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CONTROLLED RADICAL POLYMERIZATION AND CHARACTERISATION OF VINYLIC- ACRYLATE COPOLYMERS

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Abstract

Vinyl benzene methyl acrylic ester copolymerization was achieved using controlled radical polymerization (CRP). The reaction was carried out by using methyl 2-bromopropionate ($C_4H_7BrO_2$) initiator under catalytic conditions employing $CuBr/N,N,N',N',N''$ -pentamethyldiethylenetriamine. The GPC-gel permeation chromatography method has been employed to ascertain distribution of molecular mass. Copolymer composition was determined through proton NMR analysis. Both nonlinear error-in-variables (EVM) and Kelen-Tudos (KT) methods were used to obtain the comonomer reactivity ratios respectively as $r_s = 1.09$, 1.09 ± 0.05 and $r_M = 0.36$, 0.35 ± 0.17 . The resonance frequency pertaining to both quaternary carbons present in styrene as well as those pertaining to carbonylic carbons present in methyl acrylate segment have been observed to be dependent on the sequence and were identified up to the triad level. The proton (1H) and carbon-13 (^{13}C) NMR spectroscopy was used to fully assign the peaks in the copolymers using analytical techniques such as DEPT-distortionless enhancement by polarization transfer, as well as 2D NMR methods.

Keywords: Controlled radical polymerization (CRP), NMR, Microstructure, S/M copolymer.

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INTRODUCTION

Due to the mild reaction conditions, tolerance to contaminants and abundance of radically polymerizable monomers, free radical polymerization is frequently employed in industry to create a wide variety of materials [1]. There has been extensive research in the area of controlled radical polymerization (CRPs) [2-12] which revolutionized the range of materials that could be produced using these processes.

This has allowed greater control over molecular weight and polymer architecture such as star-shaped, graft or block copolymers made from a variety of monomers. One of the most adaptable and versatile techniques in this area is copper-based controlled radical polymerization (CRP) [13-16] and has been used in the (co)polymerization of acrylates [17,18], methacrylates [19-21], and styrene(s) [22]. Since the stereochemical assignments of the monomeric units have an impact on the chemical shifts, the spectral pattern of the copolymers is sometimes intricate. Vinyl copolymer's intramolecular (tacticity and sequence distribution) and intermolecular (molar mass distribution and chemical composition) chain structures have been identified using NMR spectroscopy as a potent experimental technique [23-25]. The overlapping signals seen as a consequence of different compositional and configurational sequences in 1D NMR spectroscopy [26] are resolved using 2D NMR techniques [27-30]. The microstructure of the polymers [31-37] has been investigated and assigned by 2D NMR investigations, including HSQC and TOCSY experiments.

Styrene/alkyl acrylate copolymers have several applications mostly in paints, adhesives and coatings. Most significant growth has been in the packaging industry (which allows the production of attractive containers, dinnerware and bottle labels), in fast food, automotive and electronic industry (which include the production of new devices such as computers, video cassettes and new telecommunication equipment) and in medical applications [38]. Styrene/methyl acrylate blends have been described for curing of polyester binders in smokeless propellant fuels [39]. The styrene/butyl acrylate copolymers

are widely used in the terpolymer system (e.g. in the production of waxes).

Numerous researchers [40-56] have reported on the triad distribution [40,41] and tacticity parameter [42] of these copolymers. Poehlein *et al.* [43] described the sequence distribution by the Alfrey-Mayo model. Using ZnCl_2 as an accelerator, other researchers [44,45] studied the kinetics of radical copolymers of methyl and ethyl acrylate with styrene. Using ^{13}C NMR spectroscopy, Darricades *et al.* [46] studied the sequence distribution in emulsion copolymers. A few other investigations [47-49] demonstrated the significance of sequential organization in the heat degradation of styrene/methyl acrylate copolymers.

Kobayashi *et al.* [50] extended the Gibbs-Dimarzio equation and investigated the influence of Series distribution on the glass transition point. Koinuma *et al.* [52,53] too have analyzed the NMR spectrum of methyl acrylate/styrene. Using batch emulsion polymerization, Guillot *et al.* [54,55] created ethyl acrylate and styrene copolymers to investigate the microstructure (sequence distribution) and glass transition temperature.

Brar *et al.* [56] examined the sequence distribution of styrene/methyl acrylate copolymers using proton-coupled ^{13}C NMR spectroscopy to interpret the different peaks. Vander Boomen *et al.* [57] prepared these copolymers by continuous emulsion polymerization and observed strong compositional drift in a batch copolymerization. However, no comprehensive and detailed investigation of microstructure [58,59] has been attempted for random styrene/methyl acrylate copolymers using advanced NMR techniques like HMBC, TOCSY and HSQC. To analyse microstructure of resonances pertaining to methine and methylene, quaternary carbon, and carbonyl carbon of styrene/methyl acrylate, a combination of two dimensional (HMBC, TOCSY and HSQC) and one dimensional nuclear magnetic resonance techniques ($^{13}\text{C}\{^1\text{H}\}$, ^1H and DEPT) has been used.

