

Characterization of Styrene/Methacrylic Acid Copolymers by 2D-NMR Spectroscopy

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ABSTRACT: Styrene/methacrylic acid copolymers were prepared by free-radical photopolymerization using the uranyl nitrate ion as the initiator. The copolymer composition was determined from $^1\text{H-NMR}$ spectroscopy. The comonomer reactivity ratios determined using Kelen Tudos and nonlinear error in variable methods (EVM) are $r_m = 0.61 \pm 0.05$ and $r_s = 0.14 \pm 0.07$. The broad and overlapping $^1\text{H-NMR}$ spectrum was assigned using the help of 2D TOCSY and NOESY experiments. These methods were used to ascertain the various geminal, vicinal, and spatial couplings between the protons. The methyl and methine protons also show configurational and compositional sensitivity. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2444–2453, 2001

Key words: styrene/methacrylic acid copolymer; sequence distribution; configuration; 2D-NMR; microstructure

INTRODUCTION

Bovey and Mirau used a statistical method to assign the sequence distribution of methyl methacrylate–styrene and methyl methacrylate-*co*- α -methyl styrene copolymers by $^1\text{H-NMR}$ data.¹ Ito et al. studied the coisotacticity of methyl methacrylate–styrene, methyl methacrylate-*co*- α -methyl styrene,² and vinylidene chloride–vinyl acetate copolymers by $^1\text{H-NMR}$ spectroscopy. Makushka et al.³ subsequently investigated the copolymerization of a methacrylic acid copolymer and gave valuable information regarding the sequencing and tacticity of monomer units in the polymer chain.

Two-dimensional NMR spectroscopy⁴ has been extensively used to investigate the structure of biological molecules. 2D-heteronuclear NMR

spectroscopy is being frequently used for the study of homopolymers^{6–9} and copolymers.¹⁰ Van Doremaele et al.¹¹ reported the intermolecular structure (triad distribution, tacticity parameter) of methyl acrylate–styrene copolymers using ^1H and ^{13}C experiments. Koinuma et al.^{12,13} interpreted the $^{13}\text{C-NMR}$ spectra of a methyl acrylate–styrene copolymer using a theoretical model. The sequence distribution of the homogeneous styrene/acrylic acid¹⁴ copolymers obtained by low-conversion bulk polymerization was studied by $^1\text{H-}$ and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy. Bruch and Bovey¹⁵ reported proton NOESY to interpret the spectrum of vinylidene–isobutylene copolymers.

In this article, carbon and $^1\text{H-NMR}$ in the 2D mode were used for further exploration of the structure and conformation of styrene–methacrylic acid (S/M) copolymers. The microstructure of the S/M copolymers were investigated by $^1\text{H-}$, $^{13}\text{C}\{^1\text{H}\}$ -NMR, $^1\text{H-}^{13}\text{C}$ heteronuclear shift quantum correlation (HSQC), and homonuclear total correlated spectroscopy (TOCSY). A ^{13}C distortionless enhancement by a polarization transfer (DEPT) spectrum was used

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Table I Copolymer Compositions and Molecular Weight of the S/M Copolymers

Sample No.	Feed Mol Fraction		Copolymer Composition		$\bar{M}_n \times 10^{-5}$ g/mol	$\bar{M}_w \times 10^{-5}$ g/mol
	f_s	f_m	F_s	F_m		
1	0.30	0.70	0.30	0.70	0.51	0.86
2	0.40	0.60	0.35	0.65	0.10	0.25
3	0.50	0.50	0.44	0.56	0.12	0.46
4	0.60	0.40	0.48	0.52	0.11	0.39
5	0.70	0.30	0.50	0.50	0.34	0.67
6	0.75	0.25	0.54	0.46	0.30	0.54
7	0.90	0.10	0.66	0.34	0.20	0.29
8	0.95	0.05	0.76	0.24	0.18	0.25

\bar{M}_n and \bar{M}_w are the number- and weight-average molecular weight of the copolymers.

Table II Triad Fractions Calculated from the NMR Spectra, Harwood Model, and Monte Carlo Simulations in S/M Copolymers

Sample No.	Copolymer Composition F_s	Triads	Triad Fractions		
			a	b	c
1	0.30	SSS	0.02	0.01	0.01
		SSM	0.08	0.10	0.06
		MSM	0.90	0.89	0.93
		MMM	0.35	0.34	0.28
		MMS	0.45	0.49	0.47
		SMS	0.20	0.17	0.25
2	0.44	SSS	0.05	0.02	0.03
		SSM	0.20	0.22	0.18
		MSM	0.77	0.76	0.79
		MMM	0.12	0.14	0.07
		MMS	0.50	0.47	0.40
		SMS	0.38	0.39	0.53
3	0.50	SSS	0.08	0.06	0.10
		SSM	0.32	0.36	0.35
		MSM	0.60	0.58	0.55
		MMM	0.08	0.04	0.02
		MMS	0.32	0.33	0.38
		SMS	0.60	0.63	0.60
4	0.66	SSS	0.35	0.31	0.38
		SSM	0.45	0.49	0.47
		MSM	0.20	0.20	0.15
		MMM	0.05	0.01	0.01
		MMS	0.14	0.12	0.08
		SMS	0.81	0.87	0.91
5	0.76	SSS	0.55	0.52	0.60
		SSM	0.35	0.40	0.37
		MSM	0.10	0.08	0.03
		MMM	0.01	0.00	0.00
		MMS	0.09	0.06	0.05
		SMS	0.90	0.94	0.95

^a Triad fractions obtained from $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the quaternary and carbonyl carbon resonance signals of the S- and M-centered monomeric units.

^b Triad fractions calculated using $r_s = 0.14$ and $r_m = 0.61$ from Harwood's program.

