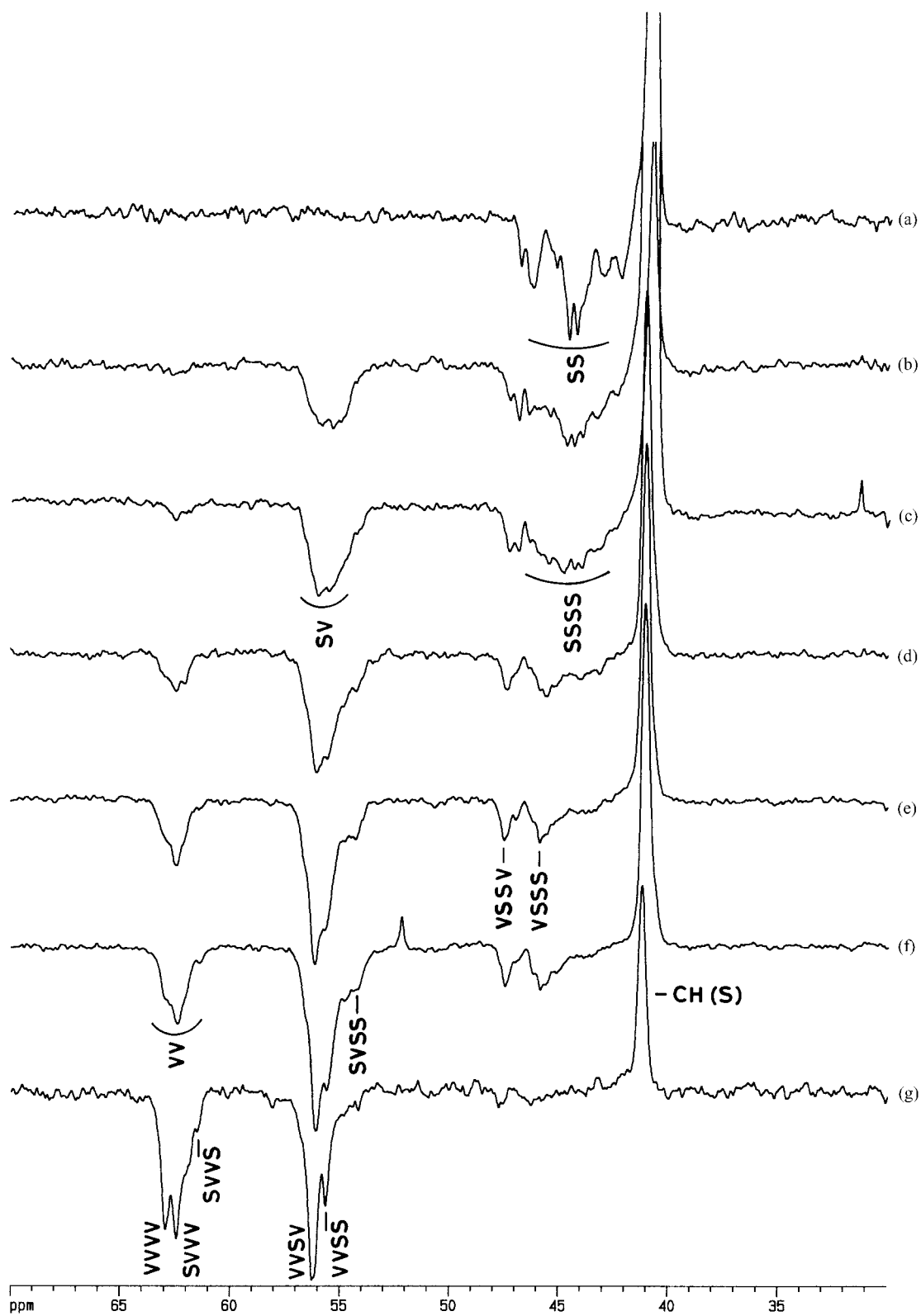


Figure 2 $^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR spectrum of S/V copolymer ($F_S =$): (a) polystyrene, (b) 0.82, (c) 0.75, (d) 0.70, (e) 0.60, (f) 0.51, and (g) 0.35 in CDCl_3 .

