Detailed microstructural analysis of styrene–methacrylonitrile copolymers by ^{13}C n.m.r. spectroscopy

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The microstructures of both random and alternating copolymers of styrene and methacrylonitrile were investigated by high field ^{13}C n.m.r. spectroscopy. N.m.r. analysis of random copolymers provided information pertaining to different modes of comonomer placements along the chain. Information about the stereochemical aspects of comonomer placements (co-tacticity) was derived from the spectra of alternating copolymers. These results provided valuable information regarding the chain microstructures and the copolymerization mechanism.

(Keywords: styrene–methacrylonitrile copolymers; ^{13}C n.m.r.; microstructural analysis)

INTRODUCTION

High resolution n.m.r. technique has been proven to be an effective tool for elucidating microstructural features of synthetic polymers[1,2]. Noise decoupled ^{13}C n.m.r. technique, particularly at high magnetic field, owing to large chemical shift dispersion and being free from undesired spin–spin couplings is the method of current interest[3,4]. For vinyl copolymers, n.m.r. studies provide valuable information on the mode of arrangements of different comonomeric units along the polymer chain (comonomer sequence) and the stereochemistry of the placement of these units along the polymer chain (cotacticity). Since the overall physicomechanical properties of the copolymers are dependent on these structural features, the investigation of their microstructures is of fundamental interest. Amongst the large number of copolymer systems investigated, greater attention has been paid to styrene–methylmethacrylate and styrene–acrylonitrile copolymers for microstructure analysis[5–12]. Whereas intensive ^{1}H and ^{13}C n.m.r. studies have been pursued for these copolymer systems surprisingly little information is available on another closely related copolymer system, namely styrene–methacrylonitrile (Sty–MAN) copolymer, except for a few ^{1}H n.m.r. studies by Harwood *et al.*[13–15].

Therefore, we intended to pursue a systematic investigation of the microstructural features of this interesting copolymer system. Our study comprises the structural analyses of both random and alternate copolymers based on these monomers. While the former provides information on the comonomer sequence distribution pattern along the polymer chain, the latter serves as an interesting system for analysing the stereochemical aspects of the arrangement of the comonomer units along the polymer backbone. By carrying out the n.m.r. measurements at higher magnetic fields (75 MHz for ^{13}C nuclei), it became possible to obtain highly resolved resonance lines which were conveniently utilized for structural analysis.

EXPERIMENTAL

Materials

Monomers: Styrene and methacrylonitrile were of reagent grade and obtained from Fluka AG. They were dried over calcium hydride prior to distillation. The monomers were further purified by fractional distillation under reduced pressure in an atmosphere of nitrogen immediately before use.

Solvents: All the solvents were of reagent grade and were purified by standard procedures. The polymerization solvent toluene was refluxed over sodium and was fractionally distilled under nitrogen.

Initiator and complexing agents: 2,2′-azobis isobutyronitrile (AIBN) obtained from Fluka AG was recrystallized from ethanol. Ethylaluminium sesquichloride (analytical grade) obtained from Aldrich Chemie was used as received.

Copolymerization

Random copolymerization; This was carried out at 60°C by taking predetermined amounts of the comonomers using toluene as the solvent (1:1 v/v) and AIBN as the free radical initiator (1% w/w). The conversion of the monomers to copolymers was restricted to below 10% and the polymers were isolated in pure form by repeated

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dissolution and reprecipitation from chloroform and methanol, respectively. The samples were finally dried at 60°C under vacuum to constant weight.

Alternating copolymerization: The copolymers were synthesized in toluene using ethyl aluminium sesquichloride as complexing agent without AIBN or irradiation, following the procedure of Hirai *et al.*[36] used for styrene–methyl methacrylate copolymers. Three sets of copolymerizations were carried out using different mole ratios of comonomers and the amount of the complexing agent used was always 50 mol% relative to the MAN monomer. The conversion of monomers to polymers was always restricted to lie between 5–10%.

N.m.r. measurements

N.m.r. spectra (300 MHz ^{1}H and 75 MHz ^{13}C) were recorded using Varian VXR-300 spectrometer. The samples were analysed as 10–15% (w/v) solution in $CDCl_3$ at 60°C using TMS as the internal standard. Noise decoupled ^{13}C n.m.r. spectra were obtained using the WALTZ decoupling procedure and the spectra were recorded after accumulating 40 000 to 50 000 transients.