^c Triad fractions calculated from the Monte Carlo calculations.

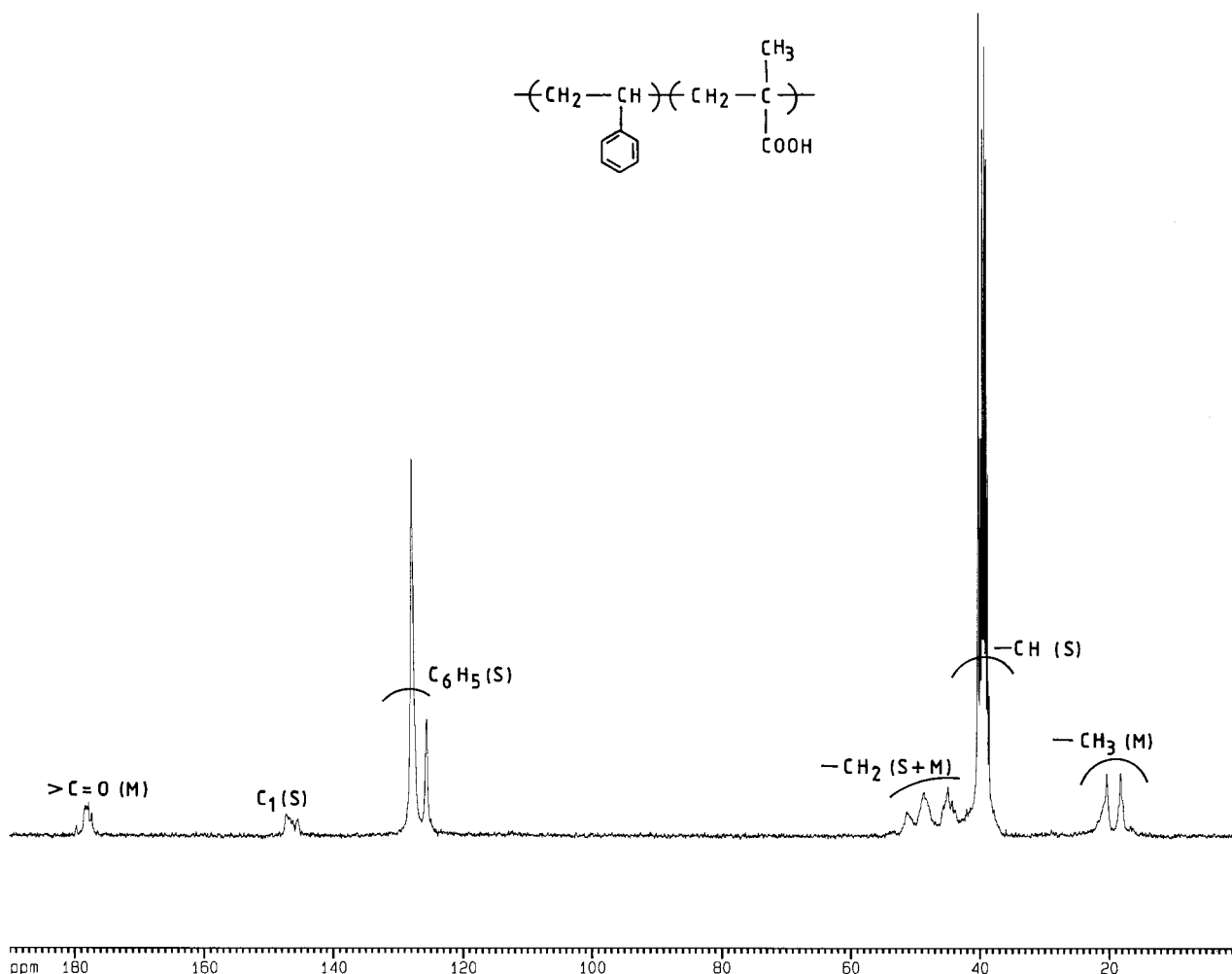


Figure 1 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the S/M copolymer ($F_S = 0.48$) in $\text{DMSO-}d_6$.

to differentiate between the carbon resonance signals of methine and methylene groups. The sequence distribution studies involved the methyl and methylene groups, which influenced, considerably, the microstructure of the copolymers as seen from the NOESY spectra. 2D-NOESY was used to ascertain the various spatial coupling between the protons. Monte Carlo simulations¹⁶ were used to investigate the effect of the degree of polymerization on the triad fractions.

EXPERIMENTAL

The styrene and methacrylic monomers were distilled under reduced pressure and stored below 5°C. The S/M copolymers were prepared by photopolymerization using the uranyl ion as a photo-

initiator.¹⁷ The percent conversion was kept below 10% by precipitating in hexane.

^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR experiments were performed in $\text{DMSO-}d_6$ on a Bruker 300-MHz DPX spectrometer at a frequency of 300.13 and 75.5 MHz, respectively. The ^1H -NMR spectra were recorded using standard pulse sequences given in the Bruker pulse program library. The DEPT measurement were carried out in CDCl_3 using the standard pulse sequences with a J modulation time of 3.7 ms ($J_{\text{CH}} = 135$ Hz) with a 2-s delay time. The 2D- ^1H - ^{13}C -HSQC spectrum was recorded using the standard HSQC pulse sequences,¹⁸ whereas the homonuclear TOCSY experiments were carried out on a Bruker 300-MHz spectrometer using the standard pulse sequences¹⁹ at two mixing times, that is, 4 and 80 ms. The phase-sensitive²⁰ NOESY spectra were