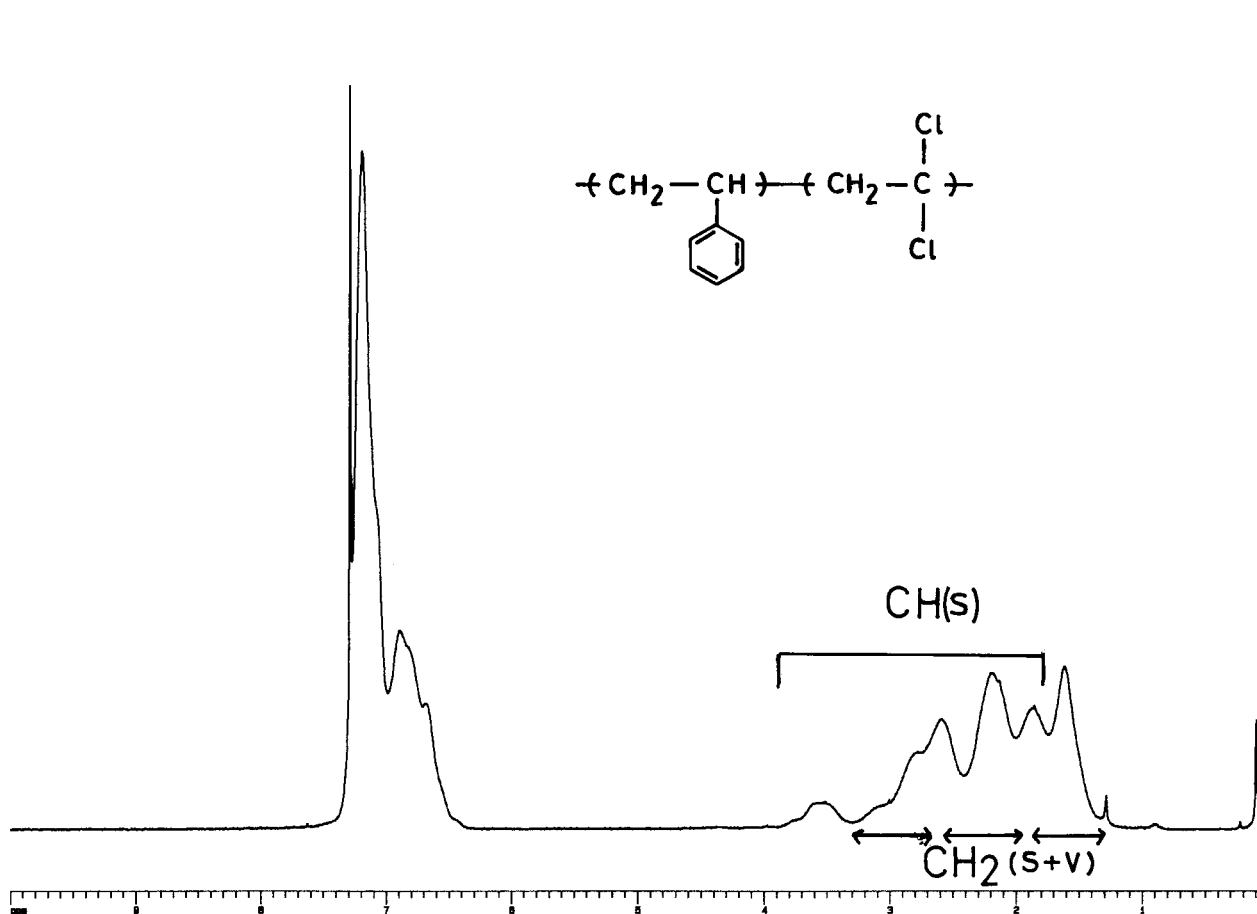


Figure 3 300-MHz ^1H -NMR spectrum of the S/V copolymer in CDCl_3 ($F_S = 0.51$).

titative $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra. The copolymer composition data were used to estimate the terminal model reactivity ratio by the KT method.²⁴ The initial estimate of the reactivity ratios along with the copolymer composition data were used for the calculation of reactivity ratios by the EVM method.² The value of the reactivity ratios are $r_S = 1.39$ and $r_V = 0.13$, which are in agreement with those reported in the literature.^{26–30} The feed mol fraction and composition of the copolymer are shown in Table I.

$^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the S/V copolymer ($F_S = 0.51$) recorded in CDCl_3 is shown in Figure 1. The quaternary carbon resonance signal of styrene appears at $\delta 142.1$ – 148.8 ppm, whereas the quaternary carbon resonance signal of the vinylidene chloride region appears at $\delta 82$ – 95 ppm. The resonating signals of the regions $\delta 42$ – 65 ppm and $\delta 41$ ppm are assigned as the methylene carbons of the copolymer and the methine carbon of the styrene units, respectively.

The quaternary carbon of the vinylidene chloride and styrene monomeric unit gives multiplet

signals in the ranges $\delta 82$ – 95 ppm and $\delta 142.1$ – 148.8 ppm, which are assigned by inspecting the intensity variations with the change in the composition. It is observed that the signal at $\delta 84$ ppm increases with increase in the vinylidene chloride content and so is assigned to the VVV triad, whereas resonating signals at $\delta 93$ – 95 ppm that decrease with an increase in the vinylidene chloride are assigned to the SVS triad. The resonance signals around $\delta 87$ – 91 ppm that first increase and then decrease with increasing vinylidene chloride content are assigned to the VVS triad. Further splitting observed in these triads is due to compositional effects.

