Characterization of glycidyl methacrylate/styrene copolymers by one- and two-dimensional NMR spectroscopy

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Abstract

Glycidylmethacrylate/styrene copolymers of different compositions were prepared by free radical bulk polymerisation using benzoyl peroxide as an initiator. Copolymer composition was obtained from quantitative Carbon-13 NMR spectroscopy. Reactivity ratios for comonomers were calculated using the Kelen-Tudos (KT) and non-linear error in variable methods (EVM). The reactivity ratios obtained from KT and EVM are found to be $r_G = 0.56 \pm 0.1$, $r_S = 0.44 \pm 0.07$ and $r_G = 0.60$, $r_S = 0.48$ respectively. The triad sequence distribution in terms of G and S centered triad were obtained from $^{13}C{^1H}$ NMR spectroscopy. Complete spectral assignment of ^{13}C and ^1H-NMR spectra were done with the help of distortionless enhancement by polarization transfer and 2D ^{13}C-^1H heteronuclear single quantum coherence.

Keywords: Glycidylmethacrylate/styrene copolymers; 2D NMR studies; Sequence distribution

1. Introduction

GMA based copolymers are receiving great attention due to the presence of reactive epoxide ring, which offers it an opportunity to enter into wide range of chemical reactions [1,2]. The GMA based copolymers have been used for binding of drugs and biomolecules [3] and in electronic industries as negative electron beam resists [4]. 2D-NMR spectroscopy has been widely used for determining the compositional [5-7] and configurational [8-10] sequence of the polymers. Microstructure of co-polymers of GMA with alkyl acrylate, N-vinyl pyrroli-done, vinyl acetate, acrylonitrile have already been reported [11-14]. Reddy and coworkers [15] have synthesized and characterized GMA/styrene (G/S) copoly-mers by various spectroscopic techniques such as UV, IR, $^{13}C{^1H}$ NMR, but to the best of our knowledge the microstructure of G/S copolymer have not been reported so far. The proton NMR spectrum of G/S copolymer is quite complex and overlapped, and can only be resolved and assigned using 2D-heteronuclear single quantum coherence (HSQC) NMR spectroscopy. In this article we report the complete assignment of ^1H and $^{13}C{^1H}$ NMR spectra of G/S copolymers in terms of compositional and configurational sequences with the help of 1D($13C{^1H}$) NMR and 2D-HSQC NMR experiments. We also report some interesting observation seen in the oxy-methylene group of GMA in the HSQC spectrum.

2. Experimental

GMA (Merck) and styrene (Fluka) were distilled under reduced pressure and stored below 5 °C. A series of G/S copolymers containing different mol % of GMA in feed were prepared by bulk polymerisation using benzoyl peroxide as an initiator at 60 °C. The conversion was kept below 10%. The copolymers were precipitated in methanol (Merck). The copolymers were further purified

using CHCl3/methanol system. The copolymer composition was determined experimentally by quantitative $^{13}Cf^1Hg$ NMR spectroscopy using inverse gated decoupling pulse program where relaxation delay was kept at 10 s.

The ^1H and $^{13}Cf1Hg$ NMR spectra were recorded in CDCl$_3$ on Bruker 300 MHz DPX spectrometer operating at 300.13 and 75.5 MHz, respectively. All the 2D(HSQC, TOCSY) NMR experiments were also performed in CDCl$_3$ on Bruker 300 MHz DPX spectrometer. Distortionless enhancement by polarization transfer (DEPT) measurements were carried in CDCl3 using the standard pulse sequence with a J modulation time of 3.7 ms *(JCH* = 135 Hz) with 2 s delay time. Two-dimensional ^1H-^{13}C heteronuclear chemical shift correlation spectrum was recorded in CDCl3 using standard pulse sequence. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 *t1* experiments. The 2D TOCSY experiment using the standard pulse sequence was carried out in CDCl3 using the mixing time of 4 ms. The relative area of resonance signals were determined using a non-linear least square Lorentzian line shape deconvolution program [16]. In all cases the fitting was considered valid only when the $v^2 < 1$.