RESULTS AND DISCUSSION

Styrene–methacrylonitrile random copolymers

The copolymers were prepared by free radical initiation in a toluene medium. The composition of the copolymers was determined by ^{1}H n.m.r. and elemental analysis. The results obtained with both the methods are in close agreement and are summarized in *Table 1*.

A typical ^{13}C n.m.r. spectrum of a copolymer sample of poly(styrene-co-methacrylonitrile) is presented in *Figure 1*. Assignment of the different signals due to various carbon atoms of the constituting comonomer units of the copolymer was pursued using off resonance decoupling experiments and by comparison with the spectra of the corresponding homopolymers.

Examination of the spectra reveals several multiple lines for various carbon atoms suggesting their sensitivity to the structural arrangements of the comonomer units along the polymer chain. Of the different carbon atoms, the fine structures exhibited by the backbone quaternary carbon atom due to MAN units and the methine carbon atom of the styrene units are particularly significant and have been utilized for comonomer sequence analyses.

For the quaternary carbon atom, unlike a single resonance line observed around 32.5 ppm in the homopolymer spectrum of poly(MAN)[16], three distinct signals with further finer structures within themselves were observed in the spectra of the copolymers. This is a clear indication of the sensitivity of this carbon atom to comonomer sequence distributions. Assignments of these peaks under three general regions of chemical shifts to different sequential triads were carried out systematically in the following manner. The peak appearing at approximately 32.5 ppm corresponds to that of poly(MAN) and hence can be assigned to an MMM type triad. Similarly, the resonance lines at approximately 34.5 ppm and 36.0 ppm have been assigned to MMS + SMM and SMS triads, respectively. The terms 'M' and 'S' correspond to MAN and styrene monomer units, respectively.

Table 1 Chemical shift assignment of MAN centred comonomer triads from the backbone quaternary carbon resonance and quantitative analysis of MAN centred triads obtained this carbon resonance

	Mole fraction of MAN in		Chemical shift of different triads^{b,c} (ppm)		
Serial number	initial mixture	copolymer^a	MMM	SSM + MMS	SMS
1	0.82	0.76 (0.78)	32.5 (0.47)	34.4 (0.44)	35.8 (0.09)
2	0.58	0.47 (0.46)	32.7 (0.07)	34.5 (0.45)	35.9 (0.48)
3	0.21	0.12 (0.14)	– –	34.7 (0.11)	36.0 (0.89)

[a] The numbers outside the bracket correspond to ^{1}H n.m.r. based results while those inside are obtained from elemental analysis

[b] The chemical shifts reported correspond to the maximum height of the peaks

[c] The numbers given below the chemical shift values inside the brackets correspond to the relative intensity of the triads