The expanded $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the quaternary carbon resonance of the styrene unit of the copolymer shows that the signals around $\delta 142.1$ – 144 ppm increase in intensity with increase in the vinylidene chloride content and they were assigned to the VSV triad. Similarly, the concentration of SSS and SSV triads increases with increase in the styrene content from $\delta 145$ – 146 ppm and around $\delta 144$ – 145 ppm, respectively.

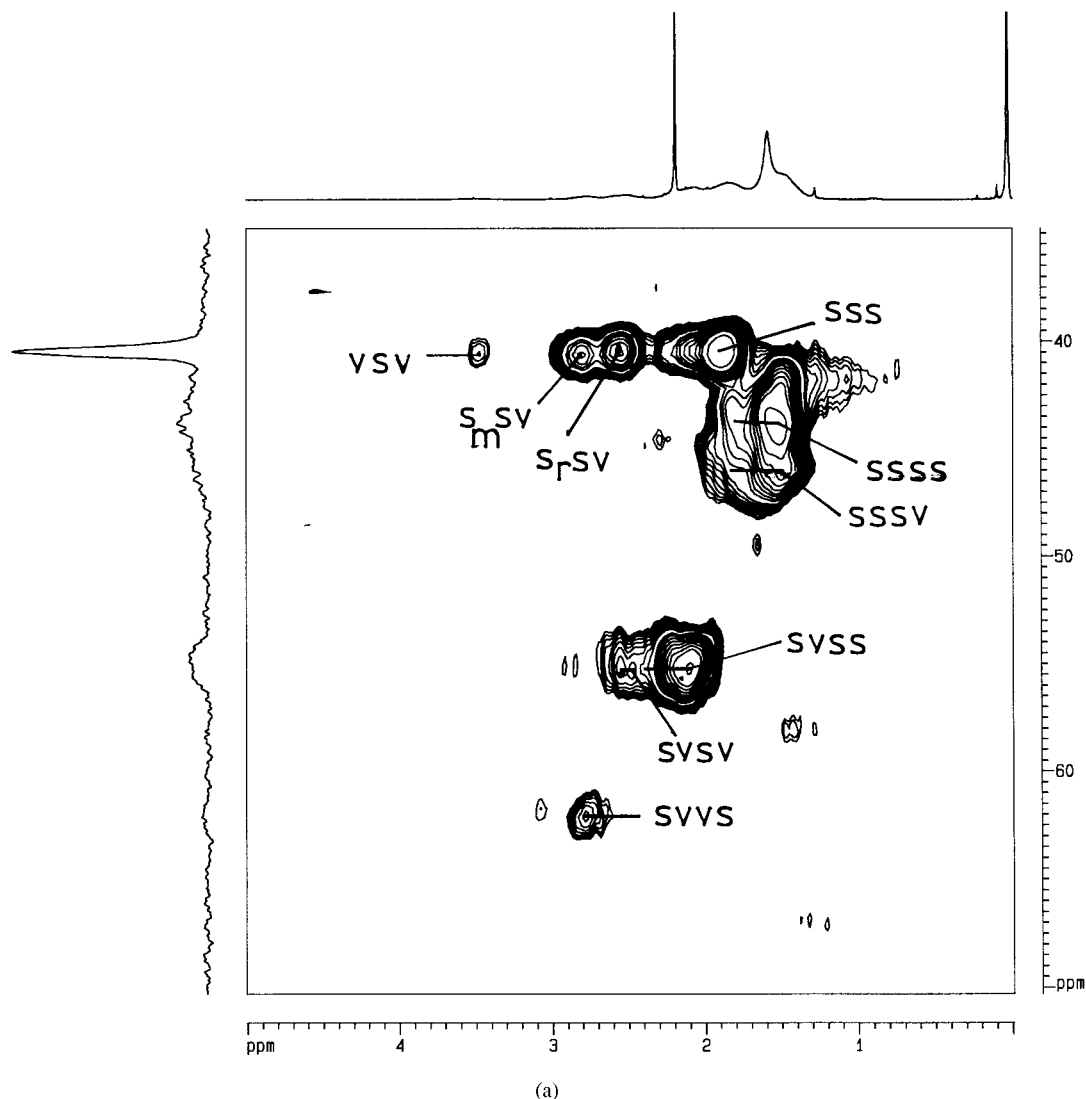


Figure 4 75 MHz 2D HSQC NMR spectroscopy of S/V copolymer ($F_S =$): (a) 0.82 and (b) 0.35 in CDCl_3 .

The quaternary carbon resonating signals of S and V monomeric units are used for the assessment of the copolymer mechanism. The experimental triad fractions are obtained by curve fitting of the resonance signals of these regions in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum. The triad fractions thus obtained are then compared to the theoretically obtained triad fraction using the Alfrey-Mayo model employing the Harwood program.³¹ There is good agreement between these values as seen from Table II.

