

Sequencing of *N*-Vinyl-2-pyrrolidone/Glycidyl Methacrylate Copolymers by One-Dimensional and Two-Dimensional Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: Copolymers of *N*-vinyl-2-pyrrolidone (V) and glycidyl methacrylate (G) monomers of different compositions were prepared by free-radical solution polymerization. The copolymer composition of these copolymers was determined with ^1H -NMR spectra. The reactivity ratios calculated from the Kelen–Tudos and nonlinear least-square error-in-variable methods were $r_V = 0.03 \pm 0.01$ and $r_G = 5.05 \pm 0.84$ and $r_V = 0.02$ and $r_G = 4.72$, respectively. The triad sequence distribution in terms of V and G centered triads was determined from $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy. The complete spectral assignment of $^{13}\text{C}\{^1\text{H}\}$ - and ^1H -NMR spectra was performed with the help of distortionless enhancement by polarization transfer and two-dimensional ^{13}C – ^1H heteronuclear single quantum coherence. The ^1H – ^1H couplings were explained with total correlation spectroscopy and nuclear Overhauser enhancement spectroscopy spectra. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 50–60, 2002; DOI 10.1002/app.10186

Key words: *N*-vinyl-2-pyrrolidone; glycidyl methacrylate; copolymers; microstructure; two-dimensional (2D) NMR; sequence determination

INTRODUCTION

N-Vinyl-2-pyrrolidone (V)-based copolymers have many commercial applications. The *N*-Vinyl-2-pyrrolidone polymer has good properties, such as biocompatibility and low toxicity, as well as good film forming and adhesive characteristics.^{1,2} It is used as a comonomer^{3,4} because of its amphiphilic properties. *N*-Vinyl-2-pyrrolidone contains a highly polar amide group that confirms hydrophilic and polar attracting properties, whereas the main-chain methylene and methine groups confirm the hydrophobic properties. Glycidyl

methacrylate (G)-based copolymers are also attracting attention due to the presence of a reactive epoxide ring, which enables glycidyl methacrylate to enter into a wide range of chemical reactions,^{5,6} thereby offering the opportunity for chemical modification of the parent copolymer for various applications. Glycidyl methacrylate-based copolymers have been used for the binding of drugs and biomolecules⁷ and in the electronics industry as negative electron-beam resists.⁸

The microstructure (stereochemical arrangement) of various pendent groups with respect to the polymer backbone fundamentally influences their physical and chemical properties.⁹ Two-dimensional (2D) NMR spectroscopy has been used for determining the compositional^{10–12} and configurational^{13–16} sequences of the polymers. Hunter and Price¹⁷ and Reddy et al.¹⁸ synthesized and characterized V/G copolymers with

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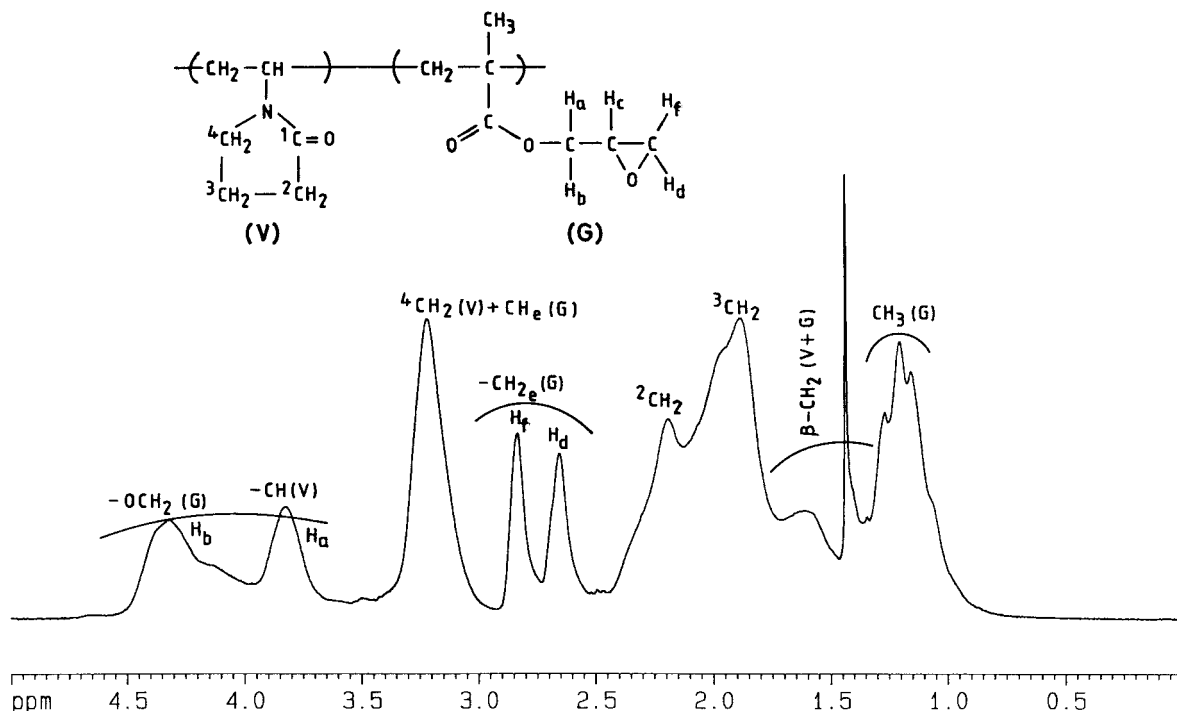


Figure 1 ^1H -NMR (300-MHz) spectrum of the V/G copolymer ($F_V = 0.52$) in CDCl_3 .

$^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy techniques. The ^1H -NMR spectrum of a V/G copolymer is quite complex and overlapping and can be resolved and assigned only with 2D heteronuclear single quantum coherence (HSQC) NMR spectroscopy techniques. In this article, we report the complete assignment of ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of V/G copolymers in terms of compositional and configurational sequences with the help of one-dimensional (1D) $^{13}\text{C}\{^1\text{H}\}$ -NMR and 2D HSQC, total correlation spectroscopy (TOCSY), and nuclear Overhauser enhancement spectroscopy (NOESY) spectra.