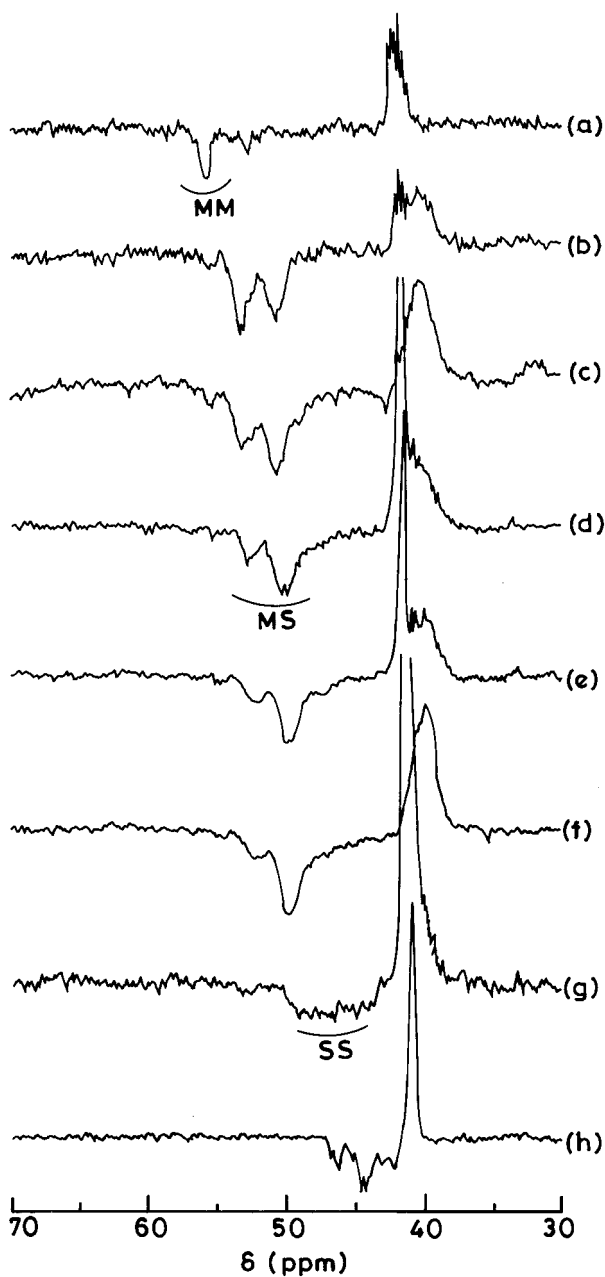


Figure 2 DEPT-135 spectra of S/M copolymer ($F_S =$) with different compositions: (a) PMAC; (b) 0.3; (c) 0.35; (d) 0.44; (e) 0.48; (f) 0.50; (g) 0.66; (h) PS.

recorded with a mixing time of 350 ms. The processed data matrix consisted of 512×512 points covering 5000 Hz in both dimensions.

RESULTS AND DISCUSSION

The feed mol fraction and copolymer compositions are given in the Table I. The copolymer composi-

tions were determined from proton NMR spectroscopy. The values of the reactivity ratios $r_m = 0.61 \pm 0.05$ and $r_s = 0.14 \pm 0.07$ are in good agreement with those reported in the literature.²¹ These values were calculated from the Kelen Tudos (KT) method²² and the nonlinear error in variables method (RREVM). The triad fractions were calculated using the terminal model reactivity ratio from the Harwood Program.²³ These triad fraction values are in good agreement with those determined from NMR as shown in Table II. The area under the resonance signals of the S-centered quaternary and M-centered carbonyl carbon of the S/M copolymers give the concentration of the respective S- and M-centered triads. The overlapping regions in the spectrum were resolved using a nonlinear least-square curve-fitting deconvolution program.

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

The complete assignment of the 75-MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the S/M ($F_S = 0.48$) copolymer in $\text{DMSO}-d_6$ is shown in Figure 1. The carbonyl carbon resonance of the M unit and quaternary carbon resonance signals of the S monomeric unit show the compositional sensitivity; hence, these signals were used for the estimation of M- and S-centered triad concentrations. The triad fractions were determined by measuring the normalized areas under various resonance signals, which were compared with the triad fraction values obtained using the reactivity ratios $r_s = 0.14$ and $r_m = 0.61$ by Harwood's program. By comparing the resonance signals of the carbonyl carbon of poly(methacrylic acid) (PMAC), the MMM triad ap-

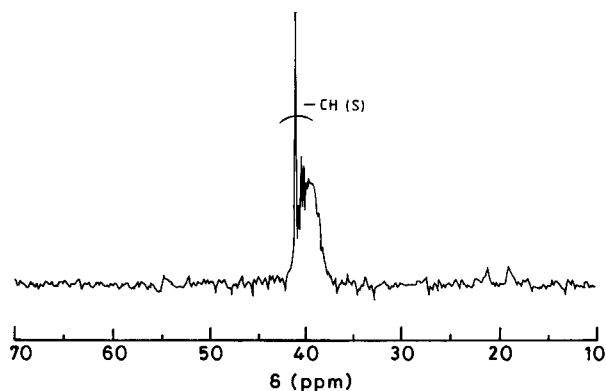


Figure 3 DEPT-90 spectra of S/M copolymer ($F_S = 0.48$) in $\text{DMSO}-d_6$.