The methylene resonance signals are clearly distinguished by DEPT-135 recorded in CDCl_3 (Fig. 2). In the DEPT-135 spectrum, the methylene carbon signals are in the negative phase and the resonates from $\delta 42$ – 65 ppm are due to the V

unit which has two highly electronegative chlorine atoms. The resonance signals in the regions, namely, $\delta 42$ – 46 , $\delta 54$ – 57.5 , and $\delta 61.5$ – 65 ppm, are assigned to the SS, SV, and VV dyads, respectively. Assignments were confirmed from the change in the intensity of the resonating signals with the change in the copolymer composition. The chlorine atoms produce a deshielding effect in the carbon at α and β positions, whereas the shielding effect in the carbon at γ position. Further splitting within each dyad is assigned to the tetrad compositional sequences. The three signals in the SS dyad region are assigned to SSSS ($\delta 42$ – 43.5 ppm), SSSV ($\delta 43.5$ – 45 ppm), and VSSV ($\delta 45$ – 47.5 ppm). Similarly, the SV dyads that show the tetrad sensitivity from $\delta 53$ – 55 , $\delta 55$ –

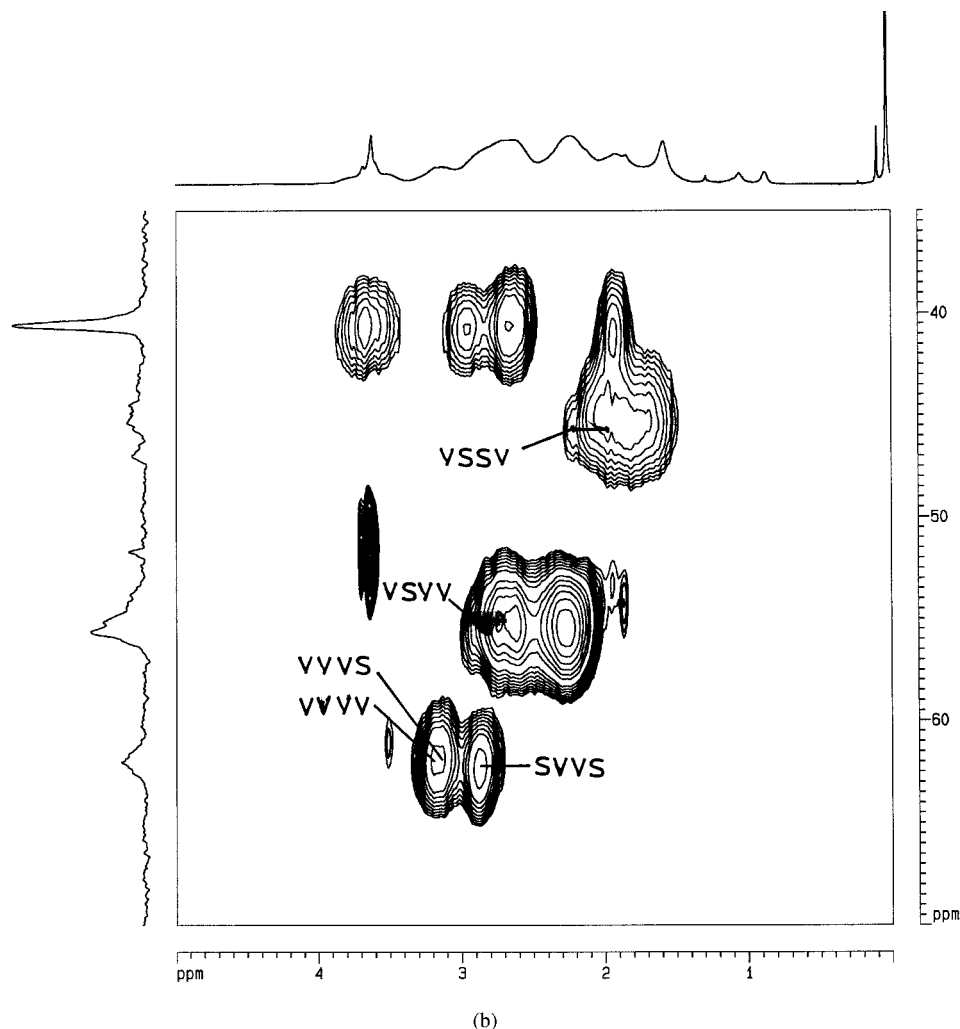


Figure 4 (Continued from the previous page)

56.1, and $\delta 56.1$ – 57.5 ppm are assigned to SSVS, SSVV + VSVS, and VSVV tetrads, respectively. The other dyad, VV, shows splitting (compositional sensitive) and it was assigned to SVVS, SVVV, and VVVV at $\delta 61$ – 62 , $\delta 62$ – 62.5 , and $\delta 62.5$ – 62.8 ppm, respectively. The labeling of these tetrads are based on the variation of the intensities of resonance signals with the varying compositions of the monomers in the copolymer.