3. Results and discussion

3.1. Copolymer composition and reactivity ratios determination

The compositions of G/S copolymers were determined from quantitative $^{13}Cf^1Hg$ NMR spectroscopy. The mole fractions of monomers in feed and in copolymer are as shown in Table 1. The copolymer composition data were used to determine the terminal model reactivity ratio (KT method). These initial estimates of re-

activity ratios, along with the copolymer composition data were used for the calculation of the reactivity ratios by non-linear error in variable method (EVM). The errors in determining the monomer composition in feed and in copolymer were estimated to be 3%. The value of reactivity ratios as obtained from Kelen-Tudos (KT) [17] and non-linear EVM [18] are $r_G = 0.56 \pm 0.1$, $r_S = 0.44 \pm 0.07$ and $r_G = 0.60$, $r_S = 0.48$ respectively. These values are in close agreement with the reported reactivity ratios $r_G = 0.54$ and $r_S = 0.44$ [15].

3.2. $^{13}Cf^1Hg$ NMR and ^1H NMR studies

The complete assignment of carbon resonance signals in $^{13}Cf^1Hg$ NMR spectrum of G/S copolymer *(F$_G$ = 0.55* in copolymer) taken in CDCl3 is shown in Fig. 1(a). The carbonyl carbon resonances of GMA unit and aromatic quaternary carbon resonances of styrene unit are

Fig. 1. (a) The $^{13}Cf^1Hg$ NMR spectrum of G/S copolymer *(F$_G$ = 0.55).* (b) Expanded carbonyl carbon region.

Table 1
The feed in mol fraction and copolymer composition data of G/S copolymers

Sample	Feed in mol fraction		Copolymer composition		M_n x 10^{-5} g/mol	M_w x 10^{-5} g/mol	Polydispersity
	FG	*fS*	F_G	F_S			
GS1	0.70	0.30	0.68	0.32	0.96	1.76	1.83
GS2	0.60	0.40	0.57	0.43	0.82	1.72	1.53
GS3	0.55	0.45	0.55	0.45	0.99	1.81	1.48
GS4	0.50	0.50	0.52	0.48	1.10	1.91	1.42
GS5	0.40	0.60	0.45	0.55	1.67	2.71	1.40
GS6	0.30	0.70	0.39	0.61	1.43	2.15	1.36
GS7	0.20	0.80	0.29	0.71	1.98	2.44	1.19

f_G and f_S are the mole fractions of G- and S-comonomers, respectively in feed.
F_G and F_S are the mole fractions of G- and S-comonomers, respectively in the copolymer.
M_n and M_w are number average and weight average molecular weight of copolymers calculated using gel permeation chromatography technique.

assigned around d173.8-178.2 ppm and d142.2-147.0 ppm respectively. The spectral region around d15.5-66.5 ppm is very complex and overlapped and can be assigned to aliphatic carbons in the main and side chain of copolymer. The overlapped carbon regions can be resolved by employing the DEPT-135 NMR (Fig. 2) where methylene carbon signal appear in negative phase and methine and methyl carbon signals appear in positive phase. The -OCH2, epoxy methylene and epoxy methine carbon signals are assigned around d64.8, d44.8, d48.9 ppm respectively. The b-methylene carbon of both styrene and GMA units resonate around d41.5-54.8 ppm. The signals around d36.2-41.8 ppm and d15.75-23.25 ppm are assigned to methine carbon resonances of styrene and methyl carbon resonances of GMA unit in the copolymer, respectively. The quaternary carbon of GMA unit is assigned at d47.0 ppm and it is overlapped with b-methylene carbon signal.

The expanded $^{13}C f^{1}Hg$ NMR spectrum of the carbonyl carbon resonances of G/S copolymer are shown in Fig. 1(b) $(F_G$ — 0.55). In the carbonyl carbon region, the signals around d173.8-175.65 ppm decrease in intensity with increase in GMA content in the copolymer, hence they are assigned to SGS triad sequence. The signals around d176.30-178.2 ppm increase in intensity with increase in GMA content in copolymer, hence they are assigned to GGG triad sequence. This is further confirmed by comparing with $^{13}C f^{1}Hg$ NMR of poly(Glycidylmethacrylate). The signals around d175.65-176.30 ppm are assigned to SGG triad sequence. The quaternary carbon resonance signals of styrene unit show overlapping of various compositional and configurational sequences and hence are difficult to resolve and assign.