EXPERIMENTAL

N-Vinyl-2-pyrrolidone (Fluka, Switzerland) and glycidyl methacrylate (Fluka) were distilled under reduced pressure and stored below 5°C . A series of V/G copolymers with different mole fractions of V in the feed were prepared by free-radical solution polymerization in CHCl_3 at 60°C with benzoyl peroxide as an initiator. The precipitation conversion was kept below 10% by precipitation of the copolymer in cyclohexane (Qualigens). The copolymers were further purified with a chloroform/cyclohexane system. The copolymer

composition was determined experimentally with the ^1H -NMR spectrum. The various 1D [^1H , $^{13}\text{C}\{^1\text{H}\}$, and distortionless enhancement by polarization transfer (DEPT)] and 2D (HSQC, TOCSY, NOESY) NMR experiments were performed in CDCl_3 on a Bruker DPX-300 NMR spectrometer with different standard pulse sequences as described in our previous articles.^{19–21}

Table I Feed Mole Fraction and Copolymer Composition Data of V/G Copolymers

Sample	Feed Molar Fraction		Copolymer Composition	
	f_V	f_G	F_V	F_G
VG1	0.98	0.02	0.68	0.32
VG2	0.94	0.06	0.52	0.48
VG3	0.90	0.10	0.44	0.56
VG4	0.85	0.15	0.37	0.63
VG5	0.75	0.25	0.27	0.73
VG6	0.60	0.40	0.21	0.79

f_V and f_G are the mole fractions of V and G comonomers, respectively in feed. F_V and F_G are the mole fractions of V and G comonomers, respectively in the copolymer.

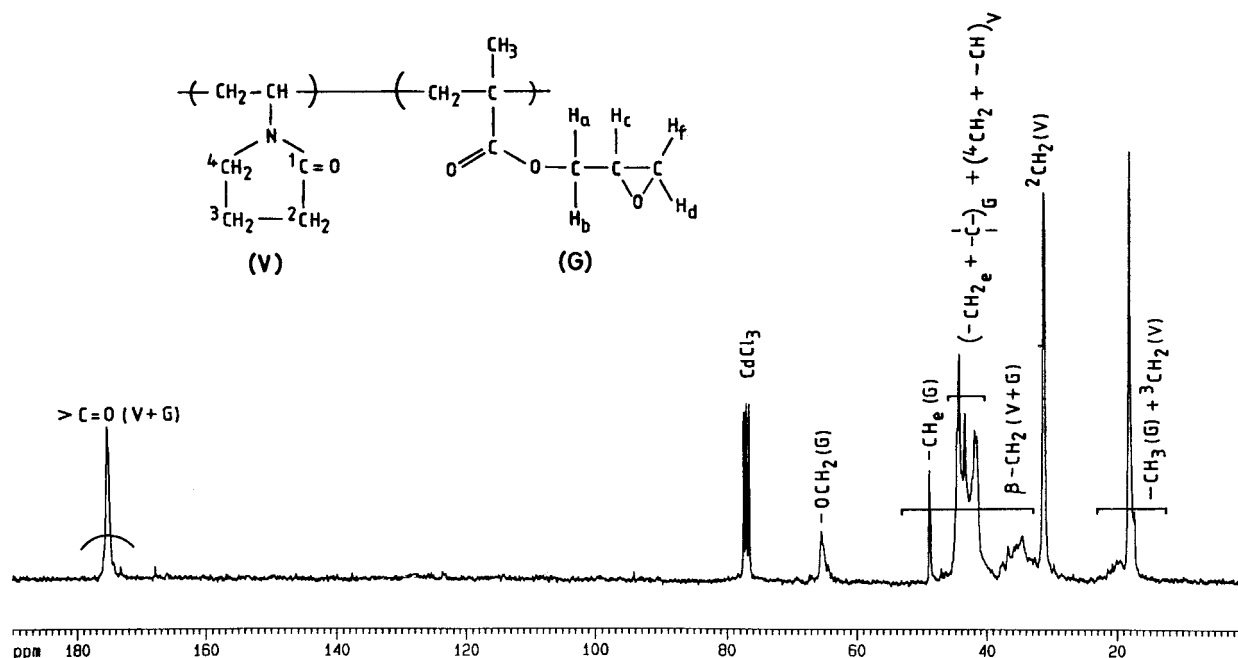


Figure 2 $^{13}\text{C}\{^1\text{H}\}$ -NMR (75.5-MHz) spectrum of the V/G copolymer ($F_V = 0.52$) in CDCl_3 .

RESULTS AND DISCUSSION

Reactivity Ratio Determination

The ^1H -NMR spectrum of the V/G copolymer along with complete assignments is shown in Fig-

ure 1. The $[(\text{CH}_2)_e]_G$ region and $\{[(\text{CH})_e]_G + \{^4\text{CH}_2\}_V\}$ region do not overlap each other, so the copolymer compositions of the V/G copolymers were determined from the ^1H -NMR spectrum with the following equation:

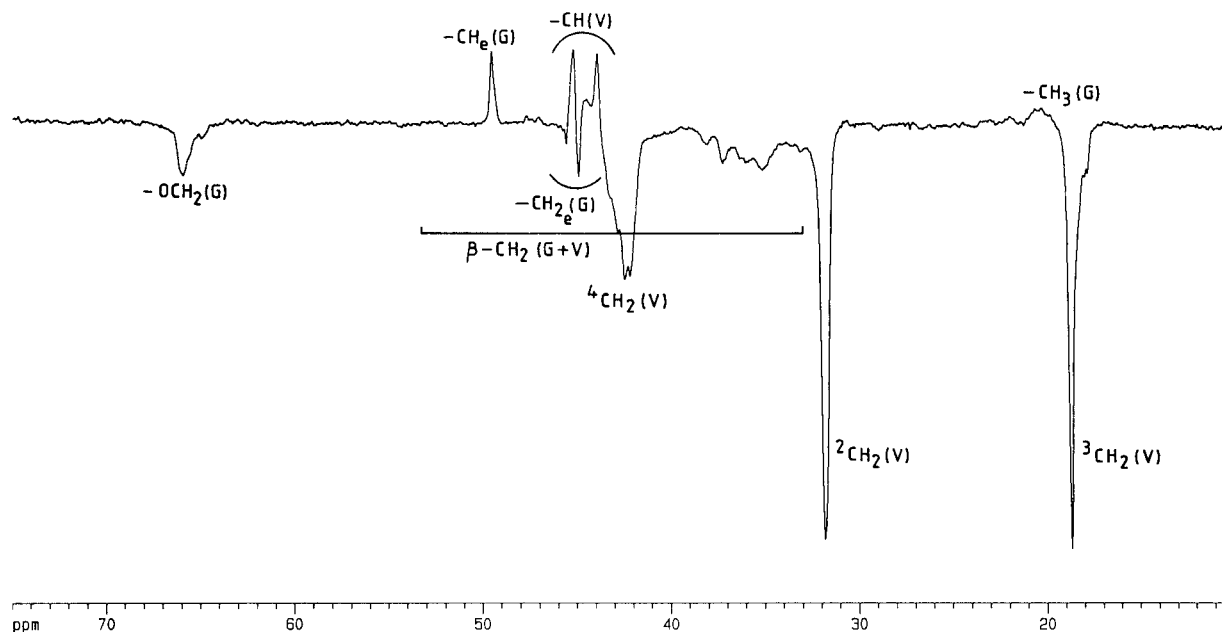


Figure 3 DEPT-135 spectrum of the V/G copolymer ($F_V = 0.52$) in CDCl_3 .

Table II Compositional and Configurational Assignment of the Methylene Region of the V/G Copolymers from a 2D HSQC Spectrum

Peak Numbers	HSQC		Assignment
	$^{13}\text{C}\{^1\text{H}\}$ ppm	^1H ppm	
1	33.0	1.58	V_rV
2, 3	35.5	1.78, 1.40	V_mV
4, 6	41.5	1.98, 1.34	VV_mGV
5	41.5	1.63	VV_rGV
7, 9	44.0	2.00, 1.25	VV_mGG
8	44.0	1.58	VV_rGG
10, 12	46.4	1.98, 1.20	GV_mGG
11	46.4	1.55	GV_rGG
13	53.0	2.00	G_mG
14	54.5	1.92	G_rG

$$F_G = \frac{[I(\text{CH}_2)_e]_G}{[I(\text{CH}_2)_e]_V + [I(\text{CH}_2)_e]_G}$$

where $[I(\text{CH}_2)_e]_V$ is the intensity of the $[(\text{CH})_e]_G + \{^4\text{CH}_2\}_V$ region minus half the intensity of the $[(\text{CH}_2)_e]_G$ region, $[I(\text{CH}_2)_e]_G$ is the intensity of the epoxy methylene protons of the glycidyl methacrylate monomer, and $[I(\text{CH}_2)_e]_V$ is the intensity of the ring protons of the $^4\text{CH}_2$ group of the *N*-vinyl-2-pyrrolidone monomer in the copolymer.

The copolymer composition data (Table I), determined from ^1H -NMR spectra, were used to calculate the terminal model reactivity ratios by the Kelen–Tudos (KT)²² and nonlinear least-square error-in-variable (EVM)²³ methods with the RREVM computer program.²⁴ The terminal model reactivity ratios calculated from the KT method ($r_V = 0.03 \pm 0.01$ and $r_G = 5.05 \pm 0.84$) served as the initial estimates for the calculation of the reactivity ratios by the EVM method. The reactivity ratios observed from the EVM method are $r_V = 0.02$ and $r_G = 4.72$, which are in close agreement with each other and the literature values.¹⁸

$^{13}\text{C}\{^1\text{H}\}$ -NMR and ^1H -NMR studies

The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the V/G copolymer [mole fraction of V (F_V) = 0.52] in CDCl_3 along with the signal assignments is shown in Figure 2. The carbonyl carbons of both monomers (V and G) overlap and resonate around $\delta = 173.2$ –177.0 ppm. Both of these carbon signals show multiplets, indicating that they are sensitive to compositional and configurational sequences. The spectral region around $\delta = 15.0$ –70.0 ppm is very complex and overlapping. The extent of overlapping cannot be ascertained from the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum alone. These overlapping regions can be resolved with DEPT-135 and 2D HSQC

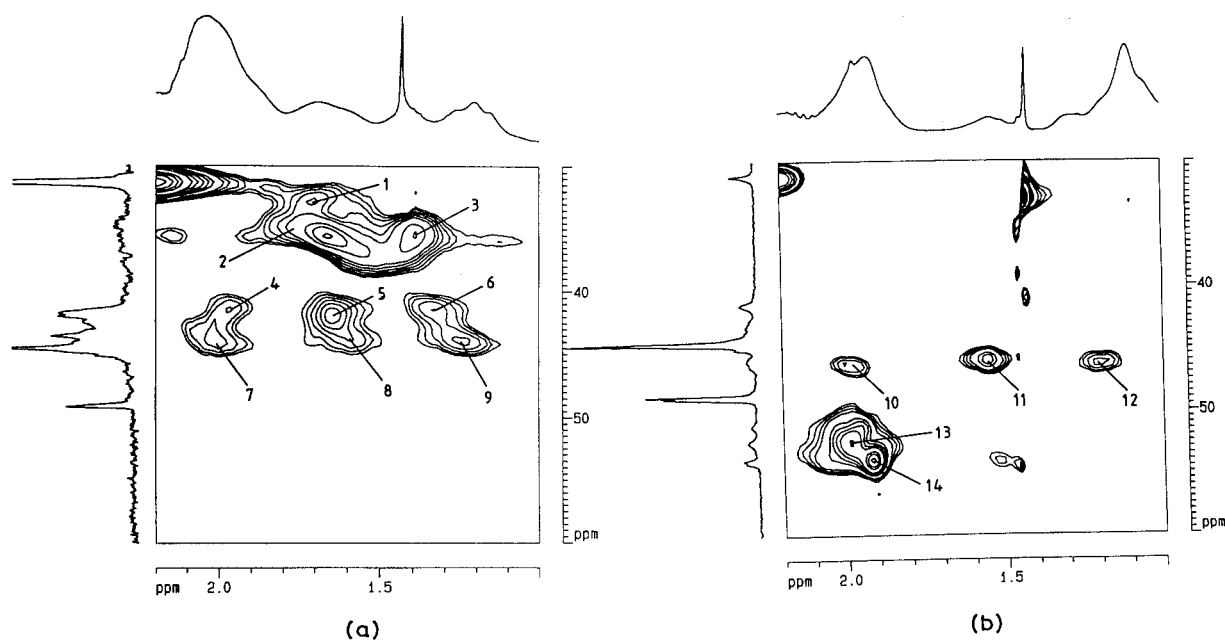
**Figure 4** Methylene regions of the HSQC spectra of V/G copolymers with the mole fractions (a) $F_V = 0.68$ and (b) $F_V = 0.21$ in CDCl_3 .