EXPERIMENTAL

Materials and Methods

Styrene (MERCK, 99%), methyl 2-bromopropionate (Aldrich, 98%) and methyl

acrylate (MERCK, 98%) were both vacuum distilled maintaining temperature under 5 °C. Chemicals such as Aldrich's 98% copper(I) bromide (CuBr), CDH's 99.5% copper metal powder (Cu(0)), and Aldrich's 99% N,N,N',N',N''-pentamethyldiethylenetriamine were utilized as they were, without undergoing any additional reactions. The preparation method of vinyl-acrylate copolymers using various infeed ratios is described in our earlier work[60-63]. The resultant copolymers were vacuum-dried for a day at 80°C.

Characterization

Gravimetric measurement was used to determine the percentage conversion, while GPC has been employed for measuring Mn along with the polydispersity index Mw/Mn. Polystyrene standards in conjunction with Tetrahydrofuran (THF) were employed for mobile phase, keeping rate of flow at 0.3 mL/min. Copolymer compositions were determined using proton (¹H) NMR spectra. The copolymers were analysed using various

one dimensional (proton (¹H), proton-coupled ¹³C, DEPT) in conjunction with two dimensional (HMBC, TOCSY and HSQC) nuclear magnetic resonance spectroscopy. Our previous publications [60-63] provide further details on the techniques used.

RESULTS AND DISCUSSION

Molecular weights estimation

By adjusting the in-feed molar ratios under ATRP conditions, copolymers of styrene and methyl acrylate were created to observe the change in composition of the copolymer as the polymerization process progressed. The molecular weight distribution of the three copolymer series (Table-1) revealed a linear increase in Mn with conversion, while the polydispersity remained small (Mw/Mn = 1.1–1.3), demonstrating regulated polymerization. Fig. 1 illustrates the correlation between the increase in molecular weight and the rise in conversion.

Table1
Percentage conversion, molecular weight and polydispersity
for the S/M copolymers at different infeed

Styrene/MA (0.65/0.35)			Styrene/MA (0.5/0.5)			Styrene/MA (0.25/0.75)		
Conversion (%)	Mn	PDI	Conversion (%)	Mn	PDI	Conversion (%)	Mn	PDI
7.2	5000	1.31	9.12	6000	1.3	8.2	5000	1.32
23.52	18000	1.24	20.15	15000	1.25	29.23	19000	1.2
33.46	23000	1.19	35.23	23000	1.18	40.12	24000	1.17
50.15	35000	1.17	45.68	28000	1.17	55.23	33000	1.16
61.2	42000	1.16	57.31	37000	1.16	60.19	36000	1.15
73.2	50000	1.15	69.89	46000	1.15	72.2	44000	1.15

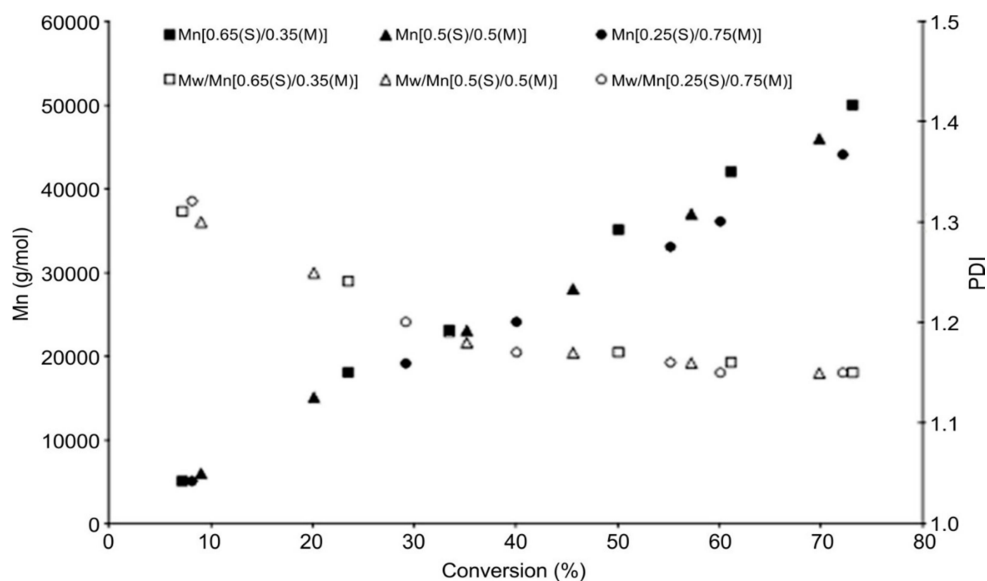


Fig. 1. Variation of molecular weight with the conversion of S/M copolymers synthesized by ATRP

Reactivity Ratios Determination

Relative peak integrations of protons present in the phenyl resonances of S group along with methoxy resonances of M group of ^1H spectrum have been utilized to calculate copolymer compositions (F_M). The S/M copolymer's composition listed in Table-2 was determined [45] from the equation:

$$F_1 = \frac{S_1/5}{(S_1/5 + S_2/3)}$$

The Kelen and Tudos approach was used to evaluate the reactivity ratios r first. The values of r using the plot are found to be, respectively, $r_S = 1.09 \pm 0.05$ and $r_M = 0.35 \pm 0.17$ and from the Error in Variable Model (EVM) tool are $r_S = 1.09$, $r_M = 0.36$.