The ^1H -NMR spectrum of the S/V copolymer (Fig. 3) is broad and overlapping between methylene with methine proton resonances from $\delta 1.0$ to $\delta 4.0$ ppm, whose assignments were done using 2D HSQC in two different compositions as shown in Figure 4. From the variation in the intensity of the contours observed in the HSQC spectrum with varying composition, the methine region is assigned as $\{^{13}\text{C}/^1\text{H}\}$ at $\delta 40.7/1.88$ ppm for the SSS triad, $\delta 41.0/2.52$ – 2.85

ppm for the SSV triad, and $\delta 41.3/3.45$ ppm for the VSV triad. Further splitting within these triads is due to configurational sequencing. The SSV triad shows two contours at $\delta 41.0/2.52$ and $\delta 41.0/2.85$ ppm due to configurational SmSV and SrSV triads, respectively. It is evident from the HSQC that the methine carbon in the region $\delta 41.0$ ppm, which gives a singlet in the $^{13}\text{C}\{^1\text{H}\}$ spectrum, is spread over a large range of chemical shifts from $\delta 1.25$ to 1.60 ppm in the ^1H -NMR and HSQC NMR spectra.

The assignment of the tetrads for methylene carbons from 2D HSQC (Fig. 4) helps to assign the methylene protons on the ^1H -NMR spectrum. The VV dyad region shows three contours at $\delta 62.5/2.85$, $\delta 62/3.1$, and $\delta 62.2/3.2$ ppm in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum, which are due to the SVVS, VVVS, and VVVV tetrads, respectively. Further fine resonance contours may be due to

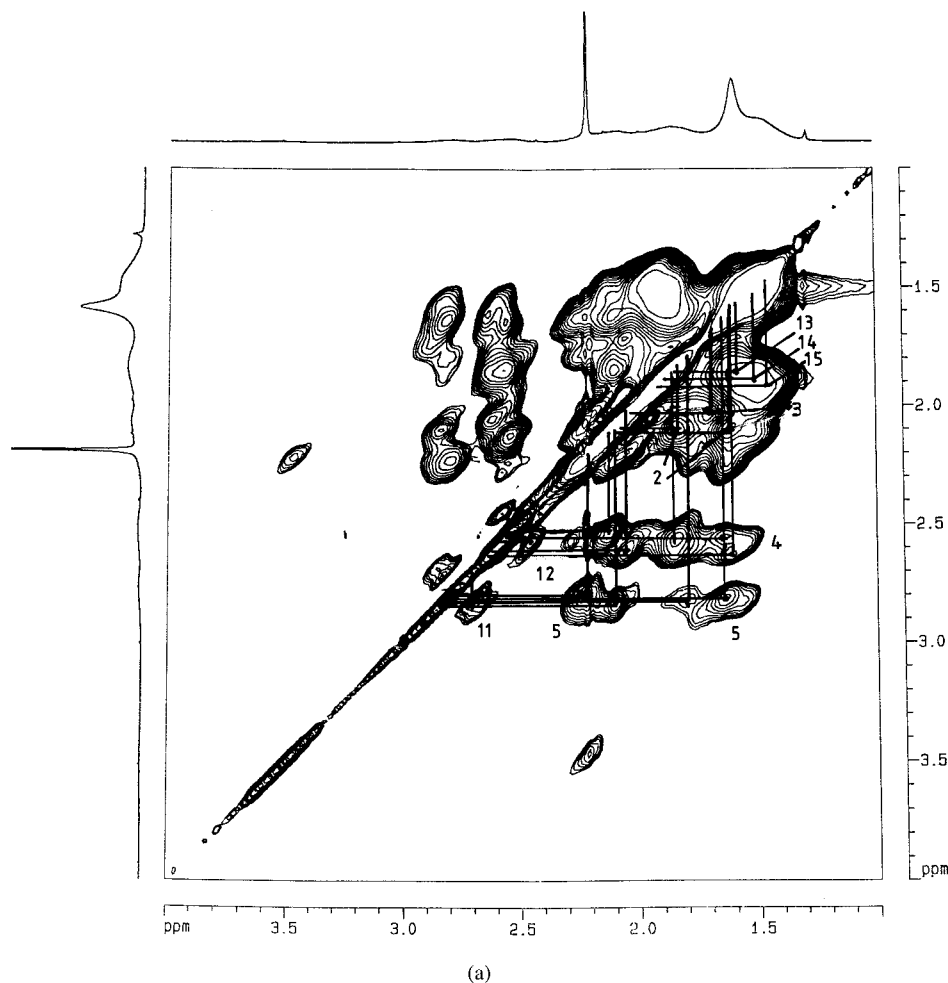


Figure 5 2D TOCSY NMR spectrum of the S/V copolymer ($F_S =$) at 80 ms: (a) 0.82 and (b) 0.35 in CDCl_3 .

higher compositional sequences and other tactic reasons. The VS dyad region shows resonance contours for the SVSS tetrad at δ 55.0/2.12 and δ 55.0/2.25 ppm; the SVSV tetrad at δ 55.2/2.5 and δ 55.2/2.55 ppm; and the VVSV tetrad at δ 56/2.72 and δ 56/2.88 ppm. This may be because the methylene protons of the VS dyads are magnetically nonequivalent.