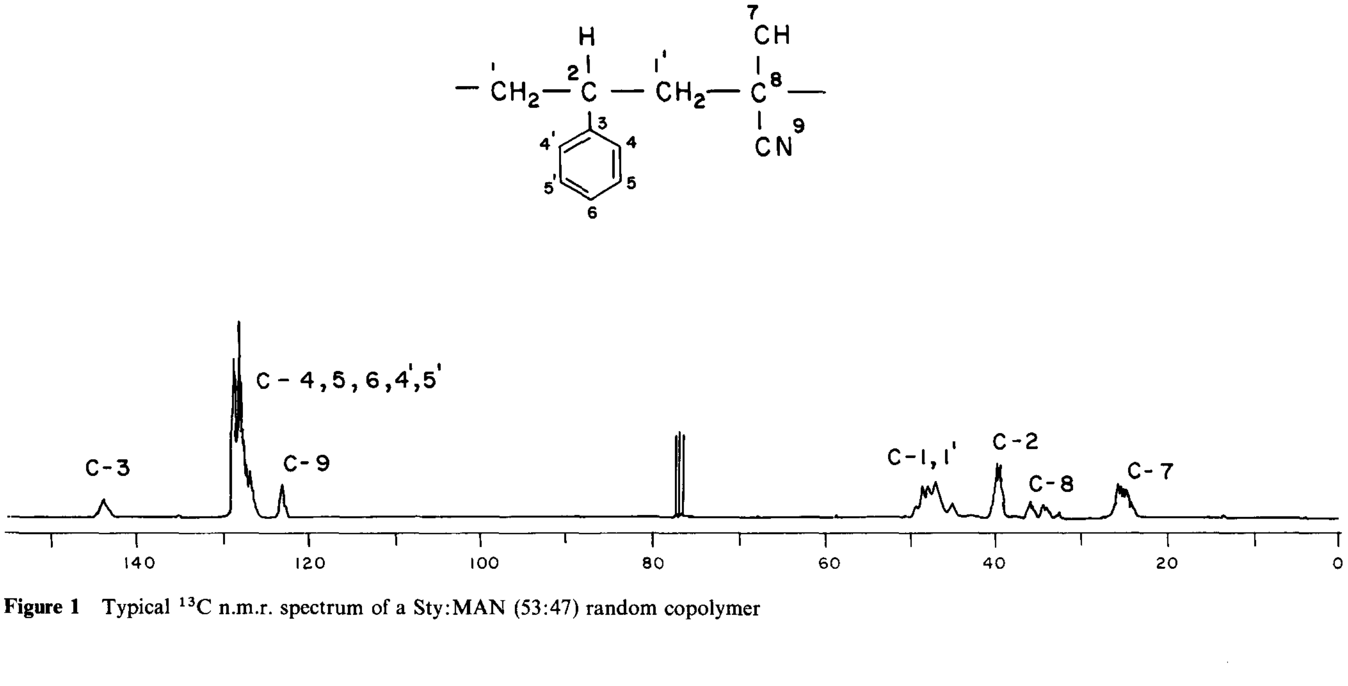

Figure 1 Typical ^{13}C n.m.r. spectrum of a Sty:MAN (53:47) random copolymer

The validity of such assignments is based on the following facts. Firstly, for the copolymers with different monomeric compositions, the relative intensity of signals due to different triads varies in an expected manner. Furthermore, examination of the chemical structures of the three triads suggests that the quaternary carbon atom of the central MAN unit is adjacent to different types of functional groups situated at the γ position in these triad structures. It is well known that the substituents located at γ position with respect to a given carbon atom significantly affect the chemical shift of the later in the upfield direction. The magnitude of this effect is dependent upon the nature of the substituent groups (viz. $-CH_3$, $-CN$, –phenyl as in the present case)[17]. Determination of the chain tacticity of vinyl homopolymers with the help of this γ contribution principle has been successfully carried out by Tonelli[18,19]. Thus, using this principle, the chemical shift values calculated for these triad structures are in close agreement with the experimental results*, thereby attesting the validity of our signal assignments[20].

Following the assignments of different resonance lines to various comonomer sequence triads, quantitative estimation of the occurrence of these triads was pursued. The enlarged spectra due to this quaternary carbon atom for the copolymers of varying compositions are shown in *Figure 2*. Using the signal relative intensities of these resonance lines, quantitative estimation was made and the results are summarized in *Table 1*. Analysis of these data suggests that MAN shows a reduced tendency towards formation of MMM type triad. This could possibly be attributed to relatively low reactivity of the MAN comonomer. These three resonance lines due to different comonomer sequences also show further fine structure splittings, particularly those due to the MMS + SMM and SMS triads. This is indicative of their sensitivity to possible configurational arrangements of the comonomeric units in a given copolymer triad (cotacticity), a phenomenon well studied for styrene–(meth)acrylic ester copolymer systems[21,22].

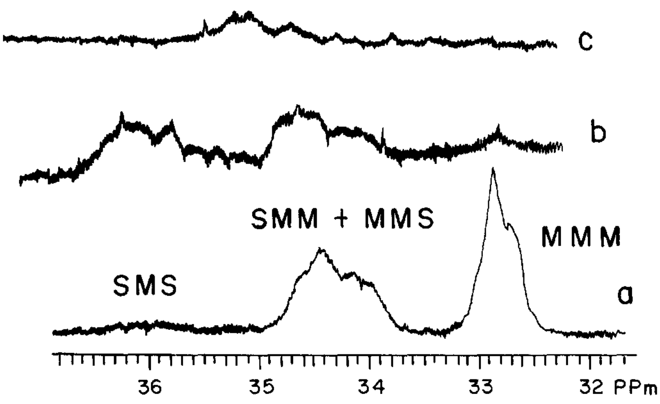

Figure 2 Expanded resonance patterns of the backbone quaternary carbon atoms in Sty:MAN random copolymers: (a) Sty:MAN (24:76); (b) Sty:MAN (53:47); (c) Sty:MAN (88:12)

Table 2 Chemical shift assignments of styrene centred comonomer triads from the backbone methine carbon resonance

Serial number	Mole fraction of styrene in copolymers	Chemical shift of different triads[a,b]		
		SSS	SSM + MSS	MSM
1	0.24	– –	39.9 (0.24)	39.5 (0.76)
2	0.53	40.8 (0.19)	40.0 (0.42)	39.5 (0.39)
3	0.88	40.8 (0.76)	40.1 (0.21)	39.5 (0.03)

[a] The chemical shifts reported correspond to the peak maxima

[b] The numbers given inside brackets below the chemical shift values correspond to the relative intensities of these triads

Relatively broad signal lines and extensive peak overlapping did not permit us to pursue such studies at the present time. On the other hand, the results concerning the stereochemical features of the comonomer arrangements in the alternating copolymer of styrene and MAN are described below.