Table-2
Copolymer composition data of the S/M copolymers (<10% conversion)

Sample No.	Styrene mole fraction infeed (f_S)	Styrene mole fraction in copolymer (F_S)
1	0.70	0.74
2	0.50	0.61
3	0.40	0.50
4	0.25	0.37
5	0.15	0.31
6	0.10	0.25

Fig. 2 shows the plot of copolymer composition versus conversion wherein an almost identical trend can be seen for all three feed compositions, demonstrating that the copolymer composition changes as conversion increases. A specific feed composition has a different copolymer composition at low

conversion than it has at high conversion. As the conversion rises, there is a compositional tendency towards less reactive monomers and an increased incorporation of methyl acrylate into the copolymer is observed. If the comonomer pair's reactivity differences are greater, this drift will be more pronounced.

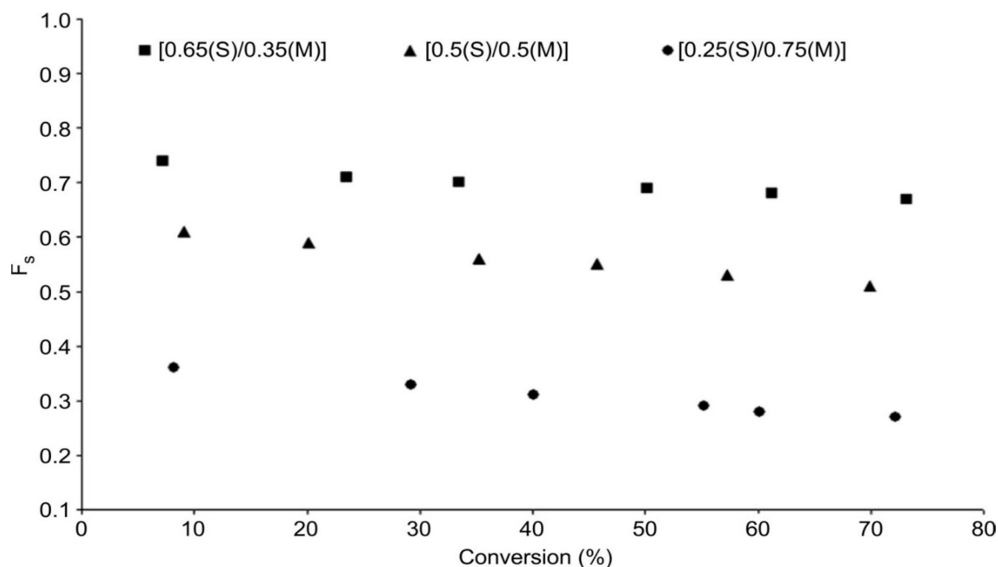


Fig. 2. Variation of copolymer composition (F_S) as a function of conversion for the S/M copolymers

^1H NMR studies

Fig. 3 depicts the complex peak groupings of the S/M copolymer's ^1H NMR spectrum at $F_M = 0.50$. Methoxy proton resonances, which are largely insensitive to the stereochemical arrangement in the polymer, show marked splitting [60] from 3.80 to 2.80 ppm (methyl acrylate). By comparing the methoxy proton signals of different compositions of the S/M

copolymers with that of poly(methyl acrylate), the methoxy proton signals were assigned up to triad level. Similar splitting is seen in phenyl proton also. The CH and CH_2 protons of both M and S units can be tentatively ascribed to the range between 0.65-2.50 ppm. The overlapping signals were resolved and completely assigned in the subsequent sections.

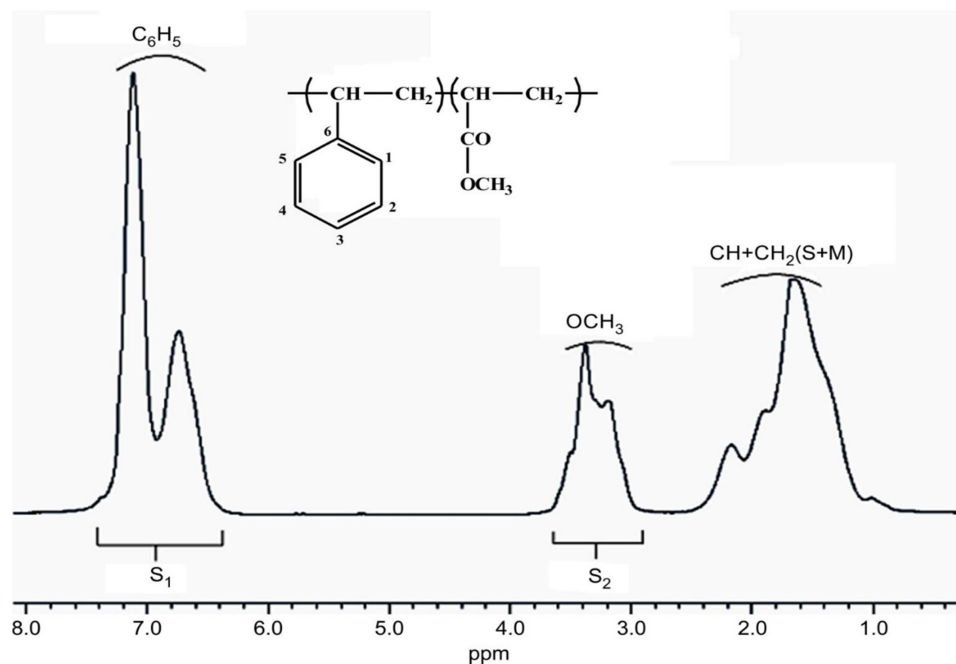


Fig. 3. ^1H NMR spectrum of the styrene/methyl acrylate copolymer ($F_M = 0.50$) in CDCl_3 at $25\text{ }^\circ\text{C}$