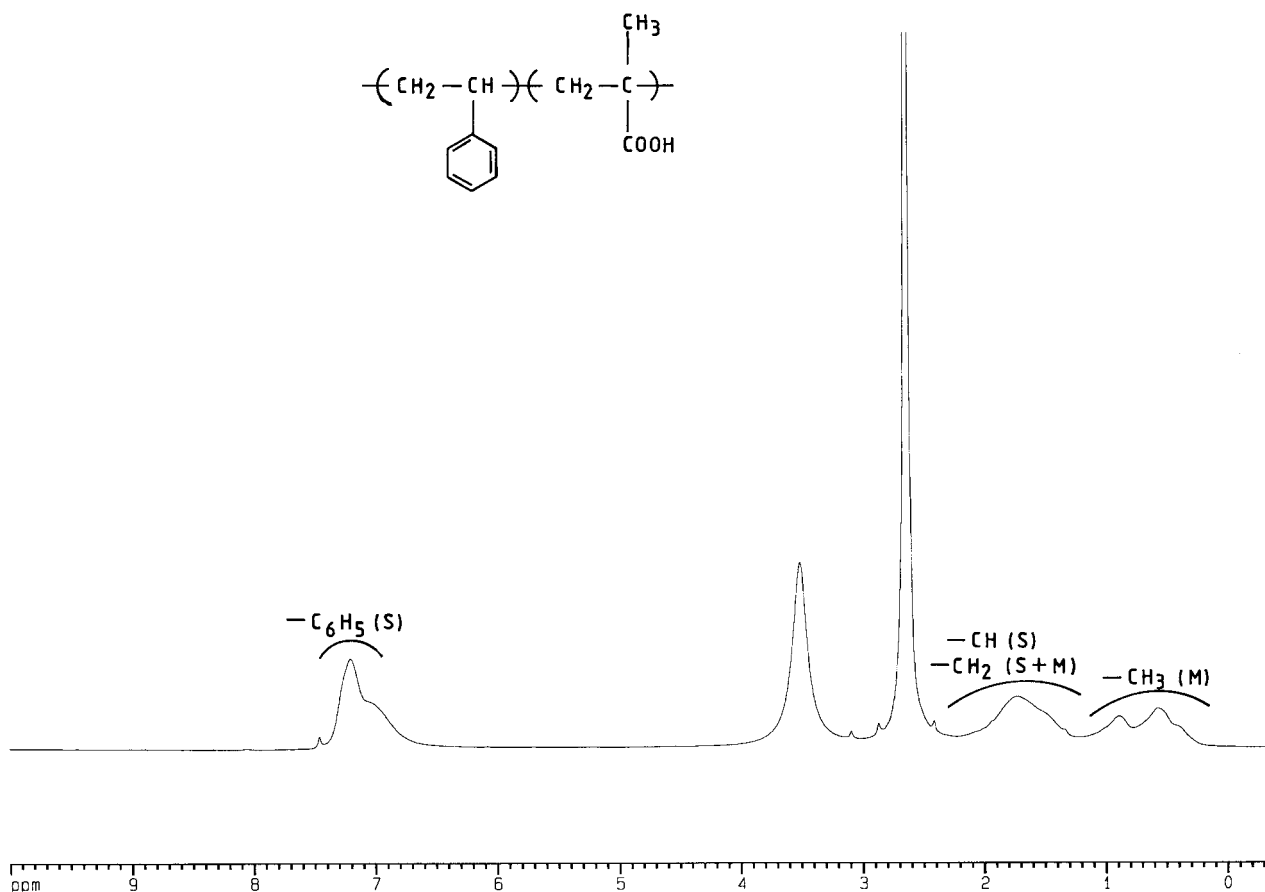


Figure 4 $^1\text{H-NMR}$ spectrum of the S/M copolymer ($F_S = 0.48$) in $\text{DMSO-}d_6$.

pears around $\delta 179$ – 181 ppm, and the MMS and SMS triads, around $\delta 178$ – 179 and $\delta 177$ – 178 ppm. Similarly, the resonance signals of quaternary carbon of the phenyl group of styrene at $\delta 145$ – 147 , $\delta 147$ – 148 , and $\delta 148$ – 150 ppm were assigned to the SSS, SSM, and MSM triads, respectively. The methylene carbon resonance signals in the region $\delta 42$ – 47 ppm increases with increase in the styrene content and it was assigned to the SS dyad. The resonance signal around $\delta 47$ – 50 ppm was assigned to the MS dyad. The resonance signal from $\delta 50$ – 53 ppm was compared with PMAC, and it was assigned to MM dyads. The resonance signals of phenyl carbon of the S unit appear as a multiplet around $\delta 124$ – 128 ppm.

The methylene carbon of the S/M copolymer unit resonances from $\delta 42$ – 55 ppm was resolved by employing DEPT and HSQC experiments. Figures 2(a–h) and 3 show the DEPT-135 and DEPT-90 spectra of the aliphatic methylene and methine carbon regions of the copolymers. The methine carbon resonances are in a positive phase and the methyl-

ene carbon resonances are in a negative phase. The methylene carbons show the resonance signals from $\delta 41$ – 55 ppm. This can be resolved by the HSQC experiments. On the basis of the variations in the compositions of the copolymer and on comparison with the homopolymers, the methylene carbon signals of SS dyads and the methine carbon signals of the styrene units show overlapped signals in the region $\delta 41$ – 48 ppm.