After obtaining the sequence distribution information about the MAN-centred comonomer triads, we proceeded to analyse styrene-centred comonomer sequence distributions in these copolymers. For this purpose, the resonance lines due to the backbone methine carbon atom belonging to the styrene monomer were employed. This carbon atom resonates over the chemical shift range of 39.0–41.0 ppm and is adequately resolved to three signal lines, thus revealing its sensitivity to comonomer sequence effect at triad level.

On the basis of the variation of signal intensities as a function of copolymer composition as well as with the help of the calculated chemical shifts using ν contributions as described above, we have assigned these three signal lines unambiguously to the three possible triads. The most downfield peak appearing at approximately 41.0 ppm corresponds to the methine carbon resonance of polystyrene[22] and hence can be assigned to be SSS triad. Accordingly, the signals at approximately 40.0 ppm and 39.5 ppm have been ascribed to SSM + MSS and MSM triads, respectively. The information about the chemical shifts of these triads for different copolymer compositions are summarized in *Table 2*.

The expanded spectra of resonance due to methine carbon region for different copolymers are depicted in *Figure 3*. With the help of the peak intensity measurement results for different triads, quantitative estimation of the sequence distribution became possible and the results thus obtained are summarized in *Table 2*. Although somewhat higher reactivity was for styrene monomer is evident due to relatively higher intensity of SSS triad, the copolymerization process appears to be principally random. This implies when the growing chain end and its preceding unit consists of styrene, a MAN unit is preferentially added at the chain end.

In addition to the method for sequence analysis described above, comparison of the experimental and calculated results with the help of the following two approaches further supplements the authenticity of signal assignments to different sequences and their quantitative estimation.

The first approach deals with the comparison of the

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* Our calculations of chemical shifts on the basis of γ contributions are in fairly close agreement with the experimental results, but they are not exactly equal. This variation is primarily due to the conformation of the polymer chain, which is known to influence the magnitude of γ effect (γ gauche effect). Calculations of conformation based γ contributions are beyond the scope of this paper; nevertheless the approximate calculations serve our purpose quite well.

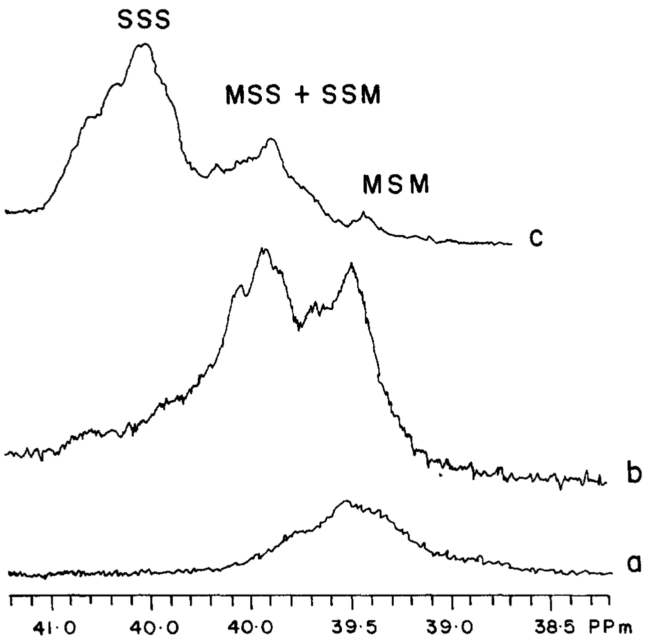

Figure 3 Expanded resonance patterns of backbone methine carbon atom of Sty:MAN random copolymers: (a) Sty:MAN (24:76); (b) Sty:MAN (53:47); (c) Sty:MAN (88:12)

results on copolymer composition obtained experimentally with those calculated using sequence analysis data. For the later purpose, triad results were converted to dyad values which were subsequently used to calculate the comonomeric contents of the copolymers. The appropriate equations used for such purpose are given below[23]:

$$\mathrm{MM} = \mathrm{MMM} + \mathrm{SMM}/2 \qquad (1)$$

$$\mathrm{SS} = \mathrm{SSS} + \mathrm{MSS}/2 \qquad (2)$$

Hence

$$\mathrm{MS} = 1 - \mathrm{MM} - \mathrm{SS} \qquad (3)$$

From these relationships it can be thus deduced that,

$$(\mathrm{S}) = \mathrm{SS} + \mathrm{MS}/2 \qquad (4)$$

$$(\mathrm{M}) = \mathrm{MM} + \mathrm{MS}/2 \qquad (5)$$

The terms (S) and (M), respectively, correspond to the mole fractions of styrene and MAN present in the copolymer. The experimentally determined and theoretically calculated results are summarized in *Table 3* and a close agreement between the two sets of results testifies to the preciseness of this analysis.

The second approach for verifying the validity of this sequence analysis involves the comparison of number average sequence lengths determined using triad analysis data from n.m.r. measurements and those obtained from reactivity ratio data. For the former purpose, use of the following equations gives the required number average sequence length results[24].

$$\bar{N}_1 = (f_{212} + f_{112/2})^{-1} \qquad (6)$$

$$\bar{N}_2 = (m_2/m_1)\bar{N}_1 \qquad (7)$$

The terms $\bar{N}_1$ and $\bar{N}_2$ correspond to the number average sequence lengths for the monomers 1 and 2 constituting the copolymer; f_{111}, f_{112} and f_{212} are the fractions of different triads with monomer 1 as the central unit ($f_{111} + f_{112} + f_{212} = 1$) and m_1 and m_2 are the mole fractions of monomers 1 and 2 in the copolymer.

In order to calculate the number average sequence lengths using the results of monomer reactivity ratio, the following relevant equations are used[25,26].

$$\bar{N}_1 = 1/P_{12} = r_1(M_1)/(M_2) + 1 \qquad (8)$$

$$\bar{N}_2 = 1/P_{21} = r_2(M_2)/(M_1) + 1 \qquad (9)$$

In these equations (M_1) and (M_2) correspond to the mole fractions of the monomers 1 and 2 in the initial reaction mixture; r_1 and r_2 correspond to the reactivity ratio for these two monomers. P_{12} and P_{21} represent the probabilities of cross propagation.

The reactivity ratios calculated for this copolymer system with the help of the YBR method[27] using the copolymer composition data were found to be 0.71 and 0.28 for styrene and MAN, respectively. This relatively higher value of reactivity ratio for styrene in this copolymer can be ascribed to be responsible for observed higher intensity of SSS triads in the n.m.r. spectra of these copolymers. The results on the number average sequence lengths obtained by both of these methods are summarized in *Table 4*. A close agreement among these results is a clear testimony for the accuracy of sequence analysis.

Styrene–methacrylonitrile alternating copolymer

(Meth)acrylic type polar vinyl monomers in the presence of metal halides such as zinc halide or ethyl aluminium sesquichloride undergo alternating copolymerization with electron donating monomers such as styrene[29,30]. A good deal of research has been pursued during the last few years for elucidating the mechanism of this interesting copolymerization process. From several studies it was established that the metal halide Lewis acid critically controls the addition of the comonomer units exclusively in an alternate manner. As a result the relative reactivity ratios for both the monomers become virtually zero. But with regard to the stereochemistry of chain propagation, the metal halide does not seem to have any influence. This implies the stereochemical configuration of such copolymers is atactic, showing no specific preference either for meso or racemic mode of monomer placements during chain propagation[31,32]. Analogous to homopolymers, the stereochemical structures of these copolymers are designated as meso(co-isotactic) or racemic(co-syndiotactic), depending on the arrangements of the polar groups of the (meth)acrylic monomers and the aromatic rings of the styrene monomers are on the same or opposite sides of the polymer backbone[21].

Because the complications due to the copolymer sequence effects are absent in the alternating copolymer, analysis of their stereochemical features (co-tacticity)

Table 3 Quantitative analysis of the observed and calculated copolymer compositions for styrene–MAN copolymers

Serial number	Mole fraction of MAN in the copolymer		Mole fraction of Sty in the copolymer	
	Observed	Calculated	Observed	Calculated
1	0.76	0.78	0.23	0.22
2	0.47	0.45	0.53	0.55
3	0.12	0.10	0.88	0.90