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

The S/M copolymer's fully assigned $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum is depicted in Fig. 4 ($F_M = 0.50$). The assignments were made by comparing the spectra of the respective homopolymers with DEPT-135 as has been described by Brar *et al.* [60]. Due to the overlap of the signals, the spectral area between 32.88 and 48.38 ppm is extremely complicated. Due to their compositional and configurational sensitivity, the backbone CH_2 and CH carbon resonances have a wide range of resonances. According to DEPT-90, the CH carbons to both units belong in the range of 37.33–41.00 ppm. The extended spectrum of M unit carbonyl peak in NMR spectroscopy, which resonates in range of 174.51–178.57

ppm, and quaternary carbon signals in styrene, which resonate in the range of 142.2–146.4 ppm, are shown in Figs. 5 and 6. The various triad sequences as well as their positions were assigned based on variations of monomer arrangement in the copolymers followed by its assessment against spectrum corresponding to homopolymers. Around 177.2–176.2 ppm, 176.2–175.2 ppm and 175.2–174.1 ppm are the carbonyl carbon resonance signals attributed to SMS, SMM and MMM triads, respectively (Fig. 5). Triad SSS is assigned to quaternary carbon peaks at 146.2–144.8 ppm, the SSM triad is assigned around 144.8–143.6 ppm, and the MSM triad is assigned around 143.6–142.4 ppm. (Fig. 6).

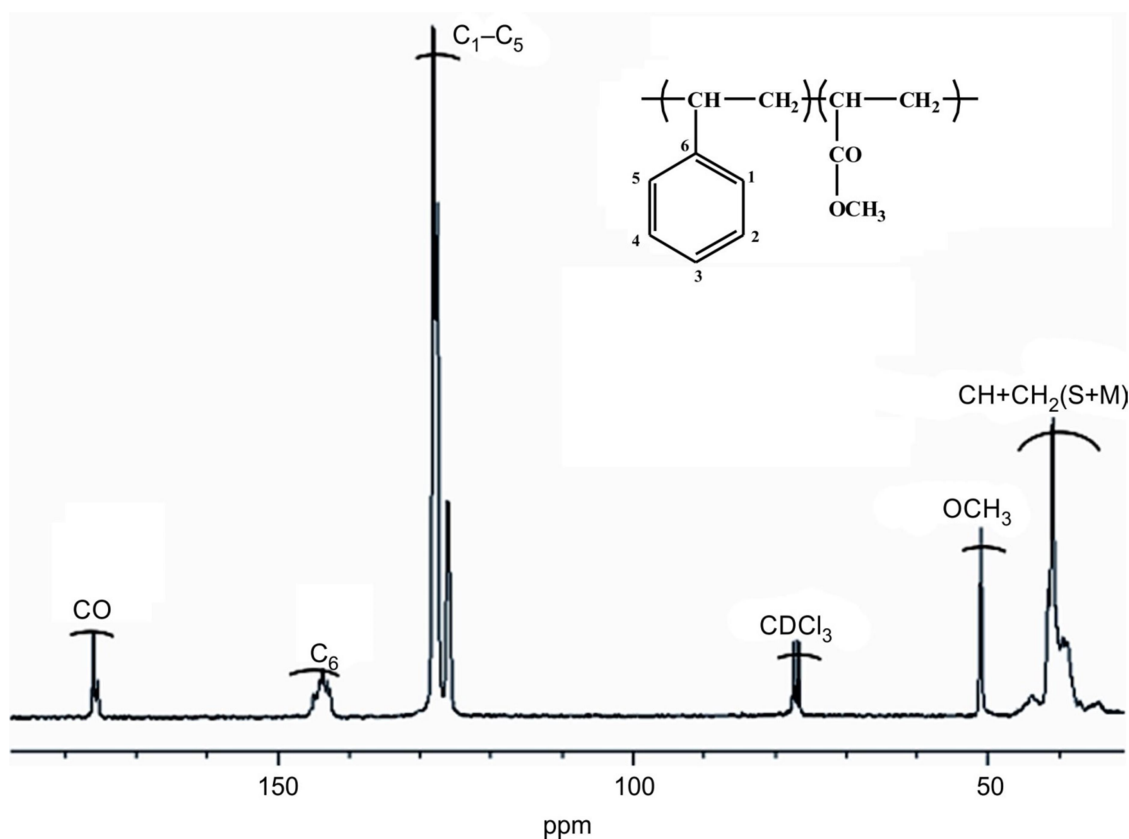


Fig. 4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the styrene/methyl acrylate copolymer ($F_M = 0.50$) in CDCl_3 at 25°C

