Sequence Determination in Styrene–Methyl Methacrylate Copolymers by ^{13}C NMR Spectroscopy

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ABSTRACT: Styrene (St)–methyl methacrylate (MMA) copolymers with varying compositions were prepared in bulk by radical polymerization using 2,2'-azoisobutyronitrile (AIBN) as an initiator. ^{13}C and ^1H NMR spectra of the copolymers were analyzed. From ^1H NMR, reactivity ratios were determined. The triad sequences were determined by using the α -methyl and phenyl (C-1) resonances frequencies from ^{13}C NMR spectra. The thermal decomposition behavior of the copolymers was related to the triad concentrations, calculated using the Bovey's statistics. The effect of ferric chloride as a stabilizer on the composition of copolymer was also studied.

KEY WORDS Copolymer / ^{13}C NMR / Reactivity Ratios / Triad Sequence
/ Bovey's Statistics / Thermal Stability /

^1H and ^{13}C NMR spectroscopy provides significant information on the monomer distribution and nature of linkages in copolymers. The monomer sequence length distribution affects the bulk and solution properties of copolymers. In our earlier publication, the sequence distribution of methyl methacrylate–ethyl methacrylate copolymers using ^{13}C NMR has been reported.¹ Sequence distribution of methyl methacrylate–acrylic acid copolymers by ^{13}C NMR has already been communicated.² NMR studies of methyl methacrylate–styrene copolymers have been reported in the literature.^{3–6} Katritzky *et al.*³ reported the variation of MSM triad concentration (M stands for methyl methacrylate and S stands for styrene), with the percentage of styrene. Their results do not agree with the data presented in the Table IV (ref 3).

A continuation of our earlier work, in this paper the sequence of methyl methacrylate–styrene copolymer shall be reported. Bovey's statistics shall be applied and results shall be compared with our ^{13}C NMR data. The effect

of ferric chloride on the reactivity ratios shall be discussed. An attempt has been made to correlated the sequence triad with the thermal decomposition temperature of the copolymers.

EXPERIMENTAL DETAILS

Methyl methacrylate–styrene copolymers of different composition were prepared in bulk using 1% 2,2'-azoisobutyronitrile (AIBN) as an initiator at 60°C. The percentage conversion in copolymers was less than 5%. Copolymers of different compositions were prepared with 2% ferric chloride, as a stabilizer.

^1H NMR spectra of all samples were recorded with a JEOL-FX 100 NMR spectrometer, operating at 99.5 MHz in CDCl_3 at 25°C with TMS as internal standard. The number of pulses given was in the range 20 and spectral width was 1000 Hz (~ 10 ppm).

^{13}C NMR spectra were also obtained with JEOL-FX-100 NMR spectrometer operating at 25 MHz in pulsed FT mode, with noise modulated proton at 48°C. The solvent used

was CDCl_3 with TMS as internal standard. The spectral range was 5000 Hz (~ 200 ppm) and 15000 pulses were given. Chemical shifts are reported down field with respect to TMS. All the calculations regarding fractional area measurements were done by using Lorentzian shape curve fitting computer programme on ICL-2960, at IIT Delhi.

The thermal gravimetric analysis (TGA) of stabilized and unstabilized samples were carried out on a TGA du Pont 1090. The molecular weights of the copolymers were determined by viscometry in toluene at 30°C . Time of flow was more than 100 s. The values of Mark-Houwink constants were taken from literature.⁹ The values of molecular weights of copolymers are given in Table I. All the copolymers are of the same order of molecular weight.

RESULTS AND DISCUSSION

^1H NMR Studies

A representative ^1H NMR spectrum of meth-

ylmethacrylate-styrene copolymer is shown in Figure 1. The resonance due to aryl protons of styrene unit is observed at $\delta 7.16$ ppm. The methoxy resonance, which is quite insensitive to stereochemistry in poly(methyl methacrylate), is very sensitive to monomer sequence in case of copolymer. The methoxy resonance appears in the form of triplet within the wider range of $\delta 2.8$ ppm to $\delta 3.75$ ppm. Additional structures appear on each of the resonance because of the tacticity within the copolymer. The α -methyl resonance which is very sensitive to tacticity in poly(methyl methacrylate), seems to be sensitive to monomer sequence distribution and tacticity within copolymers.

The spectral integration of the aryl and α -methyl protons were used to determine the copolymer composition because of large difference in the values of chemical shift for the two kinds of protons. The compositions of copolymers are given in Table I.

The average values of reactivity ratios calculated with different monomer feed ratios and

Figure 1. ^1H NMR spectrum of copolymer (40% styrene) in CDCl_3 at 25°C .