The micro structure of G/S copolymers in terms of GMA centered triad sequence distribution from the $^{13}C f^{1}Hg$ NMR spectra was found to be in good agreement with the theoretical values calculated by the Harwood program [19] and by using terminal model reactivity ratios $r_G = 0.60$ and $r_S = 0.48$ (Table 2).

The methine carbon resonances are sensitive to compositional sequences. The expanded region of methine carbon resonance signal in $^{13}C f^{1}Hg$ NMR spectrum of G/S copolymer with different mole fractions of GMA in the copolymer ((a) 0.29, (b) 0.55 and (c) 0.68) is shown in Fig. 3. On the basis of change in intensity of the signals with change in the copolymer composition, the three resonating signals centered around d36.5-38.5, d38.5-39.75 and d39.75-41.0 ppm are assigned to GSG, GSS and SSS triads respectively.

The a-methyl region in 1D (^{1}H) and $^{13}C f1Hg$ NMR spectra is quite complex and overlapped and can be only assigned with the help of 2D-HSQC NMR spectrum (Table 3). The $^{13}C f^{1}Hg$ NMR spectrum of a-methyl region of poly(Glycidylmethacrylate) is already reported [20] and accordingly its HSQC NMR spectrum is

Fig. 2. The DEPT-135 spectrum of G/S copolymer $(F_G = 0.55)$ inCDCl$_3$.

Table 2
Calculated and observed fraction of GMA centered triad in the G/S copolymer

Sample no.	F_G	Triad	Triad fraction	
			(a)	(b)
GS1	0.70	GGG	0.36	0.34
		GGS	0.51	0.49
		SGS	0.13	0.17
GS2	0.60	GGG	0.29	0.22
		GGS	0.48	0.50
		SGS	0.23	0.28
GS3	0.55	GGG	0.20	0.18
		GGS	0.50	0.49
		SGS	0.30	0.33
GS4	0.50	GGG	0.21	0.14
		GGS	0.44	0.47
		SGS	0.35	0.39
GS5	0.40	GGG	0.08	0.08
		GGS	0.42	0.41
		SGS	0.49	0.51
GS6	0.30	GGG	0.02	0.04
		GGS	0.36	0.32
		SGS	0.61	0.63
GS7	0.20	GGG	0.01	0.02
		GGS	0.22	0.23
		SGS	0.77	0.76

Triad functions determined from: (a) observed ^{13}C NMR spectra of copolymers from >C@O(GMA) using curve fitting method, (b) Harwood's terminal model program using reactivity ratios $r_G = 0.60$ and $r_S = 0.48$.
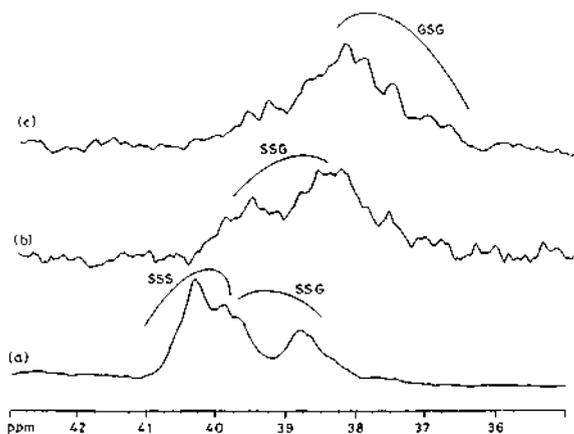
Fig. 3. Expanded ^C-pH} spectrum of G/S showing methine carbon signal of styrene unit of different copolymer composition F_G: (a) 0.29, (b) 0.55, (c) 0.68.