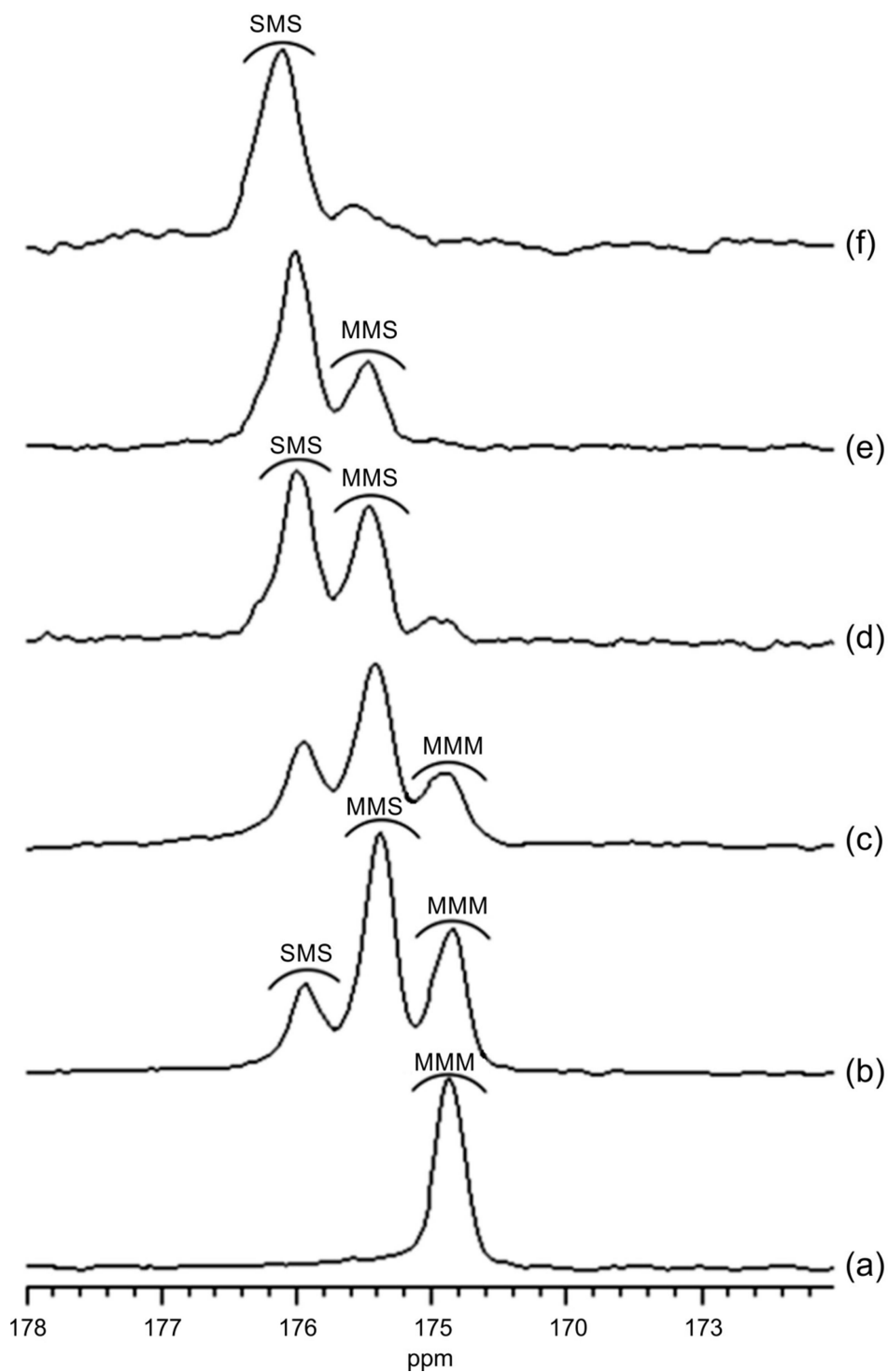


Fig. 5. Expanded carbonyl carbon of the M unit in the $^{13}\text{C} \{^1\text{H}\}$ NMR spectra of the styrene/methyl acrylate copolymers in CDCl_3 at 25 °C: a) poly(methyl acrylate), b) $F_M = 0.69$, c) $F_M = 0.63$, d) $F_M = 0.50$, e) $F_M = 0.39$, and f) $F_M = 0.26$