The methylene protons of the SS dyad region appears as nonequivalent protons connected to the same carbon, such as methylene protons in a symmetrical meso dyad for which the contours are observed at δ 43/1.5 and δ 43/1.8 ppm, δ 45/1.4 and δ 45/1.75 ppm, and δ 46/1.9 and δ 46/2.15 ppm, which correspond to the SS_mSS , SS_mSV , and VS_mSV tetrads, respectively. Table III shows the complete information obtainable from the HSQC and TOCSY spectra with assignments.

It is evident from the 2D-HSQC spectra that for the methylene chemical shifts at the tetrad

level the signals having higher chemical shifts in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra correspond to the lower chemical shifts for ^1H -NMR spectra. A TOCSY spectrum recorded at 80 ms shows three or more bond couplings and through relay couplings between the protons, as shown in Figure 5(a,b). The crosspeaks observed are from the SS and VS dyads of the methylene region and no crosspeaks were observed in the VV dyad methylene region. This predicts that the observed crosspeaks are due to the nonequivalence of the methylene protons in the VS and SS dyad regions; as for the VV dyad region, the methylene protons are both chemically and magnetically equivalent.

The 1,2 geminal coupling between the nonequivalent protons of VS-centered tetrads SVSS, VVSS, and VVSV are assigned at δ 2.60/2.45, δ 2.85/2.70, and δ 3.1/2.72 ppm, which are due to the nonequivalence of the methylene protons in

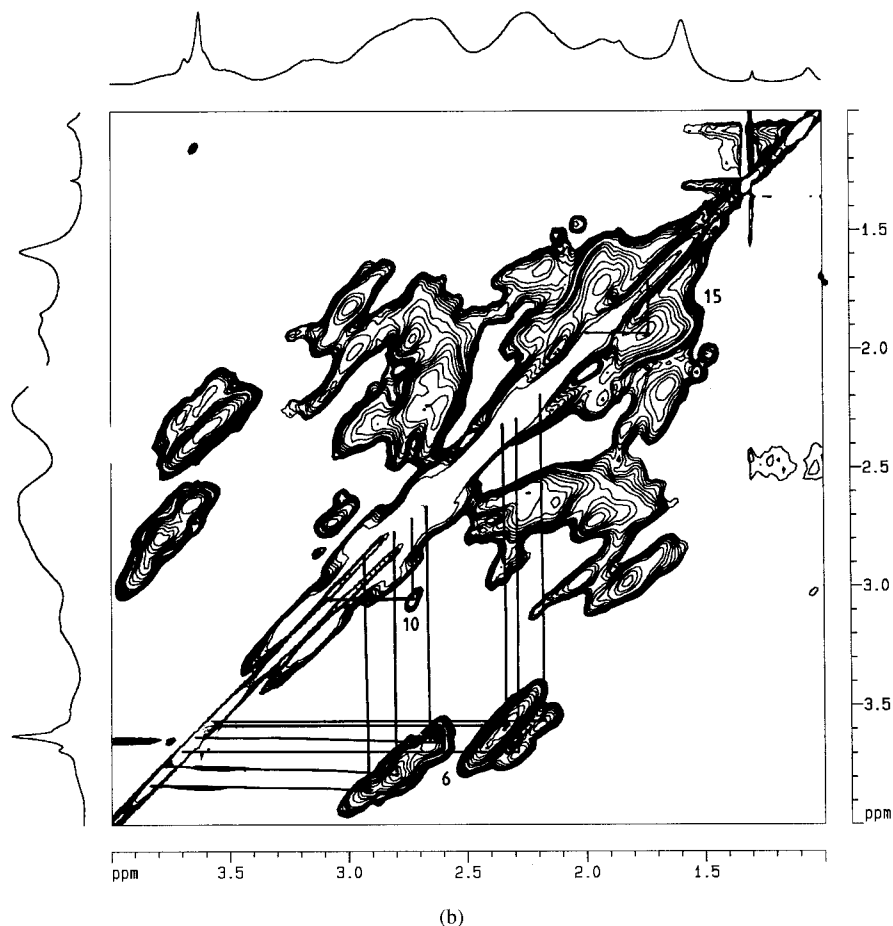


Figure 5 (Continued from the previous page)

the copolymer sequence [Fig. 5(a,b)]. This confirms the splitting observed in the 2D HSQC spectrum.