Table 3
The compositional and configurational assignments of the G/S copolymers from 2D-HSQC spectrum

Peak no.	^{13}C (ppm)	^1H (ppm)	Assignments
			$\delta CH_3 P_G$
1	16.5	0.90	GrGrG
2	18.4	1.08	GrGmG
3	18.5	0.64	SGGSS
4	19.8	0.74	SGGSG þ GGGSS
5	21.9	0.73	GGrGSG
6	21.6	0.83	GGmGSG
7	21.0	0.31	SSGSS
8	20.02	0.41	SSrGrSG
9	19.9	0.50	SSrGmSG
10	22.2	0.58	GSGSG
			$\beta(CH_2)_{G+S}$
11	41.5	1.4	SSSS
12	44.0	1.45	SSSG
13	45.58	1.50	GSSG
14.a	46.5	1.27	SSGS
14.b	46.5	1.38	
15.a	47.57	1.48	GSGS
15.b	47.57	1.85	
16.a	49.4	1.71	GSGG
16.b	49.4	1.95	
17	51.5	1.36	SGGS
18	52.0	1.70	SGGG
19	52.6	1.92	GGrGG
20	54.0	1.85	GGmGG

assigned. The expanded methyl region of the G/S copolymer is shown in Fig. 4(a) $(F_G — 0.29)$ and (b) $(F_G — 0.68)$. The methyl group region in the spectra can be divided into three broad envelopes of GGG, GGS and SGS sequences on the basis of change in intensity of

signals with the copolymer composition and by comparing with the methyl region of HSQC NMR spectrum of poly(Glycidylmethacrylate). Each of these triad regions show further splitting. The splitting in GGG triad at $_d16.5/0.90$ ppm, d18.4/1.08 ppm is assigned to GrGrG and GrGmG configurational sequences respectively by comparing with the a-methyl region of HSQC NMR spectrum of poly(Glycidylmethacrylate). Similarly, further three splitting in GGS triad sequence around d18.5/0.64, d19.8/0.74 and d21.7-22.0/0.7-0.9 ppm are assigned to pentad compositional sequences SGGSS, SGGSG and GGGSG respectively. The GSGGG pentad sequence shows splitting into two cross peaks. These cross peaks at d21.8/0.73 and d21.8/0.83 ppm are assigned to GGrGSG and GGmGSG configurational sequences respectively (Fig. 4b). This assignment is done on the basis of observation that these cross peaks do not show relative change in intensity with the copolymer composition and that the meso stereochemical configuration in poly(Glycidylmethacrylate) leads to downfield shift along both carbon and proton axis. In SGS triad sequence, the cross peaks at d21.0/0.31 ppm, d19.5-20.4/0.38-0.62 ppm and d22.2/0.58 ppm are assigned to pentad compositional sequence SSGSS, SSGSG and GSGSG respectively, on the basis of change in intensity of these cross peaks with change in the copolymer composition (Fig. 4a). The GSGSS pentad regions further show two cross peaks. These cross peaks at d20.2/0.41 and d19.9/0.50 ppm are assigned to GSrGrSS and GSrGmSS configurational sequences respectively, on the basis of observation that these cross peaks do not show relative change in intensity with the copolymer composition.