2D-NMR Studies

The $^1\text{H-NMR}$ spectrum of the S/M copolymer is shown in Figure 4. The methylene and methine of the copolymers overlap around $\delta 1$ – 2.4 ppm and the resonance of the methyl protons show a multiplet around $\delta 0.2$ – 1.0 ppm, whereas the aromatic protons of the styrene resonate as multiplet from $\delta 6.2$ – 7.6 ppm. The overlap between methine and methylene can be resolved by the $^1\text{H-}^{13}\text{C-HSQC}$ experiment, which shows protons attached directly to the carbon connectivity. The HSQC spec-

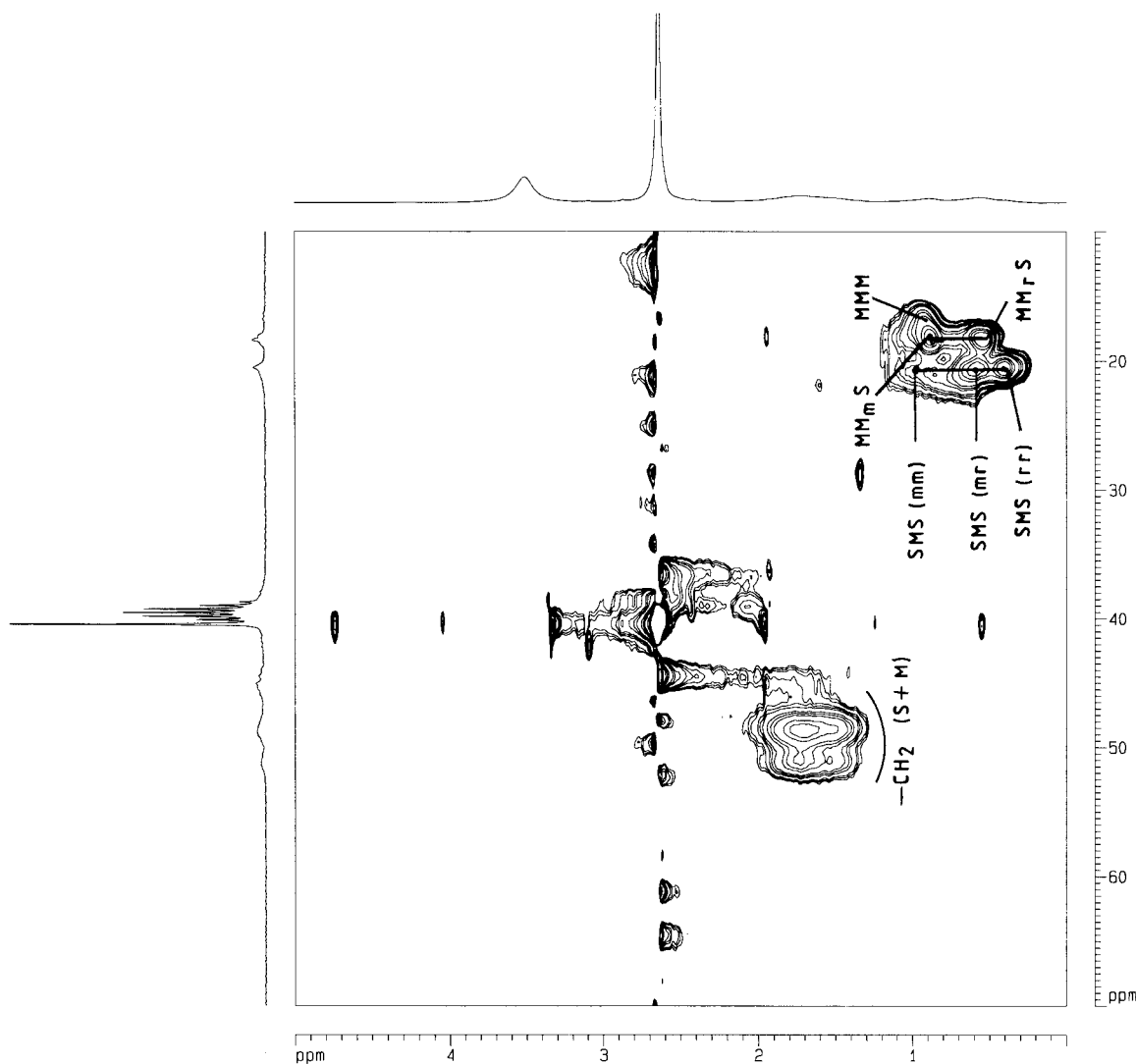


Figure 5 2D-HSQC-NMR spectrum showing the methyl, methylene, and methine resonances of the S/M copolymer with composition ($F_S = 0.48$) in $\text{DMSO-}d_6$.

trum of the copolymer in $\text{DMSO-}d_6$ is shown in Figure 5.

The $^1\text{H-NMR}$ spectrum of the methyl region shows a triplet which varies with the composition, and the methyl carbon resonances of the M-centered unit in the copolymer split into multiplets $^{13}\text{C}\{^1\text{H}\}$ around $\delta 17\text{--}23/0.3\text{--}1.2$ ppm. In the HSQC spectrum, the two intense contours at $\delta 18.5/0.6$ and $\delta 18.5/1.0$ ppm are assigned to MMS triads, which are sensitive to configurational sequences due to magnetic nonequivalent protons, which do not vary with the composition and are further assigned to MM_rS and MM_mS triads, respectively. The contour at $16/1.10$ ppm is assigned to the MMM triad. The SMS triad shows three con-

tours at $\delta 21/1.97$, $\delta 21/1.55$, and $\delta 21/1.40$ ppm, which are assigned to configurational SmMmS , SmMrS , and SrMrS triads, respectively.

The methylene carbons in the copolymers are sensitive to the compositional sequences. The resonance signal of the methylene carbons are assigned to three dyads around $\delta 51/1.30\text{--}1.85$, $\delta 48.0\text{--}50/1.3\text{--}1.6$, and $\delta 45\text{--}47/1.3\text{--}1.8$ ppm to MM, MS, and SS dyads, respectively.

The TOCSY spectra of the S/M copolymer is shown in Figure 6. Only a few crosspeaks were observed in the TOCSY spectrum—those of the MSM (mm) (1) triad: Methine proton couples with two nonequivalent methylene protons, giving two crosspeaks at $\delta 2.41/1.38$ and $\delta 2.43/1.45$ ppm.