Table III Compositional and Configurational Assignment of the Methyl Carbon Region of V/G Copolymers from a 2D HSQC Spectrum

Peak Number	HSQC		Assignment
	$^{13}\text{C}\{^1\text{H}\}$ ppm	^1H ppm	
1	16.54	0.95	$\text{G}_r\text{G}_r\text{G}$
2	18.00	1.05	$\text{G}_r\text{G}_m\text{G}$
3	17.68	1.11	$\text{G}_r\text{G}_r\text{V}$
4	19.55	1.27	$\text{G}_r\text{G}_m\text{V}$
5	21.10	1.30	GGGVG
6	20.25	1.19	VVGVV
7	21.52	1.15	GVGVV

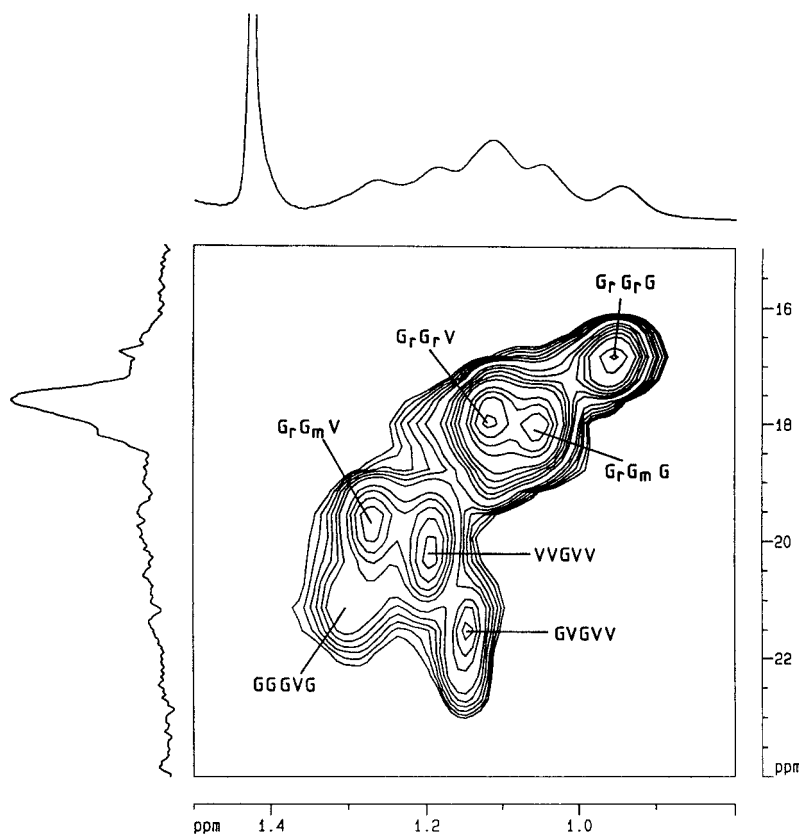
NMR experiments. The DEPT-135 spectrum of the V/G copolymer ($F_V = 0.52$) in CDCl_3 is shown in Figure 3. The methine, methylene, and methyl carbon resonances show multiplets, indicating that they are sensitive toward the compositional and configurational sequences. The side-chain ring methylene carbon signals are assigned around $\delta = 42.00$ ppm ($^4\text{CH}_2$), $\delta = 31.52$ ppm

($^2\text{CH}_2$), and $\delta = 18.50$ ppm ($^3\text{CH}_2$). These assignments are made in comparison with the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of poly(*N*-vinyl-2-pyrrolidone).²¹ All the methylene carbon resonances of the ring are singlet and insensitive to compositional and configurational sequences.

The oxymethylene ($-\text{OCH}_2$), epoxy methylene [$(\text{CH}_2)_e$], and epoxy methine [$(\text{CH})_e$] carbon signals appear around $\delta = 65.0$ ppm, $\delta = 48.9$ ppm, and $\delta = 44.5$ ppm, respectively. The β -methylene carbon of both the V and G units resonate around $\delta = 31.5$ – 55.5 ppm. The signals around $\delta = 43.0$ – 45.8 ppm and $\delta = 16.05$ – 22.15 ppm appear because of methine carbon resonances of V and methyl carbon resonances of G, respectively, in the copolymer.

The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the methine carbon resonance (V) is very complex because of the overlapping of compositional and configurational sequences. Therefore, this cannot be resolved properly.

The β -methylene carbon signals of the copolymer (V/G) due to its symmetry are sensitive to dyad and tetrad sequences. The ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spec-