The b-methylene group shows sensitivity to dyads, tetrads etc. The b-methylene region is quite complex and overlapped in both proton and $^{13}Cf^1Hg$ NMR spectra and can be resolved and assigned only with the help of 2D-HSQC NMR spectroscopy (Table 3). The carbon resonance signals can be divided into three broad envelops of SS, SG and GG dyads as shown in Fig. 5(a) $(F_G = 0.29)$ and (b) $(F_G = 0.68)$, in the region of d40.5-46.0, d46.0-50.0 and d50.0-55.0 ppm respectively, on the basis of change in intensity of signals with change in the copolymer composition and by comparing with b-methylene region of HSQC NMR spectra of poly(styrene) and poly(Glycidylmethacrylate). Further splitting within each dyad can be assigned to tetrad compositional sequence on the basis of change in intensity of signal with composition. The three cross peaks in SS dyad at d41.5/1.4 ppm, d44.0/1.45 ppm and d45.58/1.50 ppm are assigned to SSSS, SSSG and GSSG tetrads respectively. Further splitting within SG dyad are assigned to tetrad compositional sequence, each of which shows further splitting into two peaks along proton axis due to inequivalent protons. The cross peaks around d46.5/1.27 ppm and d46.5/1.38 ppm are assigned to
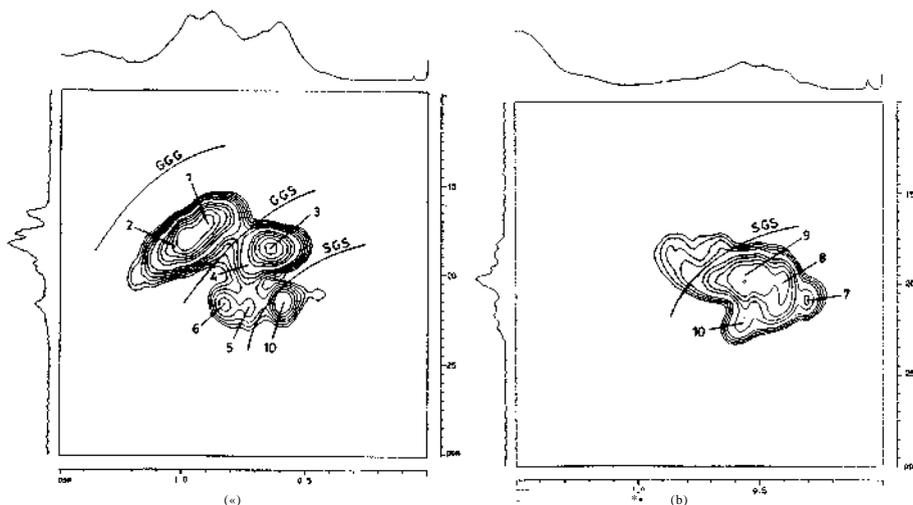
Fig. 4. The expanded 2D-HSQC NMR spectrum showing methyl region of G/S copolymers of composition F_G: (a) 0.29, (b) 0.68.
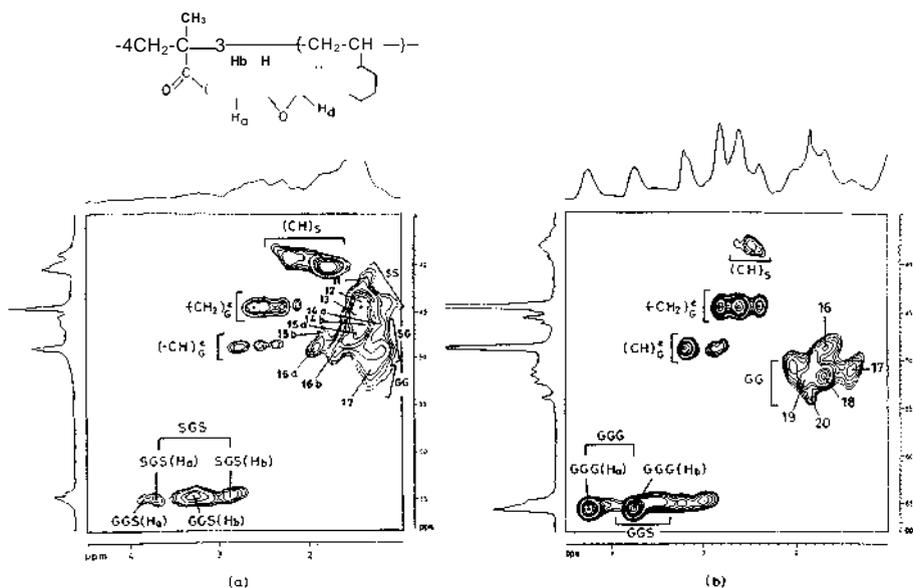

Fig. 5. The expanded 2D-HSQC NMR spectrum showing b-methylene of GMA and styrene unit, epoxymethylene and epoxymethine and -OCH$_2$ region of G/S of different copolymer composition: (a) 0.29, (b) 0.68.