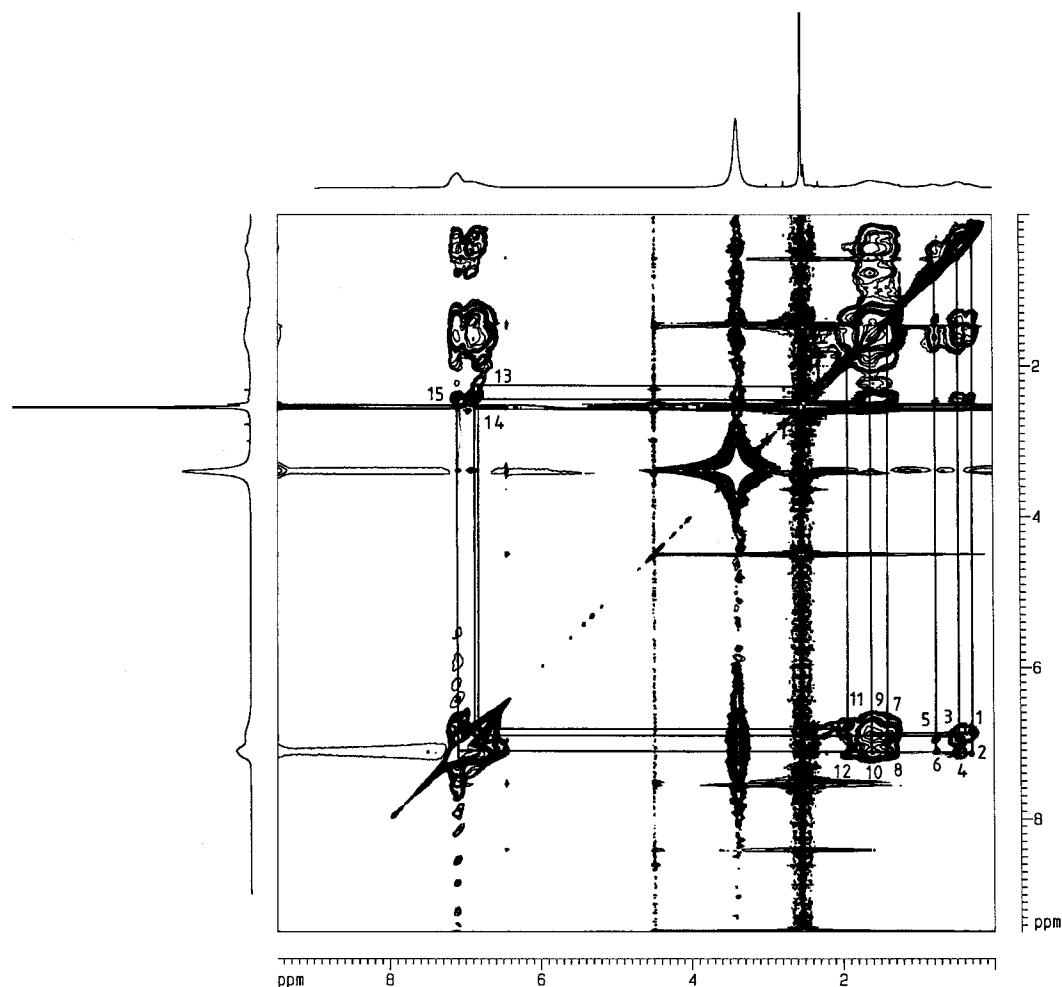


Figure 6 NOESY spectra of the S/M copolymer at 350 ms with the composition ($F_M = 0.48$) in $\text{DMSO-}d_6$.

Similarly, the MmSrM (2) triad couples with the other two protons in the mesoracemic position, giving rise to two crosspeaks at $\delta 2.42/1.69$ and $\delta 2.4/1.65$ ppm, respectively. The crosspeaks at $\delta 2.19/1.25$ and $\delta 2.27/1.24$ ppm are due to non-equivalent protons of the SS dyad and are assigned as the SmSmM (3) triad.

The methine proton of the S unit couples with two methylene protons of the SM dyad, giving a crosspeak at $\delta 2.28/1.52$ ppm, which are assigned as SSM (rr) (4) triads. Two crosspeaks at $\delta 1.92/1.32$ and $\delta 1.98/1.25$ ppm are assigned to the SSS (5) triads due to coupling between the methylene protons of the SS dyad on either side. The geminal coupling between the methylene protons in the MmM (6) dyads are observed at $\delta 1.75/1.45$ ppm. The dyad MS shows geminal coupling at $\delta 1.68/1.85$ and $\delta 1.9/1.68$ ppm to SMSS and MMSM (7)

tetrads. The TOCSY spectra at low or high ms shows that the 1,2 geminal coupling between the methylene protons is possible.

The 300-MHz proton NOESY spectrum of the S/M copolymers is shown in Figures 6 and 7b. In the methyl proton region, three principal resonances are assigned to compositional SMS, MMS, and MMM sequences in the order of increased shielding or decreasing chemical shifts. The MMM triad in the methyl proton resonance does not contribute any interactions with the phenyl group of the styrene unit. The close proximity of the methyl protons to the faces of the phenyl groups in the SrMrS and SmMrS triads are indicated by the relatively strong crosspeaks between the methyl protons (which is pentad-sensitive) and the phenylic protons. Only the syndiotactic (rr) and heterotactic (mr) of the SMS and MMS