In the SS methylene dyad region, since the racemic form of the methylene protons are equivalent, no crosspeaks are expected. In the meso

Table III Methylene and Methine Assignments from 2D HSQC and TOCSY

Sample No.	Assignments	HSQC		TOCSY (ppm)
		^{13}C (ppm)	^1H (ppm)	
1	SSS	40.7	1.88	—
2	SmSmS			2.12/1.83, 2.05/1.70
3	(SmSrS + SrSrS)			2.0/1.7
4	SmSV	41.0	2.52	2.61/1.6, 2.55/1.65, 2.54/1.85, 2.62/2.1, 2.55/2.12
5	SrSV	41.0	2.85	2.81/1.6, 2.80/1.80, 2.88/2.1, 2.82/2.2
6	VSV	41.3	3.45	3.4–3.9/2.3, 2.18–2.3, 2.6–3.0
7	VVVV	62.2	3.20	
8	VVVS	62.0	3.10	
9	SVVS	62.5	2.85	
10	VVSV	56.2	2.72, 2.88	3.1/2.72
11	SVSV	55.2	2.50, 2.55	2.85/2.70
12	SVSS	55.0	2.12, 2.25	2.6/2.45
13	SSmSS	43.0	1.5, 1.8	1.85/1.60
14	SSmSV	45.0	1.4, 1.75	1.90/1.55
15	VSmSV	46.0	1.9, 2.15	1.93/1.45

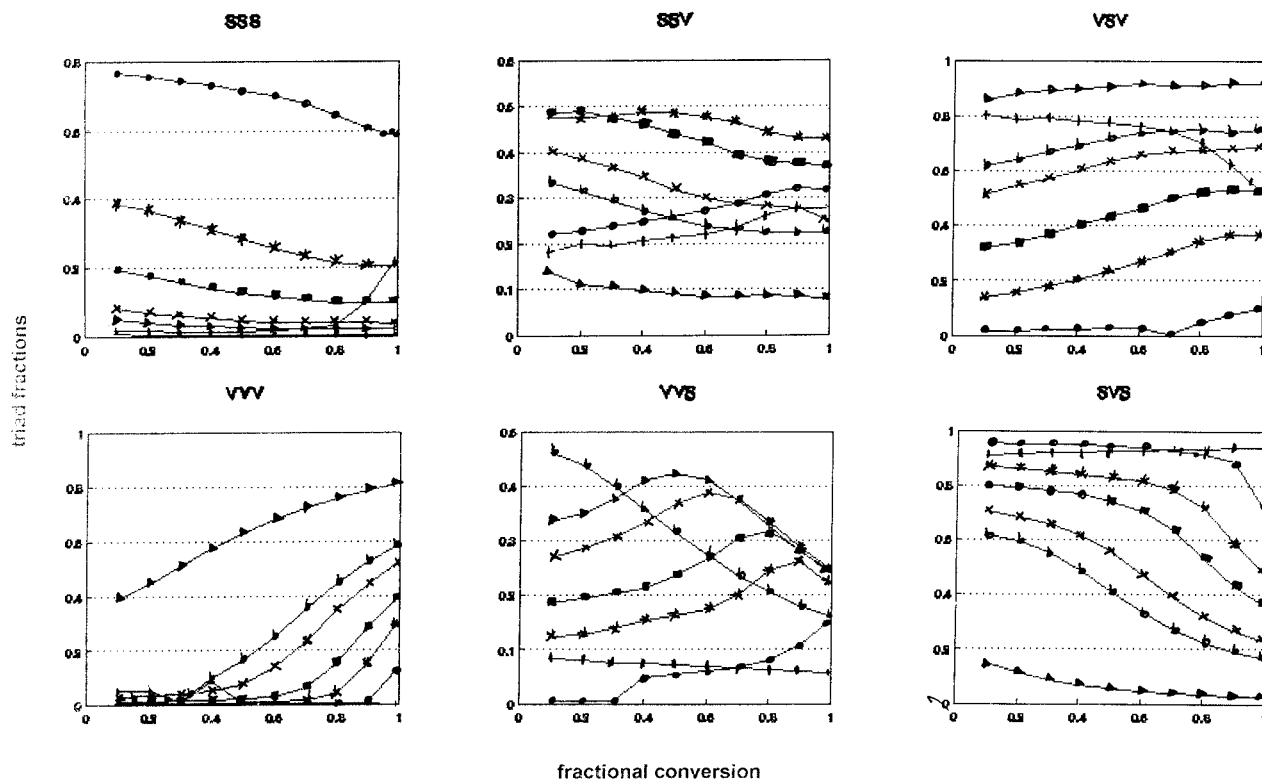


Figure 6 Variation of S- and V-centered triad fraction plotted as a function of degree of conversion for the different feed mol fractions: (●) $F_S = 0.75$; (+) $F_S = 0.6$; (*) $F_S = 0.5$; (■) $F_S = 0$ $F_S = 0.25$; (□) $F_S = 0.1$ (▲).

dyads, methylene protons are nonequivalent and these crosspeaks that were observed are compositional-sensitive and were assigned to the SS_mSS , SS_mSV , and VS_mSV tetrads at $\delta 1.85/1.60$, $\delta 1.90/1.85$, and $\delta 1.93/1.45$ ppm, respectively.