SSGS tetrad and cross peaks at d47.57/1.48 ppm and 47.57/1.85 ppm, d49.4/1.71 ppm and d49.4/1.95 ppm are assigned to SSGG (GSGS) and GSGG tetrad respectively. In the GG dyad region the cross peaks around d51.5/1.36 ppm and d52.0/1.7 ppm are assigned to SGGS and SGGG respectively. The GGGG tetrad sequence further shows sensitivity to tacticity, where the two peaks around d52.6/1.94 and d54.0/1.84 ppm are assigned to GGrGG and GGmGG configurational sequence respectively, by comparing with poly(Glycidylmethacrylate) HSQC NMR spectrum. Further splitting

pattern in these tetrads is quite complex and overlapped and can be due to higher compositional and configurational sequences.

The -OCH$_2$ methylene protons in G/S copolymer show both compositional sensitivity and diastereomerism. The -OCH$_2$ methylene proton signals can be divided into three broad envelopes as shown in Fig. 5(a) and (b). The three envelope are assigned to GGG, GGS and SGS triad compositional sequences, on the basis of change in intensity of signals with change in copolymer composition and by comparing with oxy-methylene

region in HSQC NMR spectrum of poly(Glycidyl-methacrylate). Further each triad sequences shows two peaks for diastereomeric protons. The two diastereomeric protons of GGG triad sequence occur at d4.24 and d3.75 ppm, and of GGS occur at d4.0 and d3.35 ppm and that of SGS triad sequence at d3.72 and d2.9-3.32 ppm.

The epoxy methylene proton region is assigned around d44.7/2.27-2.85 ppm as shown in Fig. 5(a) and (b). These methylene protons show both compositional sensitivity and diastereomerism. The cross peak positions of triad compositional sequence and diastereomeric protons in various compositional sequences are overlapped and cannot be resolved and hence are difficult to assign.

3.3. 2D-TOCSY spectra studies

The proton spectrum with complete assignment is shown in Fig. 6. In order to understand the connectivity between different protons and to confirm the various couplings in the polymer chain, the TOCSY spectrum was recorded. Three bond coupling between the protons of different groups which are directly coupled in the G/S copolymer can be clearly seen in TOCSY experiments in short mixing time (4 ms) as shown in Fig. 7a $(F_G = 0.55)$ (Table 4). The cross peaks at d1.3/1.98 ppm (1) and d1.58/2.34 ppm (2) are due to coupling of -CH unit of styrene in main chain with b-CH_2 protons in SS dyad and SG dyad respectively. The two protons of-$OCH2$ in
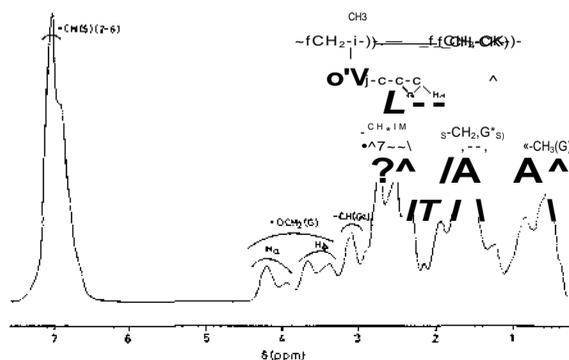
Fig. 6. The ^{1}H NMR spectrum of G/S copolymer $(F_G = 0.55)$ inCDCl$_3$.