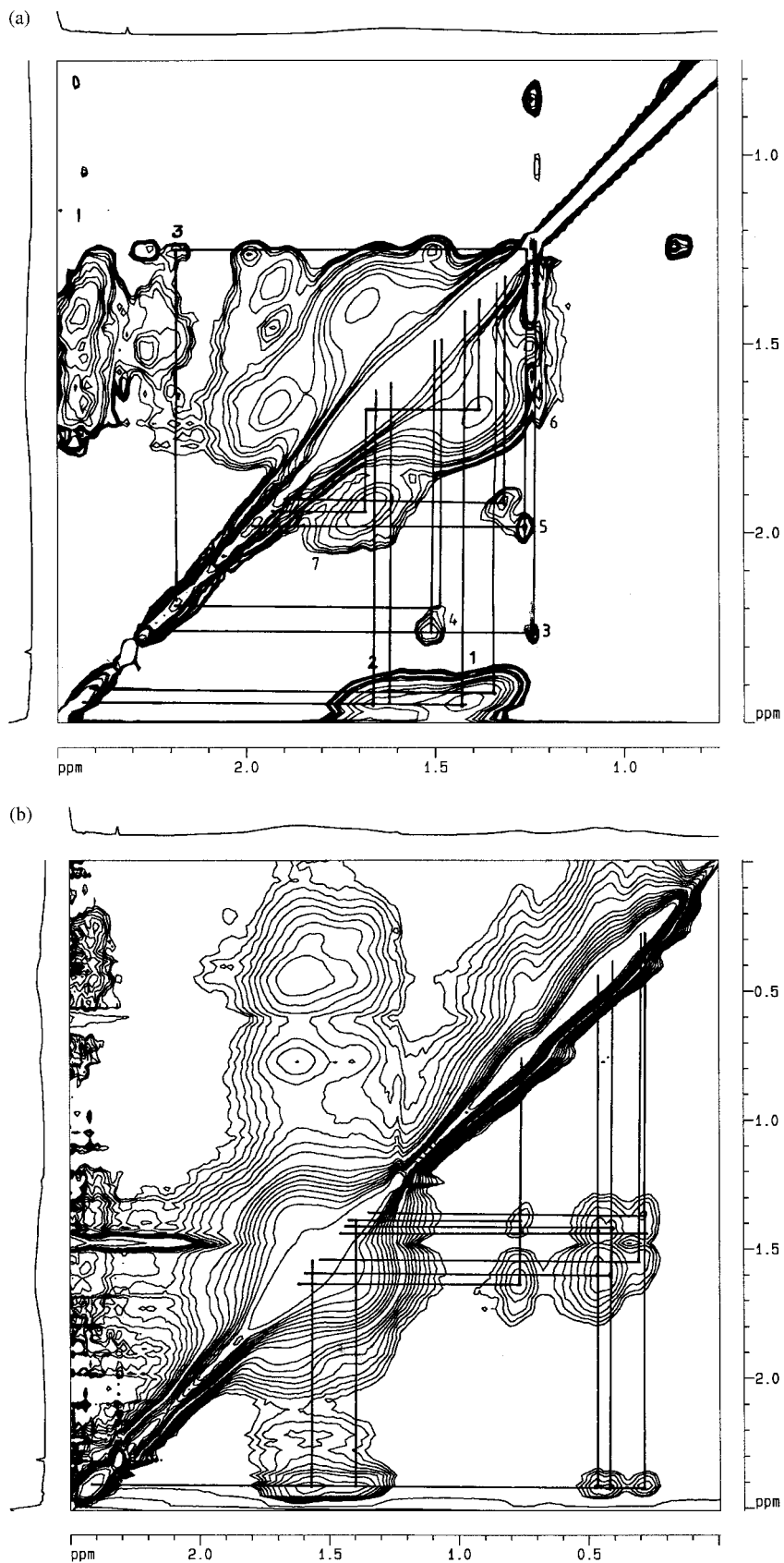


Figure 7 2D TOCSY (a) and 2D-NOESY spectra of the S/M copolymer in DMSO- d_6 ($F_S = 0.48$).