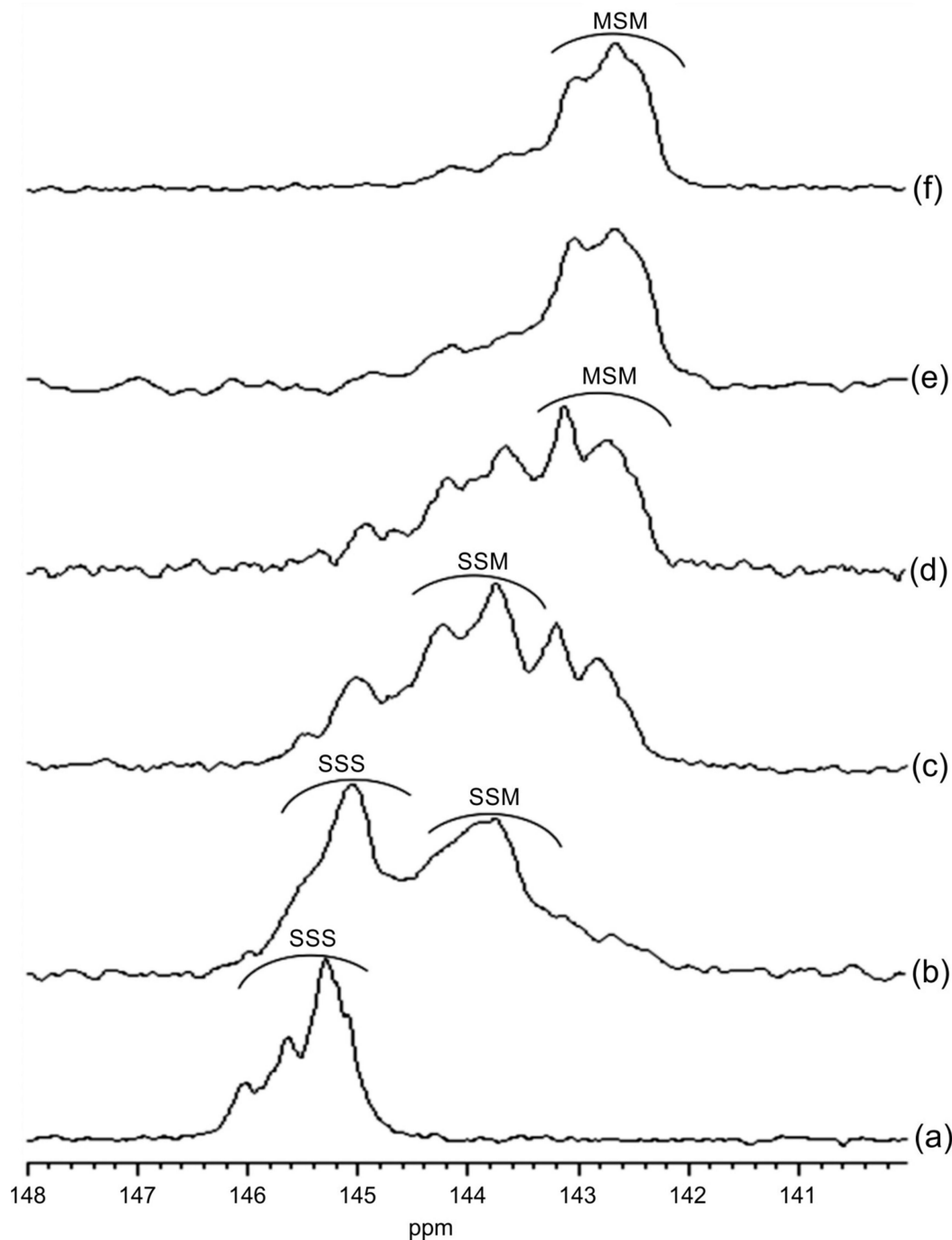


Fig. 6. Expanded Quaternary carbon of the S unit in the $^{13}\text{C} \{^1\text{H}\}$ NMR spectra of the styrene/methyl acrylate copolymers in CDCl_3 at 25°C : a) polystyrene, b) $F_S = 0.74$, c) $F_S = 0.61$, d) $F_S = 0.50$, e) $F_S = 0.37$, and f) $F_S = 0.31$

2D HSQC NMR analysis:

The expanded 2D HSQC spectra of the S/M copolymers is shown in Fig. 7 wherein complex overlapping is observed in the styrene and the CH_3 acrylate unit's main chain CH and CH_2 groups. Due to the change

in signal intensity with varying composition of the copolymer, the resonance signals of the CH_2 carbon area can be separated into MM, MS, and SS diad compositional sequences. The MM diad has a resonance in the range of 33–37/1.1–1.6 ppm. While the CH_2 protons of

the MM diad in mesomeric and racemic configurations yield two and one crosspeaks

respectively. Table-3 is showing various peaks and their corresponding assignments.

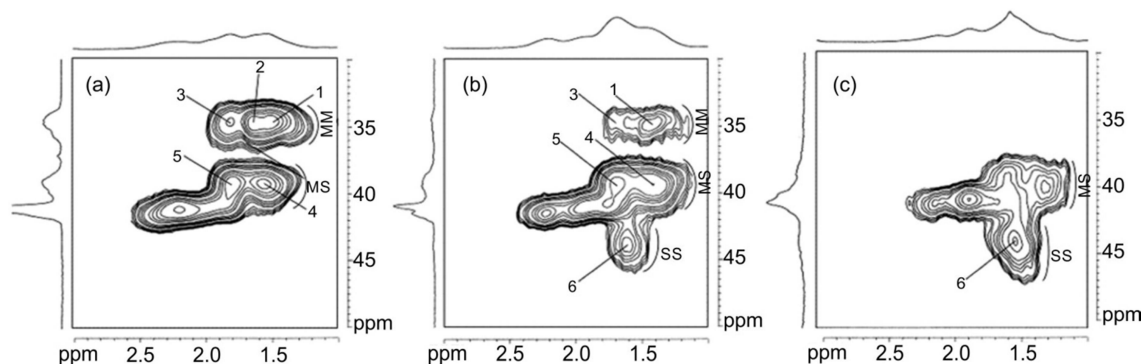


Fig. 7. Expanded 2D HSQC NMR spectra of the three different compositions of the styrene/methyl acrylate copolymers with F_M (a = 0.75, b = 0.50 and c = 0.26) in $CDCl_3$ at 25 °C

Table-3
Spectral Assignments Based on 2D HSQC Spectra

Peak number	Chemical shift (ppm)	Assignments
1	34.6/1.82	MmM
2	34.6/1.64	MrM
3	34.6/1.48	MmM
4	39.2/1.81	MmS
5	39.2/1.50	MmS
6	43.8/1.60	SS