GMA unit are diastereomeric and are coupled to each other. The cross peak at d4.22/3.71 ppm (3), d3.99/3.5 ppm (4), d3.8/3.30 ppm (5) are assigned to due to coupling of proton 'a' with 'b' of -OCH_2 unit in GGG, GGS and SGS triad respectively on the basis of change in intensity of peaks with copolymer composition. The cross peak at d3.17/2.58 ppm (6) and d3.17/2.78 ppm (7) are due to coupling of epoxy methine proton with proton 'c' and 'd' of epoxy methylene respectively and that at d3.17/3.77 ppm (8) and d3.17/4.22 ppm (9) is due to coupling with proton 'b' and 'a' of -OCH_2 group respectively. The cross peak at d2.58/2.77 ppm (10) is due to coupling of proton 'c' with proton 'd' of epoxy methylene group. The coupling within the aromatic
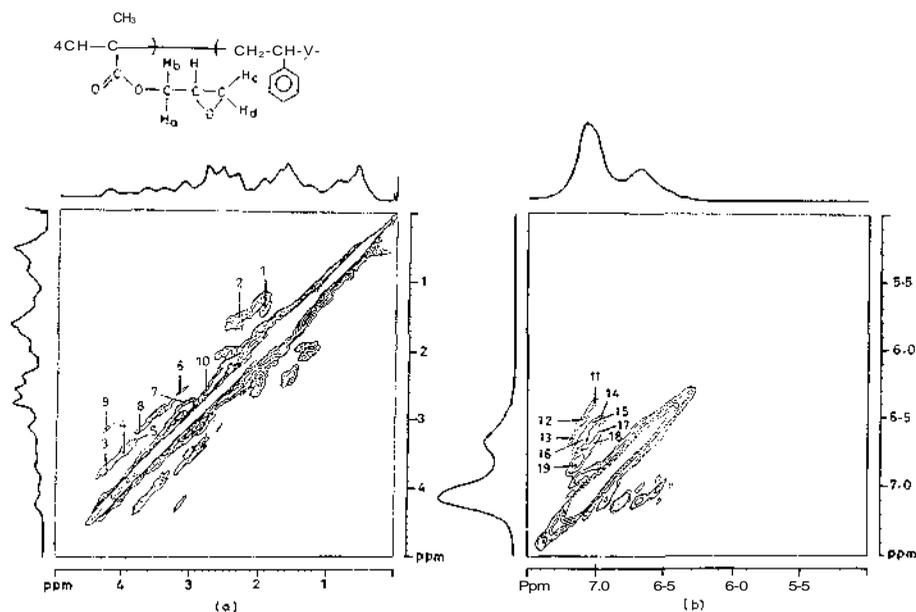

Fig. 7. (a) The 2D-TOCSY NMR spectrum of G/S copolymer $(F_G = 0.55)$ in CDCl$_3$. (b) The expanded aromatic region in 2D-TOCSY NMR spectrum of G/S copolymer $(F_G = 0.29)$ in CDCl$_3$.

Table 4
TOCSY ^{1}H–^{1}H shift correlation

Peak no.	proton (ppm)	Coupled to proton (ppm)
1	1(b-CH$_2$) in SS dyad (1.3)	(CH)$_S$ (1.98)
2	b-CH$_2$ in SG dyad (1.58)	(CH)$_S$ (2.34)
3	Proton 'a' of (OCH$_2$) in GGG triad (4.22)	Proton 'b' of (OCH$_2$) in GGG (3.71)
4	Proton 'a' of (OCH$_2$) in GGS triad (3.99)	Proton 'b' of (OCH$_2$) in GGS triad (3.5)
5	Proton 'a' of (OCH$_2$) in SGS triad (3.8)	Proton 'b' of (OCH$_2$) in SGS triad (3.30)
6	(CH)$_e$ (3.17)	Proton 'c' of (CH$_2$)$_e$ (2.58)
7	(CH)$_e$ (3.17)	Proton 'd' of (CH$_2$)$_e$ (2.78)
8	(CH)$_e$ (3.17)	Proton 'b' of (OCH$_2$) (3.77)
9	(CH)$_e$ (3.17)	Proton 'a' of (OCH$_2$) (4.22)
10	Proton'c' of (CH$_2$)$_e$ (2.58)	Proton 'd' of (CH$_2$)$_e$ (2.78)
	H-2 and H-6 of styrene in	H-3 and H-5 of styrene in
11	SrSrS (6.39)	SrSrS (7.01)
12	SrSmS (6.53)	SrSmS(7.1)
13	SmSmS (6.65)	SmSmS(7.17)
14	SSSGS (6.5)	SSSGS (6.96)
15	SSSGG þ GSSGS(6.56)	SSSGG þ GSSGS(7.02)
16	GSSGG (6.68)	GSSGG (7.11)
17	SGSGS (6.6)	SGSGS (6.97)
18	GGSGS (6.69)	GGSGS (7.01)
19	GGSGG (6.84)	GGSGG (7.13)