The methine carbon signals show both triad and compositional pentad sensitivity. The central methine protons of the SSS triad fractions show three bond couplings to the methylene protons of the SS dyad, whereas the methine protons of the SSV triad fraction shows coupling to the methylene protons at both SS and SV dyad regions. From one-to-one correlation between the methine proton, signals of the SSS triad fraction are assigned around $\delta 2.12$ ppm, $\delta 2.05$ ppm (SmSmS), and $\delta 2.0$ ppm (SmSrS + SrSrS). These methine protons show the crosspeaks at $\delta 2.12/1.83$, $\delta 2.05/1.70$, and $\delta 2.0/1.70$ ppm due to three bond couplings to the methylene protons.

The central methine proton in the SSV triad shows three bond couplings with two types of methylene protons (S and V types). The crosspeaks at $\delta 2.61/1.60$, $\delta 2.55/1.65$, and $\delta 2.54/1.85$ ppm are due to three bond couplings between the methine proton of the SmSV triad fraction and the methylene protons of the SS dyad. The three

bond couplings between the methine proton of the SmSV triad fraction and the methylene protons of the SV dyad are at $\delta 2.62/2.1$ and $\delta 2.52/2.12$ ppm.

Similarly, the central methine proton of the SrSV triad fraction shows two types of coupling with the methylene protons between the SrS and SV dyads. The crosspeaks at $\delta 2.81/1.60$ and $\delta 2.80/1.80$ ppm were assigned to the SrSV triad due to the three bond couplings between the methine proton of the SrSV triad fraction and the methylene proton of SrS dyad. The crosspeaks at $\delta 2.88/2.1$ and $\delta 2.82/2.2$ ppm are due to the coupling between the SrSV triad and the SV dyad.

In the VSV triad fraction, the central methine proton is between the two V units. This will not show any kind of configurational sensitivity. All crosspeaks in this region are, therefore, due to compositional sequences. The methine proton of the VSV triad at $\delta 3.4$ – 3.9 ppm couples with the methylene protons of the VS region at $\delta 2.3$, $\delta 2.18$ – 2.3 ppm, and $\delta 2.6$ – 3.0 ppm, which are due to compositional or other tactic reasons.

MC Simulation Studies

The MC simulation method was also used to monitor the change in the copolymer sequence

behavior during the course of the polymerization. The triad fractions obtained from the MC method are also found to be in good agreement with the theoretical and experimental triad fraction values as shown in the Table II. The correlation coefficient between the simulated data (MC) and the experimental data (NMR) is 0.93. Figure 6(a–f) shows the variation of the S- and V-centered triad concentrations as a function of the fractional conversion for the different feed mol fractions.

It is observed that, with the progress of polymerization, the monomer with the higher reactivity ratios (styrene) is consumed faster than is the other one (vinylidene chloride). This is evident from Figure 6, where the VVV triad increases as conversion increases. At lower feed mol fractions, the triad fraction (VVV) increases, but only at high conversions as the styrene is consumed faster than is the VDC comonomer concentration. Similarly, the SSS triad concentration decreases as fractional conversion increases, as expected. For $f_V > 0.9$, the decrease is very small, whereas there is a significant decrease when $f_V < 0.9$ as conversion increases. For the VVS and SSV triads, the concentration first increases, goes through the maxima, and then decreases as the conversion increases the maxima shift toward higher conversion, as f_V decreases. For $f_V > 0.8$, no maxima are seen; instead, there is a steady decrease of triad concentration as the degree of polymerization increases. For the SVS and VSV triads, the concentration decreases and increases, respectively, with increase of fractional conversion. The decrease in the SVS triad is much sharper for the lower feed mol fraction (f_V) at higher conversion. For the VSV triad, with the lower feed mol fraction, concentration increases only at higher conversion as the reactivity ratio of vinylidene chloride is less than that of styrene.

CONCLUSIONS

From the 2D TOCSY and ^1H - ^{13}C -HSQC NMR, the compositional and configurational assignments were analyzed for S/V copolymers. The broad and complex ^1H -NMR spectrum was assigned up to triad and tetrad sequences. The HSQC spectrum predicted the possibilities of the nonequivalent methylene protons and was confirmed by the geminal couplings observed in the TOCSY spectrum.

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