Due to the two non-equivalent protons, the crosspeaks 1 and 3 centering at 34.6/1.82 ppm and 34.6/1.48 ppm, respectively, are attributed to the MmM of the CH_2 diad of M unit while the crosspeak 2 centering at δ 34.6/1.64 ppm is assigned to the MrM. The MS diad area spans from 37.5 to 42/1.2 to 2.1 ppm and exhibits further splitting at the proton axis. The MmS diad is assigned the crosspeaks 4 and 5, which are located at 39.2/1.81 ppm and 39.2/1.50 ppm. The SS diad resonates at the 42–46/1.4–1.7 ppm range, which exhibits further splitting. The SS diad is given the crosspeak 6, which is centred at 43.8/1.60 ppm. Due to the

resonance of both units' CH and CH_2 in this region, the spectrum could not be allocated further.

2D TOCSY NMR analysis

The 2D TOCSY spectrum reveals the coupling among CH proton in M and triads with S atoms with CH_2 proton in MM, MS and SS diads as visible from Fig. 8. The peak positions, corresponding assignments and the responsible coupling are listed in Table-4. The ensuing assignments were then correlated with that of poly(methyl acrylate) and poly(styrene).

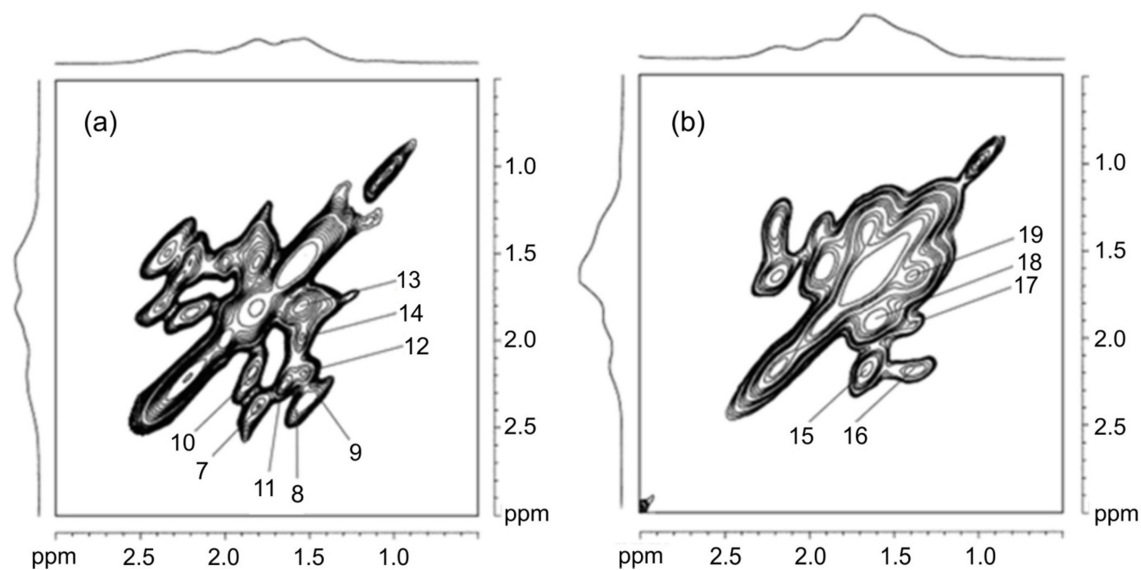


Fig. 8. Expanded TOCSY spectra of two different compositions of styrene/methyl acrylate copolymer F_M ($a=0.75$ and $b=0.39$) in $CDCl_3$ at $25\text{ }^\circ\text{C}$

Table-4

^1H - ^1H cross correlations between non-equivalent *geminal* protons in S/M copolymers observed from 2D TOCSY spectra

Correlation peak No.	Coupled protons		Peak position $^1\text{H}/^1\text{H}; \delta$
	Proton I	Proton II	
7	CH proton of M unit	CH ₂ protons of MM diad in meso (m)	2.38/1.80
8	CH proton of M unit	CH ₂ protons of MM diad in racemic (r)	2.38/1.56
9	CH proton of M unit	CH ₂ protons of MM diad in meso (m)	2.34/1.42
10	CH proton in MmMS triad	Two different CH ₂ protons of MmM diads	2.14/1.81
11	CH proton in MrMS triad	CH ₂ protons of MrM diad	2.22/1.64
12	CH proton in MmMS triad	CH ₂ protons of MmM diad	2.20/1.52
13	CH ₂ proton of MS/SS diad (Ha)	CH ₂ proton in MS/SS diad (Hb)	1.78/1.52
14	CH ₂ proton of MmM diad (Ha)	CH ₂ proton of MmM diad (Hb)	1.97/1.52
15	CH proton of the S unit in SSM triad/CH proton of the M unit in MMS triad	CH ₂ protons in SM diad/CH ₂ protons in MS diad.	2.20/1.66
16	CH proton of the S unit in SSM triad	CH ₂ protons in SS diad	2.20/1.39
17	CH ₂ proton in MS diad in MSS and MSM triads/CH ₂ proton of the M unit in MM diad. (Ha)	CH ₂ proton in MS diad in MSS and MSM triads/CH ₂ proton of the M unit in MM diad. (Hb)	1.90/1.60
18	CH ₂ proton in the MS diad in the MSS and MSM triads (Ha)	CH ₂ proton in the MS diad in the MSS and MSM triads (Hb)	1.92/1.40
19	CH ₂ proton in the SS diad (Ha)	CH ₂ proton in the SS diad (Hb)	1.66/1.39

2D HMBC NMR analysis

Fig. 9 displays the HMBC NMR spectra with complete signal assignments. The assignments of the triad sequences made using the 2D HMBC spectra were then validated using these assignments. Only M-centered triads are seen

due to the reaction between methoxy protons with carbonyl carbon. This is in agreement with the reported results [60-63]. The various peak assignments, positions and the coupling responsible is listed in Table-5.