**Figure 5** Methyl region of the HSQC spectrum of the V/G copolymer ($F_V = 0.37$).

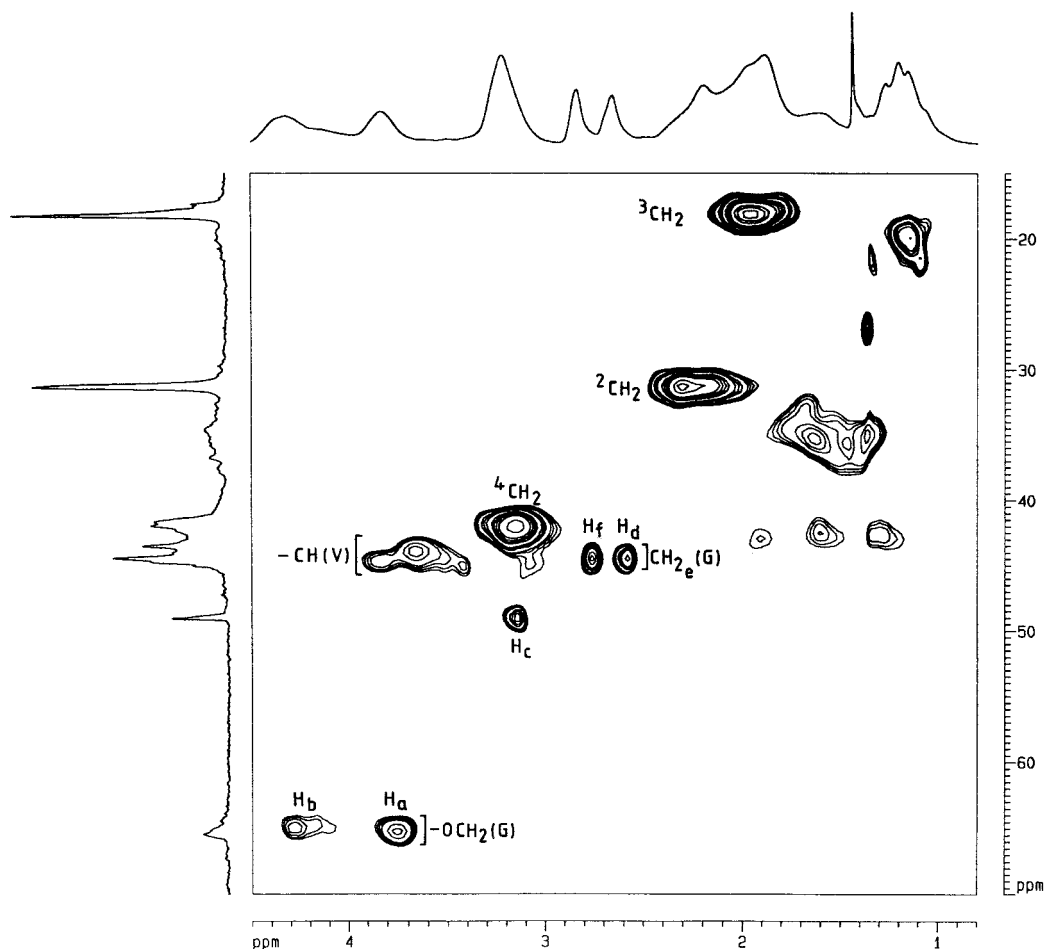


Figure 6 2D HSQC NMR spectrum showing the methyl, methylene, methine, and methoxy resonances of the V/G copolymer ($F_V = 0.52$) in CDCl_3 .

tra of β -methylene are quite complex and overlapping and can be resolved with the help of 2D HSQC study (Table II). The methylene carbon resonance signals show three broad envelopes, VV ($\delta = 31.5$ – 39.0 ppm), VG ($\delta = 39.0$ – 47.0 ppm), and GG ($\delta = 47.0$ – 55.5 ppm), on the basis of changes in the intensity with changes in the copolymer composition, as shown in Figure 4(a,b). Further splitting within each dyad can be assigned to compositional or configurational sequences on the basis of changes in the intensity of signals with the changes in the copolymer composition. In the VV dyad, one cross peak at $\delta = 33.0/1.58$ ppm is assigned to V_rV , and the two cross peaks at $\delta = 35.5/1.78$ ppm and $\delta = 35.5/1.40$ ppm are assigned to V_mV due to two nonequivalent protons in the meso (m) configuration in comparison with the HSQC spectrum of poly(*N*-vinyl-2-pyrrolidone).²¹ The VG dyad is assigned to VVG (VVG; $\delta = 41.5$ ppm), GVGV (VVG; $\delta = 43.0$ ppm), and GVGG ($\delta = 44.5$ ppm) tetrad

compositional sequences on the basis of changes in the intensity with changes in the copolymer composition. Further splitting in these tetrads (VG tetrads) along the proton axis is assigned to the configurational sequence, where two cross peaks appear because of two nonequivalent protons in the meso (m) configuration and one cross peak appears because of the racemic (r) configuration. Therefore, in the VVG tetrad, the cross peaks around $\delta = 41.5/1.98$ ppm and $\delta = 41.5/1.34$ ppm are assigned to two nonequivalent protons in the m configurational sequence VV_mGV , and one cross peak around $\delta = 41.5/1.63$ ppm is assigned to the r configurational sequence VV_rGV . In the GVGV(VVG) tetrad, the cross peaks at $\delta = 44.0/2.00$ ppm and $\delta = 44.0/1.25$ ppm are assigned to GV_mGV , and the cross peak at $\delta = 44.0/1.58$ ppm is due to GV_rGV configurational sequences. Similarly, in the GVGG tetrad, the cross peaks at $\delta = 46.4/1.98$ ppm and $\delta = 46.3/1.20$ ppm are assigned to GV_mGG , and the