Table 4 Number average sequence lengths in Styrene–MAN random copolymers

Serial number	Mole fraction of styrene in the copolymer	Calculated from ^{13}C n.m.r. sequence results: MAN centred results		Sty centred results		Calculated from reactivity ratio results	
		$\bar{N}_{Sty}$	$\bar{N}_{MAN}$	$\bar{N}_{Sty}$	$\bar{N}_{MAN}$	$\bar{N}_{Sty}$	$\bar{N}_{MAN}$
1	0.24	1.02	3.23	1.14	3.61	1.08	3.50
2	0.53	1.60	1.42	1.66	1.47	1.71	1.28
3	0.88	7.76	1.06	7.41	1.01	7.37	1.03

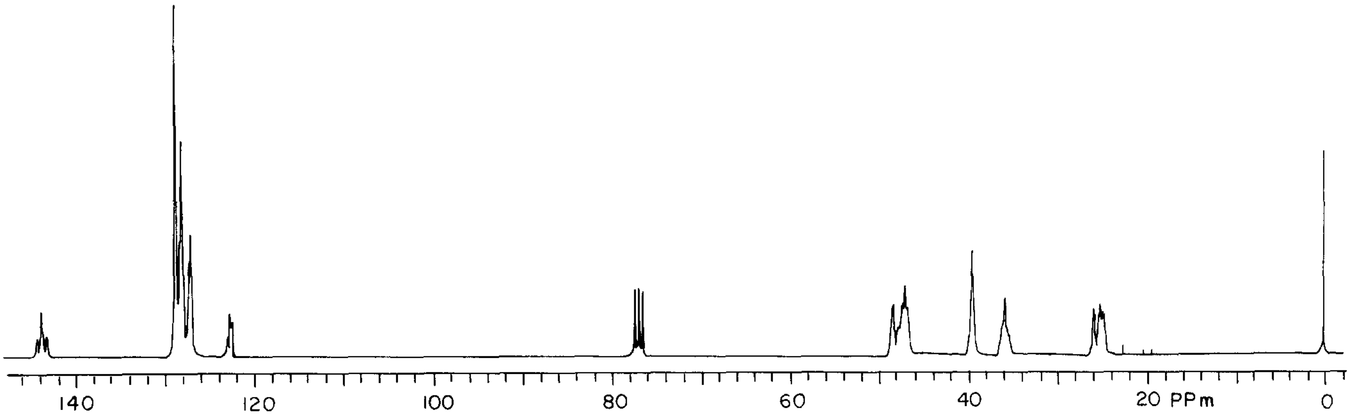

Figure 4 ^{13}C n.m.r. spectrum of alternating Sty:MAN copolymer

becomes relatively easier. Although many reports are available which describe the co-tacticity phenomena of the styrene–methyl methacrylate copolymer[33,34], literature pertaining to such studies with styrene–MAN system is scanty.

Styrene–methacrylonitrile alternating copolymers were successfully synthesized using ethylaluminium sesquichloride as the catalyst. For different initial mole ratios of the comonomers all the copolymers obtained were found to contain equimolar amounts of both the monomers, as is evident from elemental analysis and ^{1}H n.m.r. measurements. This suggests the formation of alternating copolymers under the above experimental conditions. The 75 MHz ^{13}C n.m.r. spectrum of this copolymer is presented in *Figure 4*. Unlike the random copolymer spectra this spectrum is fairly well resolved and shows sharper resonance lines. Upon examination of chemical shifts of different C atoms present in this copolymer, it was found that for the backbone quaternary carbon atom of MAN unit, the two upfield signals due to MMS and MMM sequences present in the random copolymers are completely absent and the chemical shift of the peak present corresponds to that of the SMS triad as described in the previous section. Similarly, methine carbon atom of styrene unit resonates at a chemical shift corresponding to MSM triad. Furthermore, the signals due to MSS and SSS triads in the downfield regions present in the random copolymers are absent. This further manifests the exclusive formation of alternating copolymers. Several carbon atoms of this copolymer show multiple fine structures indicating their sensitivity to chain configuration. Using these results, it has become possible to analyse the configurational features of this copolymer chain to a great extent.