proton (^{2}H and ^{6}H with ^{3}H and ^{5}H) of styrene unit is also possible as shown in Fig. 7(b) (F_G = 0.29). It appeared as a multiplet around d6.95-7.21/6.32-7.41 ppm. The multiplet may be assigned to coupling of aromatic protons in different configurational and compositional sequences. The multiplet around d6.99-7.2/6.32-7.41 ppm, d6.95-7.18/6.47-6.78 ppm and d6.96-7.21/6.49-6.92 ppm are assigned to SSS, SSG and GSG triad on the basis of variation in intensity of these signals with change in copolymer composition. In SSS triad the three cross peaks at d6.39/7.01 ppm (11), d6.53/7.1 ppm (12), d6.65/7.17 ppm (13) are assigned to the coupling in SrSrS, SrSmS and SmSmS sequences respectively, by comparing with aromatic region in TOCSY spectrum of poly(styrene). In SSG triad, the three cross peaks around d6.5/6.96 ppm (14), d6.56/7.02 ppm (15) and d6.68/7.11 ppm (16) are assigned to SSSGS, GSSGS and GSSGG pentad compositional sequences respectively, on the basis of change in intensity of the cross peak with change in the copolymer composition. Similarly, the three cross peaks in GSG triad around d6.6/6.97 ppm (17), *d6.69/7.01 ppm* (18) and d6.84/7.13 ppm (19) are assigned to SSGSS, GSGGS and GSGSG pentad respectively.

3.4. 2D-NOESY spectrum studies

The spatial interactions between various groups can be assigned using 2D NOESY NMR spectrum as shown in Fig. 8. There is no spatial interaction between methyl protons of GMA and aromatic ring protons of styrene as is clear from absence of the cross peaks in that region.
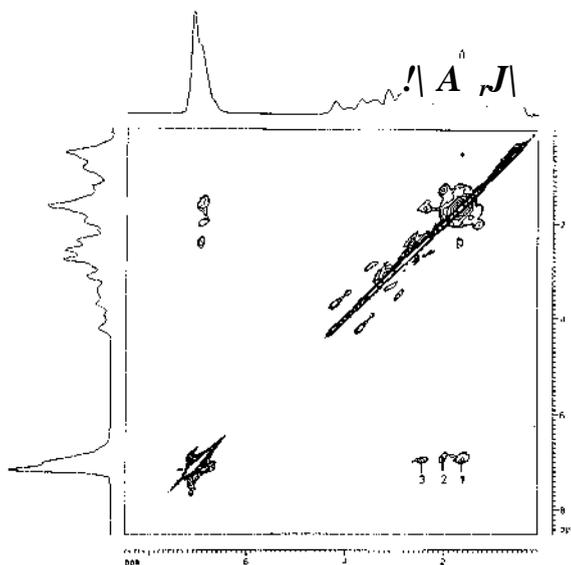

Fig. 8. The 2D-NOESY NMR spectrum of G/S copolymer (F_G = 0.55)inCDCl$_3$.

This shows that there is no tail to tail linkage in G/S copolymer. The cross peak in range d1.5-2.6 ppm is due to spatial interaction between aromatic ring proton of styrene and *b-CH2* unit of styrene and GMA. The cross peaks at d1.6/7.0 ppm (1) and d2.02/6.9 ppm (2) are due to spatial interaction of aromatic ring protons of styrene with b-CH$_2$ proton of SS dyad and SG dyad respectively. The cross peak at d2.40/7.0 ppm (3) is due

to spatial interaction of methine proton and aromatic ring protons.

4. Conclusion

The reactivity ratios of G/S copolymer system are found to be $r_G = 0.60$ and $r_S = 0.48$. Copolymerization mechanism of G/S copolymers was found to follow the first order Markov model. The DEPT and 2D(HSQC, TOCSY) NMR techniques are used to resolve the broad and overlapped signals in ^1H and $^{13}C\{^1H\}$ NMR spectra. Methine carbon resonances are assigned to triad sequences; methyl to pentad sequence and the methylene carbon resonances are assigned to tetrad sequence with the help of 2D-HSQC NMR spectra.

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