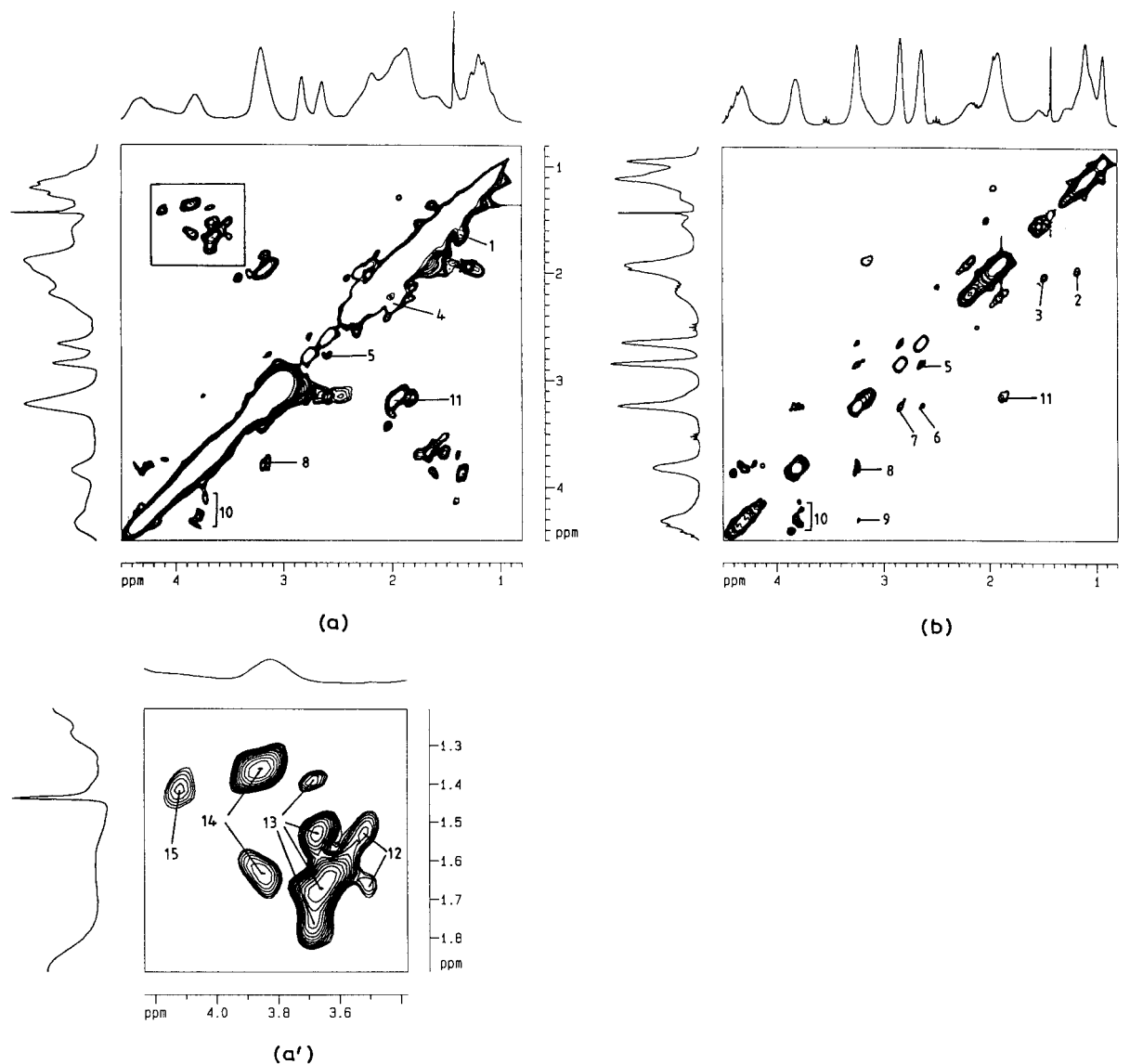


Figure 7 2D TOCSY NMR spectra of V/G copolymers at 4 ms with the mole fractions (a) $F_V = 0.52$ and (b) $F_V = 0.21$ in CDCl_3 and (a') an expanded region showing methine-methylene couplings.

cross peak at $\delta = 46.4/1.55$ ppm is assigned to GV_rGG configurational sequences. In the GG dyad region, the two cross peaks around $\delta = 53.0/2.00$ ppm and $\delta = 54.5/1.92$ ppm are assigned to G_mG and G_rG configurational sequences, respectively, by comparison with poly(glycidyl methacrylate), as shown in Figure 4(b).

The α -methyl region of the G unit in the 1D ($^{13}\text{C}\{^1\text{H}\}$ - and ^1H -NMR) spectra is quite complex and overlapping and can be assigned only with the help of the 2D HSQC NMR spectrum (Table III). However, the nonoverlapping methyl proton signals could be properly assigned around δ

$= 0.9\text{--}1.35$ ppm, as shown in Figure 5, and show both compositional and configurational sensitivity. The α -methyl carbon signal region of the G unit is divided into three broad envelopes, GGG, GGV, and VGV, on the basis of changes in the intensity of signals with changes in the copolymer composition. Further splitting within these compositional triads can be assigned to configurational or higher compositional sequences. The cross peaks at $\delta = 16.54/0.95$ ppm and $\delta = 18.00/1.05$ ppm are assigned to $\text{G}_r\text{G}_r\text{G}$ and $\text{G}_r\text{G}_m\text{G}$ configurational sequences, respectively, by comparison with the 2D HSQC spectrum of poly(glycidyl

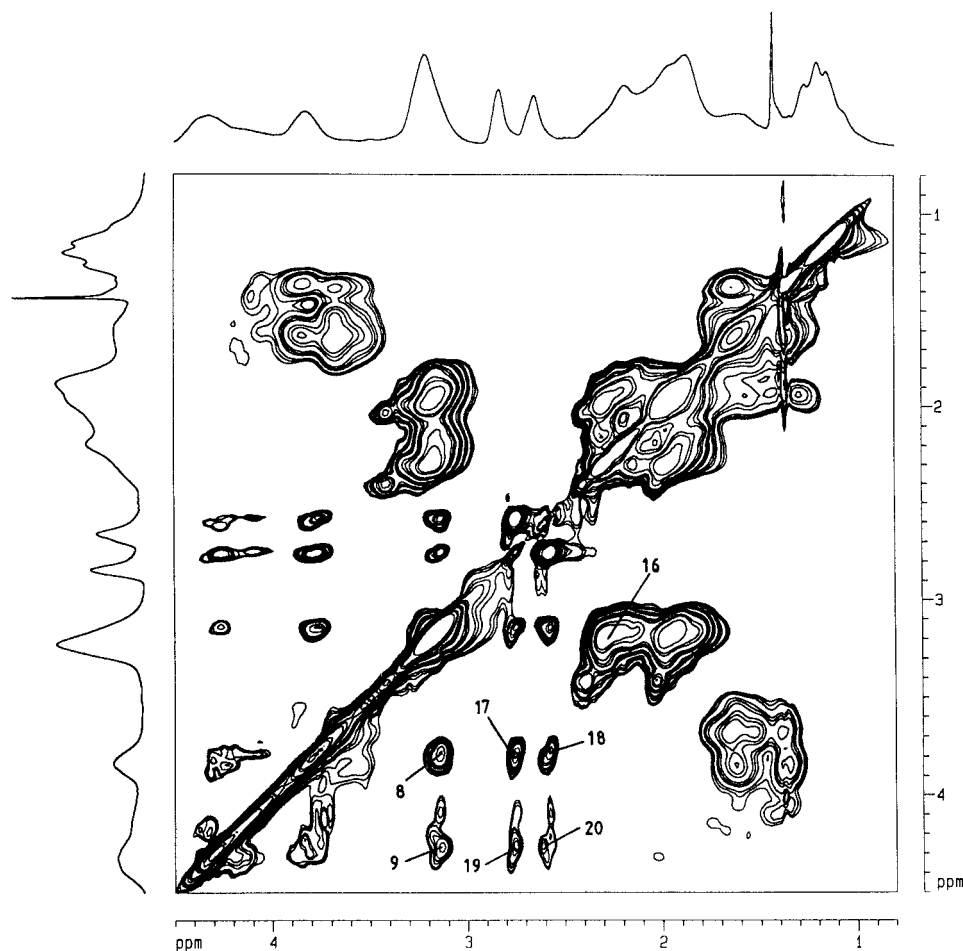


Figure 8 2D TOCSY NMR spectrum of the V/G copolymer ($F_V = 0.52$) at 80 ms.

methacrylate). Similarly, the cross peaks at $\delta = 17.68/1.11$ ppm and $\delta = 19.55/1.27$ ppm in the GGV(VGG) triad, which do not show relative changes in the intensity with the copolymer composition, are assigned to G_rG_rV and G_rG_mV configurational sequences, respectively, as shown in Figure 5. The cross peak at $\delta = 21.10/1.30$ ppm is assigned to the GGGVG compositional pentad sequence on the basis of the changes in the intensity with the copolymer composition. Further splitting in the VGV triad region is assigned to pentad compositional sequences. These cross peaks are assigned around $\delta = 20.25/1.19$ ppm (VGVVV) and $\delta = 21.52/1.15$ ppm (VGVVG) on the basis of the changes in the intensity with the changes in the copolymer composition. Further splitting may be due to configurational sequences.