The carbon atoms showing configurational sensitivities include nitrile, methine, methylene, backbone quaternary, α-methyl and aromatic C-1 carbon atoms. While the nitrile and methine carbon atoms reveal their sensitivity to triad type structure, the α-methyl backbone quaternary and aromatic C-1 carbon atoms are visibly sensitive to stereosequence distribution at pentad level. The different signals were assigned to various pentad structures and their intensities were utilized for the quantitative estimation of their frequency of occurrence. The expanded resonance patterns for the nitrile and methine carbon atoms are depicted in *Figure 5* and the results on quantitative analyses are summarized in *Table 5*. For the methine carbon atom, resonating over the

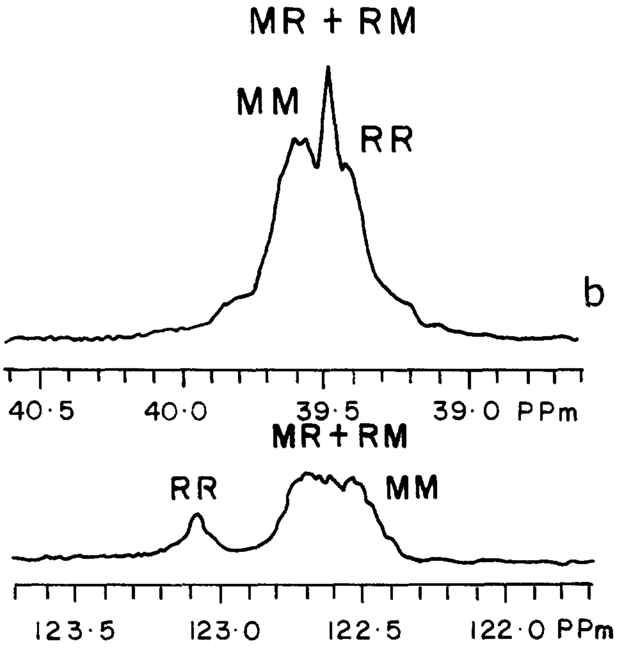

Figure 5 Expanded resonance patterns of (a) nitrile carbon atom and (b) backbone methine carbon atom in Sty:MAN alternating copolymer

Table 5 Triad type co-tacticities analyses of styrene–MAN alternating copolymers from nitrile (MAN centred) and backbone methine (styrene centred) carbon resonances

	MAN centred triads from nitrile carbon atom resonance				Styrene centred triads from methine carbon atom resonance			
			Relative intensity				Relative intensity	
Types of triads	Peak number	Chemical shift in ppm	Observed	Calculated[a]	Peak number	Chemical shift in ppm	Observed	Calculated[b]
mm	1	122.50	0.33	0.32	3	39.65	0.19	0.17
mr + rm	2	122.70	0.51	0.49	2	39.50	0.46	0.48
rr	3	123.10	0.16	0.18	1	39.40	0.35	0.35

[a] Calculated with a value of 0.57
[b] Calculated with a value of 0.59

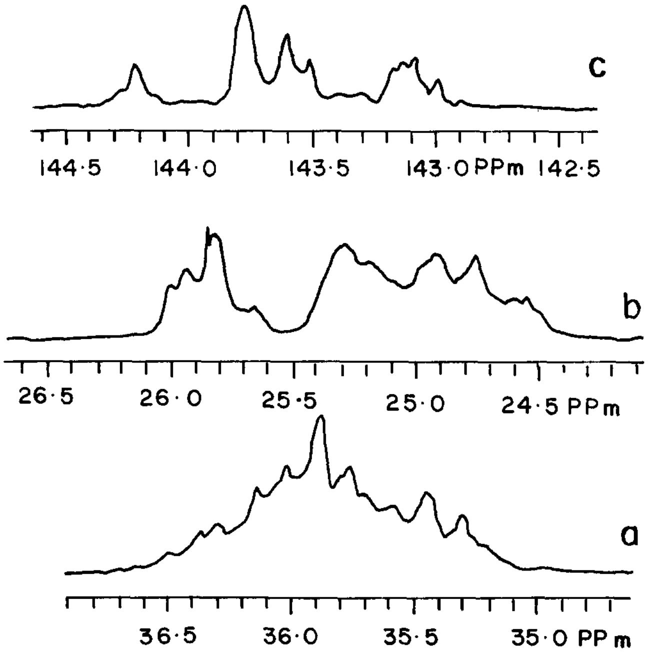

Figure 6 Expanded resonance patterns of (a) backbone quaternary carbon atom, (b) methyl carbon atom and (c) aromatic C-1 carbon atoms in Sty:MAN alternating copolymer

chemical shift range of 39.1–39.9 ppm, the three signals have been assigned to co-isotactic, co-heterotactic and co-syndiotactic triads with increasing order of field strength. The nitrile carbon atom shows three resonance lines in the range of 122.3–123.2 ppm, and these three signals have been assigned to co-isotactic, co-heterotactic and co-syndiotactic triads in the opposite manner to the previous case with respect to field strength. The relative intensity ratios of these lines suggests a non-selective tendency towards stereocontrol of monomer placement during chain growth and thus a Bernoullian type chain growth was evident. This is further supported by a single value in both the cases, which corresponds to the probability of a chain-end bearing styrene unit adding to a MAN unit and vice versa[22]. Relatively higher co-isotacticity may be attributed to a possible dipolar interaction between the aromatic ring and the nitrile groups during chain growth.