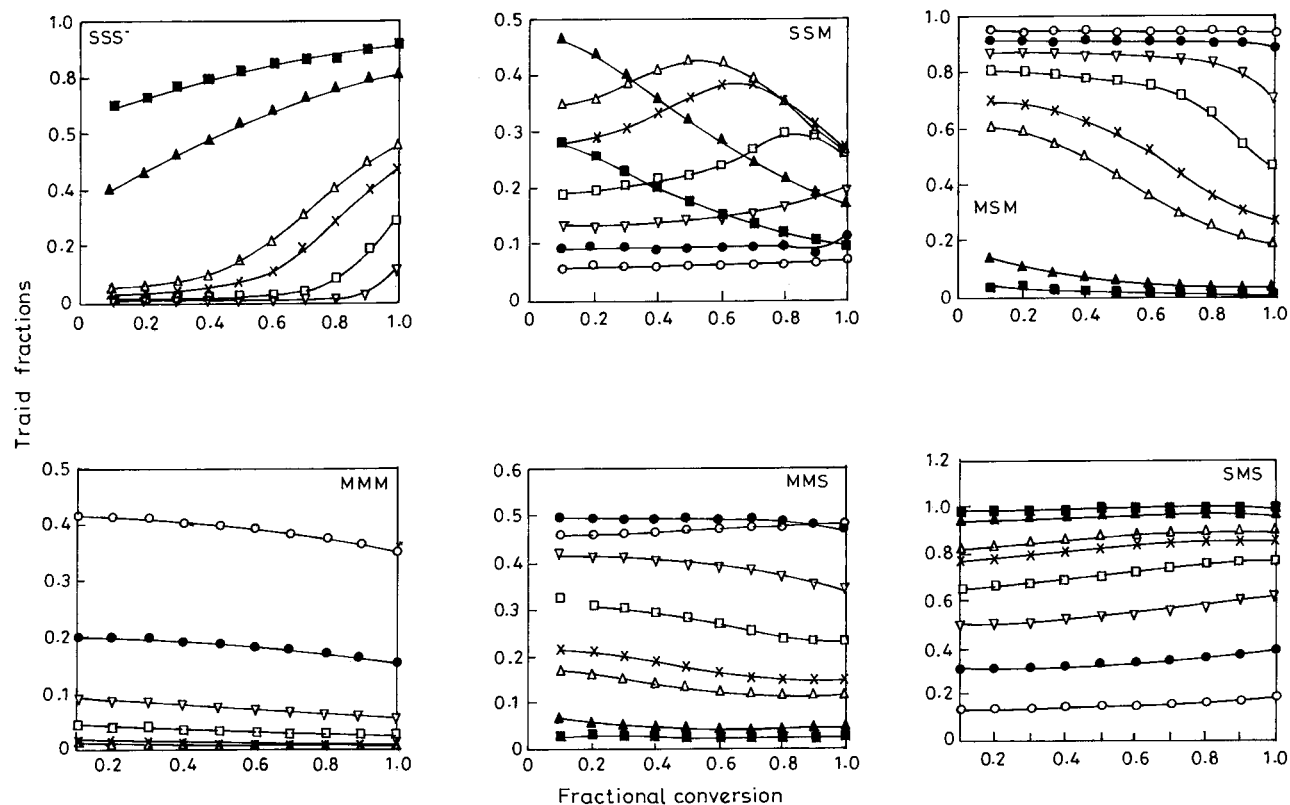


Figure 8 Variation of S- and M-centered triad fractions plotted as a function of fractional conversion for different feed mol fractions: (○) $f_s = 0.3$; (●) $f_s = 0.4$; (▽) $f_s = 0.5$; (□) $f_s = 0.6$; (×) $f_s = 0.70$; (△) $f_s = 0.75$; (▲) $f_s = 0.90$; and (■) $f_s = 0.95$.

triads show the strongest crosspeaks. The heterotactic (mr) triads of the methyl resonances show weaker but observable crosspeaks, while the isotactic SMS (mm) triad exhibits no resonance interaction. So, the crosspeaks observed at $\delta 0.28/6.9$ and $\delta 0.3/7.15$ ppm are configurational pentad-sensitive. These are assigned to the SSMSS (rr) (1) and SSMSM (mr) (2) pentads, respectively. Similarly, the crosspeaks observed at $\delta 0.48/7.16$, $\delta 0.45/7$, $\delta 0.75/6.95$, and $\delta 0.77/7.2$ ppm are due to configurational MMS triads, that is, SMMSS (rr) (3), MMMSS (rr) (4), SMMSM (rr) (5), and MMMSM (rr) (6) pentads, respectively.

The various spatial couplings between the methylene protons with phenylic protons are assigned to various tetrads. The spatial coupling between the methylene dyads SS and MS with the phenylic protons was observed and it was assigned to SSrSS (7), SSrSM (8), and MSrSM (9) tetrads for the coupling with SS at $\delta 1.4/6.88$, $\delta 1.45/7.1$, and $\delta 1.58/7.15$ ppm, respectively. The SMmSS (10), SMmSM (11), and MMmSM (12) tetrads for the spatial coupling of the MS dyad

with styrene protons at $\delta 1.6/6.92$, $\delta 1.85/7.2$, and $\delta 1.9/6.8$ ppm were assigned. The dyad MM cannot have any crosspeak with phenylic protons, that is, it is evident from the NOESY spectra. The methine proton has spatial coupling with the *ortho* protons of styrene and only compositional SSM and SSS triads can have spatial coupling with the protons of styrene by observing the crosspeaks at $\delta 2.3/6.7$, $\delta 2.45/6.9$, and $\delta 2.45/7.1$ ppm compared to the SrSrS (13), MmSrS (14), and MrSrS (15) triads.

It was observed that the α -methyl resonance exhibits NOE crosspeaks to the region of the methine of the styrene unit through methylene protons. The styrene provides significant information concerning through space interaction, that is, the average internuclear distance of these protons both with the geminal protons and between the neighboring methylene protons [Fig. 7(b)].

Monte Carlo Simulation Studies

In Figure 8, the SSS triad fraction increases with increase in the fractional conversion, whereas the

MSM triad fraction decreases with increase in the fractional conversion. Because the reactivity ratio of the M unit is higher and will be consumed first and at higher conversion, there shall be an excess of SSS. The SSM triad shows a maxima shift toward higher conversion as the feed mol fraction of styrene f_s decreases. The MMM and MSM triad fractions decrease with increase in the degree of conversion. This is so because, with the reactivity ratio of the M unit being very high, it is consumed faster than is the S unit. The SMS and MMS triad fractions remain constant with increase in the conversion.

CONCLUSIONS

The microstructure and monomer sequence distribution of S/M copolymers were investigated. The triad fractions determined for various S- and M-centered triads change with the degree of conversion. With the help of TOCSY and HSQC NMR spectra, the compositional and configurational assignments were assigned for the copolymers. The complex ^1H -NMR spectrum was assigned up to triad, tetrad, and pentad sequences. The HSQC spectrum predicted the possibilities of the inequivalent methylene protons and was confirmed by the geminal couplings observed in the TOCSY spectrum. The 2D-heteronuclear ^1H - ^{13}C -NMR spectra gave correct comonomer sequence assignments for the ^1H -NMR spectra of the copolymers. The homonuclear 2D-NOESY NMR spectrum suggested the various structural assignments of the polymer chains for the copolymer. The new assignments are supported by close agreement between the theoretical triad distributions calculated for the various copolymer compositions and those experimentally observed.

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