The other proton signals in the ^1H -NMR spectrum (Fig. 1) are overlapping. This is completely assigned by one-to-one correlations between the carbon and proton signals in the HSQC spectrum

(Fig. 6). The $-\text{OCH}_2$ or oxymethylene protons that are adjacent to the chiral center show diastereomerism and give two cross peaks at $\delta = 65.0/4.27$ ppm and $\delta = 65.0/3.78$ ppm. Similarly, the epoxy methylene proton region is assigned around $\delta = 2.63$ – 2.80 ppm, as shown in Figure 6. These methylene protons show both compositional sensitivity and diastereomerism. The peak positions of the triad compositional sequence and diastereomeric proton in various compositional sequences are overlapping and cannot be resolved, and so they are difficult to assign. Therefore, the two cross peaks around $\delta = 44.5/2.80$ ppm and $\delta = 44.5/2.63$ ppm are assigned to two nonequivalent protons. The epoxy methine proton is assigned to the cross peak at $\delta = 49.0/3.16$ ppm, that is, to the H_c proton.

2D TOCSY Spectral Studies

To understand the connectivity and confirm the various couplings in the copolymer chain, the

Table IV 2D TOCSY ^1H - ^1H Coherence of the V/G Copolymers

Peak Number	Proton (ppm)	Coupled to Proton (ppm)
1	(β -CH ₂) in VV dyad (1.35)	(β -CH ₂) in VV dyad head to head (1.64)
2	(β -CH ₂) in VG dyad (1.18)	(β -CH ₂) in VG dyad head to head (1.96)
3	(β -CH ₂) in GG dyad (1.49)	(β -CH ₂) in GG dyad head to head (2.03)
4	$^3\text{CH}_2$ (1.96)	$^2\text{CH}_2$ (2.26)
5	H _d of (CH ₂) _e (2.60)	H _f of (CH ₂) _e (2.75)
6	H _d of (CH ₂) _e (2.60)	H _c of (CH) _e (3.24)
7	H _f of (CH ₂) _e (2.82)	H _c of (CH) _e (3.24)
8	H _c of (CH) _e (3.21)	H _a of OCH ₂ (3.78)
9	(CH) _e (3.21)	H _b of OCH ₂ (4.27)
10	H _a of OCH ₂ (3.78)	H _b of OCH ₂ (4.27)
11	$^3\text{CH}_2$ (1.95)	$^4\text{CH}_2$ (3.16)
12	CH(V) in V _r V _r V (3.51)	(β -CH ₂) in V _r V (1.52)
	(3.50)	(1.66)
13	CH(V) in V _m V _r V (3.68)	(β -CH ₂) in V _m V (1.38)
	(3.68)	(1.76)
	(3.67)	V _r V (1.52)
	(3.65)	(1.67)
14	CH(V) in V _m V _m V (3.85)	(β -CH ₂) in V _m V (1.35)
	(3.85)	(1.65)
15	CH in VVG (4.12)	(β -CH ₂) in V _r G (1.40)
16	$^2\text{CH}_2$ (2.32)	$^4\text{CH}_2$ (3.16)
17	H _f of (CH ₂) _e (2.77)	H _a of OCH ₂ (3.78)
18	H _d of (CH ₂) _e (2.60)	H _a of OCH ₂ (3.78)
19	H _f of (CH ₂) _e (2.77)	H _b of OCH ₂ (4.27)
20	H _d of (CH ₂) _e (2.60)	H _b of OCH ₂ (4.27)

TOCSY spectrum plays a very important role. The direct three-bond couplings between the various protons in the V/G copolymer can be seen clearly in the low-mixing (4-ms) TOCSY spectrum, as shown in Figure 7(a,b). In the head-to-head linkage, vicinal coupling between the methylene groups of the V and G units is possible. The cross peaks at $\delta = 1.35/1.64$ ppm (1), $\delta = 1.18/1.96$ ppm (2), and $\delta = 1.49/2.0$ ppm (3) are assigned to the VV dyad, VG dyad, and GG dyad, respectively. Coupling within the ring protons of *N*-vinyl-2-pyrrolidone is also possible. The cross peak around $\delta = 1.96/2.26$ ppm (4) is assigned to the coupling of $^3\text{CH}_2$ with $^2\text{CH}_2$ within the pyrrolidone ring. The cross peak at $\delta = 2.60/2.75$ ppm (5) is assigned to the coupling of the H_d proton with the H_f proton of the epoxy methylene group. The cross peaks at $\delta = 2.60/3.24$ ppm (6) and $\delta = 2.82/3.24$ ppm (7) are assigned to the coupling of H_d and H_f protons of the epoxy methylene group with the epoxy methine proton (H_c), and the cross peaks at $\delta = 3.21/3.78$ ppm (8) and $\delta = 3.21/4.27$ ppm (9) are assigned to the coupling of the epoxy methine proton (H_c) with the H_a and H_b protons of the —OCH₂ group, respectively.