After the determination of above mentioned co-tacticity triad analysis, the resonance patterns of α-methyl, backbone quaternary and aromatic C-1 carbon atoms were utilized for further analyses of stereochemical features of this alternating copolymer. Large number of signals observed under each of these carbon atoms have been conveniently utilized for analysing the chain configurations at pentad level. The expanded resonance patterns for these three carbon atoms are shown in *Figure 6*. The results on the quantitative estimation of cotacticity distributions obtained by measurements of peak intensities are summarized in *Tables 6–8*. For the backbone quaternary carbon atom and aromatic C-1 carbon atom, the resonance lines corresponding to co-syndiotactic and co-isotactic pentads appear below the closely analogous system of styrene–methyl methacrylate copolymer, as reported by Hirai *et al.*[33]. For the α-methyl carbon atom, this trend seems to occur in a reverse manner with respect to field strength. This is obvious from the fact that, when the α-methyl group lies in the same side as aromatic ring, the nitrile group lies on the opposite side, which corresponds to the cosyndiotactic type monomer placement.

The legitimacy of our assignments of signals to different types of pentad structures is based on the following

Table 6 MAN centred pentad level co-tacticity analyses of styrene–MAN alternating copolymers from backbone quaternary carbon atom resonance

Peak number	Types of pentads	Chemical shift in ppm	Relative intensities
1	mmmr	35.30	0.067
2	mmmm	35.45	0.099
3	rmmr	35.60	0.086
4	mmrm	35.70	0.097
5	mmrr	35.76	0.141
6	rmrm	35.88	0.208
7	mrrr	36.00	0.135
8	rrmr	36.14	0.083
9	mrrr	36.28	0.047
10	rrrr	36.38	0.034

Table 7 MAN centred pentad level co-tacticity analyses of styrene–MAN alternating copolymers from methyl carbon atom resonance

Peak number	Types of pentads	Chemical shift in ppm	Relative intensities
1	rrmr	24.54	0.037
2	mrrm	24.60	0.039
3	mrrr	24.75	0.123
4	rrrr	24.90	0.162
5	mmrm	25.20	0.150
6	mmrr	25.30	0.168
7	rmrm	25.65	0.029
8	mmmr	25.80	0.147
9	rmmr	25.94	0.088
10	mmmm	26.00	0.053

Table 8 Styrene centred pentad level co-tacticities analysis of styrene–MAN alternating copolymers from aromatic C-1 carbon atom resonance

Peak number	Types of pentads	Chemical shift in ppm	Relative intensity
1	rmmr	142.98	0.042
2	mmmm	143.10	0.104
3	mmmr	143.14	0.092
4	mmrm	143.18	0.074
5	mmrr	143.50	0.096
6	mrrr	143.56	0.083
7	rrmr	143.60	0.152
8	rmrm	143.78	0.252
9	mrrm	144.20	0.077
10	rrrr	144.28	0.026

corelationships[35]:

$$\mathrm{mmmr} + 2(\mathrm{rmmr}) = \mathrm{mmrm} + \mathrm{mmrr} \qquad (10)$$

$$\mathrm{mrrr} + 2(\mathrm{mrrm}) = \mathrm{rrmr} + \mathrm{mmrr} \qquad (11)$$

where 'm' and 'r' correspond to the meso and racemic placement of comonomer units in a dyad as has been described earlier. Because these sets of equations are independent of any type of propagation models, such as Bernoullian or Markovian, they serve as an excellent test for verifying the authenticity of signal assignments to different configurational triads. These requirements are met reasonably well for all the three carbon atoms, thereby approving the authenticity of our analysis.

CONCLUSIONS

With the help of high resolution ^{13}C n.m.r. spectroscopy at higher magnetic fields, it has become possible to carry out detailed analyses of the microstructures of styrene–MAN copolymers. Spectral analyses of random copolymers provided information regarding the sequence distribution of comonomer units along the polymer chains and the corresponding alternating copolymer served as a valuable system for elucidating the configurational features of the comonomer placements along the polymer chain.

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