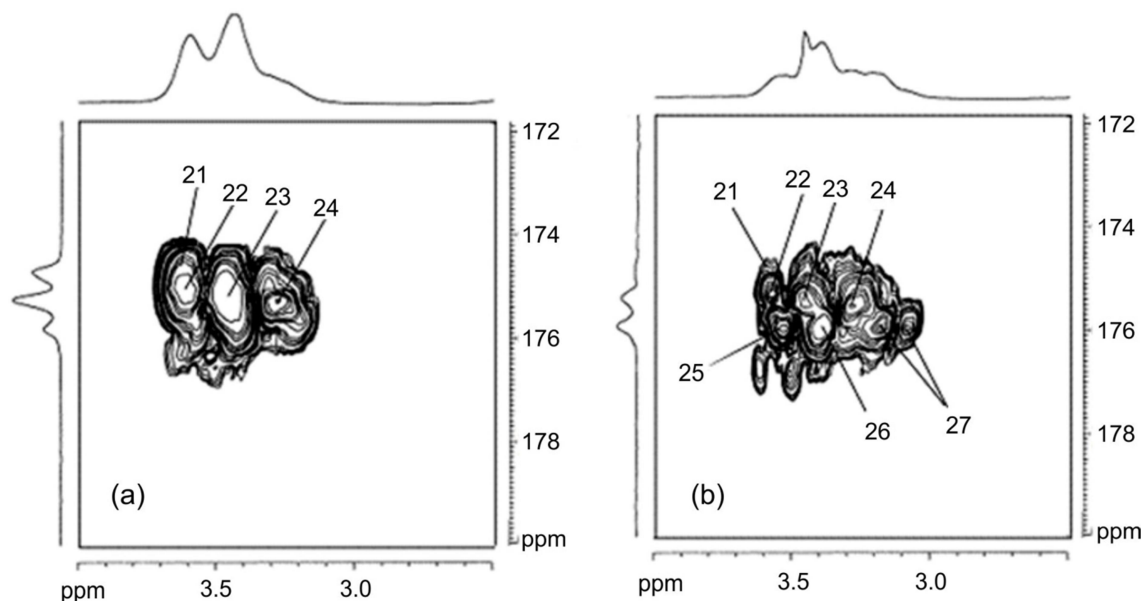


Fig. 9. Expanded HMBC NMR spectra of styrene/methyl acrylate copolymers with F_M (a = 0.75 and b = 0.50) in $CDCl_3$ at 25 °C

Table-5

2D HMBC assignments of carbonyl and nitrile carbons of Styrene methacrylate copolymer

Cross peak No.	Peak position	Type of carbon	Coupled to proton of
21	174.6/3.59	CO(MMM)	OCH ₃ (MMM)
22	175.3/3.57	CO (MMS)	OCH ₃ (MrMrS)
23	176.4/3.44	CO (MMS)	OCH ₃ (MmMrS)
24	177.5/3.28	CO (MMS)	OCH ₃ (MmMmS)
25	175.9/3.53	CO (SMS)	OCH ₃ (SrMrS)
26	175.9/3.18	CO (SMS)	OCH ₃ (SmMrS)
27	175.9/3.08	CO (SMS)	OCH ₃ (SmMmS)

Conclusions

The study focused on analyzing the sequence distribution and microstructure of copolymers consisting of styrene and methyl acrylate (S/M) produced with controlled molecular weight using various 1D and 2D NMR techniques.

The reactivity ratios for the copolymerization of S and M were calculated using KT ($r_S = 1.09 + 0.05$ and $r_M = 0.35 + 0.17$) and the EVM method ($r_S = 1.09$ and $r_M = 0.35$), indicating that styrene had a higher reactivity towards the monomer addition compared to methyl acrylate.

To unambiguously identify various sequences in the copolymers, HSQC and TOCSY NMR experiments were conducted. These experiments allowed for the identification of various correlations between protons and carbons in the copolymers, enabling the determination of the exact sequence distribution.

Long-range couplings were assigned using HMBC, which is a powerful NMR technique that is used to correlate protons and carbons that are separated by several chemical bonds. By analyzing the HMBC spectra, one can have further insight into the microstructure of the copolymers. The designations of the carbonyl carbon were reaffirmed with the help of HMBC spectra, which enabled unambiguous identification of the carbonyl carbon in the copolymers. Overall, the study provided an analysis of the sequence distribution and microstructure of S/M copolymers, which can have important implications for the design of copolymers with desired properties.

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Conflict of Interest

The authors have no competing interests to declare that are relevant to the content of this paper.

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