The two protons of —OCH₂ in the G unit are diastereomeric and are coupled to each other. In the proton spectrum, the —OCH₂ resonance signals overlap the methine (—CH) resonance signals. Thus, the cross-peak region at $\delta = 3.78/4.27$ ppm (10) is assigned to the geminal coupling of the —OCH₂ group in the side chain. The cross peak around $\delta = 1.95/3.17$ ppm (11) is assigned to the coupling of $^3\text{CH}_2$ with $^4\text{CH}_2$ of the pyrrolidone ring. The methine (—CH) proton of the V unit also shows coupling with the β -methylene protons (of both V and G units) in the main chain. Therefore, the cross peaks (12) at $\delta = 3.51/1.52$ ppm and $\delta = 3.50/1.66$ ppm are assigned to the coupling of CH(V) in the V_rV_rV triad with β -CH₂ in the V_rV dyad by comparison with poly(*N*-vinyl-2-pyrrolidone).²¹ Similarly, the cross peaks (13) at $\delta = 3.68/1.38$ and $3.68/1.76$ ppm and $\delta = 3.67/1.52$ and $3.65/1.67$ ppm are assigned to the coupling of CH(V) in the V_mV_rV triad along with β -CH₂ in the V_mV and V_rV dyads, respectively. The cross peaks (14) at $\delta = 3.85/1.35$ ppm and $\delta = 3.85/1.65$ ppm are assigned to the coupling of CH(V) in the V_m-V_mV triad with β -CH₂ in the V_mV dyad. The cross peak (15) at $\delta = 4.12/1.40$ ppm appears to be due

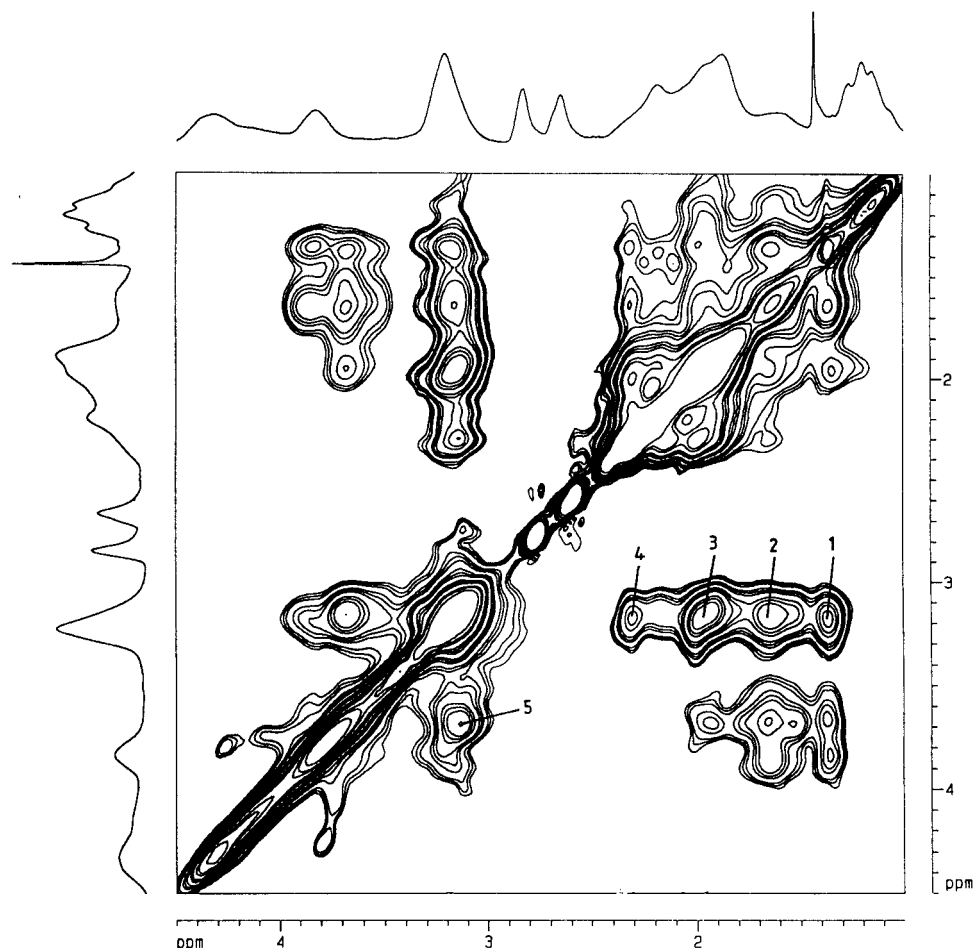


Figure 9 2D NOESY spectra of the V/G copolymer ($F_V = 0.52$) in CDCl_3 with a mixing time of 350 ms.

to the coupling of CH(V) in the VVG triad with $\beta\text{-CH}_2$ in the V_rG dyad, as shown in Figure 7(a').

In the 80-ms TOCSY spectrum (Fig. 8), we can see the long-range couplings. The cross peak around $\delta = 2.32/3.16$ ppm (16) is assigned to the coupling of $^2\text{CH}_2$ with $^4\text{CH}_2$ in the pyrrolidone ring. The signals at $\delta = 2.77/3.78$ ppm (17), $\delta = 2.60/3.78$ ppm (18) and $\delta = 2.77/4.27$ ppm (19), and $\delta = 2.60/4.27$ ppm (20) are assigned to the coupling of the two nonequivalent protons of the epoxy methylene (CH_2)_e (H_f and H_d) with the two nonequivalent protons of the oxymethylene $-\text{OCH}_2$ (H_a and H_b), respectively. All these couplings are shown in Table IV.

2D NOESY Spectral Studies

The special arrangement in the space is shown by the NOESY experiment, which is shown in Figure 9. Special coupling between the methylene pro-

tons and the pyrrolidone ring protons can be observed. Here the cross peaks around $\delta = 3.16/1.39$ ppm (1) and $\delta = 3.16/1.66$ ppm (2) are assigned to the couplings of $^4\text{CH}_2$ of the ring (V) with the β -methylene protons of V and G, respectively. The cross peaks around $\delta = 3.16/1.95$ ppm (3) and $\delta = 3.16/2.32$ ppm (4) are assigned to the couplings of $^4\text{CH}_2$ of the ring (V) with $^3\text{CH}_2$ and $^2\text{CH}_2$ of the ring (V), respectively. The cross peak at $\delta = 3.68/3.15$ ppm (5) appears to be due to the coupling of methine of V with the epoxy methine of G, as shown in Figure 9.

CONCLUSIONS

The reactivity ratios of the V/G copolymer are $r_V = 0.02$ and $r_G = 4.71$. The overlapping and broad signals in carbon and proton spectra were as-

signed completely to various compositional and configurational sequences with HSQC and TOCSY experiments. The methine carbon resonance of the V unit is assigned to triad compositional sequences, whereas the methyl carbon resonance of the G unit is assigned to triad compositional and configurational sequences. The methylene carbon resonances are assigned to tetrad compositional and configurational sequences with the help of HSQC experiments.

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