Table I. Styrene (St) and methyl methacrylate (MMA) (mol%) in copolymers as determined by ¹H NMR

	Feed in mol%		From ¹ H NMR		M × 10 ⁻⁶
	St	MMA	St	MMA	
A	80	20	76	24	1.20
B	60	40	58	42	1.33
C	50	50	54	46	1.12
D	45	55	49	51	1.15
E	40	60	45	55	1.02
F	10	90	17	83	1.10

monomer ratios in the copolymers are $r_s = 0.52$, and $r_M = 0.44$ using integral copolymer equation and $r_s = 0.53$, $r_M = 0.42$ using the method of Kelen and Tudos,⁷ with α equals 0.9407, where M stands for methyl methacrylate and S stand for styrene. The values are in agreement with the those reported in the literature.⁸

Bovey's Statistics

Monomer sequence distribution can be described by using Bovey's statistics. One needs only to calculate the probability that methyl methacrylate will add to itself (P_{MM}). The probability of addition to styrene then is simply $(1 - P_{MM})$. Various methyl methacrylate (M) centered triad fractions can be given as

$$F_{MMM} = F_M P_{MM}^2 \quad (1)$$

$$F_{MMS} + F_{SMM} = 2F_M P_{MM}(1 - P_{MM}) \quad (2)$$

$$F_{SMS} = F_M(1 - P_{MM})^2 \quad (3)$$

$$P_{MM} = r_M f_M / (1 - f_M + r_M f_M) \quad (4)$$

F_M is the mole fraction of MMA in the copolymer. A similar treatment follows for the styrene centred triad.

The values of P_{MM} in any given sample is calculated from equation (4), substituting the appropriate reactivity ratios (r) and feed ratios (f).

Concentrations of all the six monomer sequence triads for all the copolymers are give in Table II. Normalized statistical monomer dis-

Table II. Tabulation of the six monomer sequence distribution triads calculated using Bovey's statistics

	Mol% styrene					
	80	60	50	45	40	10
M centred triads						
f_M	0.20	0.40	0.50	0.55	0.60	0.90
F_M	0.24	0.42	0.46	0.51	0.55	0.83
P_{MM}	0.10	0.22	0.30	0.34	0.39	0.79
F_{MMM}	0.01	0.05	0.09	0.12	0.15	0.62
F_{MMS}	0.23	0.34	0.42	0.45	0.48	0.33
F_{SMS}	0.76	0.61	0.49	0.43	0.37	0.05
S centred triads						
f_S	0.80	0.60	0.50	0.45	0.40	0.10
F_S	0.76	0.58	0.54	0.49	0.45	0.17
P_{SS}	0.68	0.45	0.36	0.31	0.26	0.06
F_{SSS}	0.46	0.20	0.12	0.10	0.07	0.003
F_{SSM}	0.43	0.49	0.43	0.43	0.38	0.112
F_{MSM}	0.11	0.31	0.45	0.47	0.55	0.885

tribution triad population vs. styrene concentration in methyl methacrylate–styrene copolymers are shown in Figure 2.

¹³C NMR Studies

From the ¹³C NMR of polystyrene, the methylene resonance (–CH₂) seems to be tetrad sensitive, instead phenyl C-1 resonance is clearly split into three peaks showing the triad sensitivity. α -Methyl resonance is not much resolved in the ¹³C NMR of poly(methyl methacrylate). Carbonyl resonance shows triad sensitivity. The methylene, quaternary, and methoxy, resonances are not much resolved.

Proton-decoupled, ¹³C NMR spectrum of methyl methacrylate–styrene (40%) copolymer is shown in Figure 3. The most environment sensitive and least overlapped absorptions are those of the methyl methacrylate CH₃ (providing information concerning M-centred triads) and the styrene C₁ (providing information concerning S-centred triad).

The α -methyl resonance seems to be both sequence and tacticity sensitive. The multiple resonance obtained in this case can be explained in terms of three methyl methacrylate

Figure 2. Normalized statistical monomer sequence distribution triad concentrations vs. styrene in the styrene-methyl methacrylate copolymers.

Figure 3. $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of copolymer (40% styrene) in CDCl_3 at 48°C .

centred sequence triads, MMM, MMS (SMM), and SMS appearing in the order of increasing field. This assignment seems to be reasonable, as the resonance will move up field with decreasing polarity of the environment.

The expanded spectrum in the α -methyl region is shown in Figure 3. Intensity of MMM triad increased with increasing concentration of M in copolymers. It can be seen that the methine carbon of the styrene unit and the carbonyl,

methoxy, and quaternary carbon of the methyl methacrylate units are also environmentally sensitive.

The multiple resonance obtained in the case of styrene C-1 absorption can be explained in terms of three styrene centred triads, SSS (δ 146.97 ppm), SSM (MSS) (δ 145.55 ppm), and MSM (δ 143.79 ppm). The expanded spectrum in phenyl C-1 absorption region is shown in Figure 3. The resonance band due to SSS triad grows with decrease in the mole percent of feed monomer of methyl methacrylate.

The observed triad fractions of the three S centred and three M centred triads for the copolymers are given in the Table III. For the 10% styrene samples, the splitting of C-1 signal is mainly due to the tacticity of the MSM triad. Likewise in the 80% styrene sample, the CH_3 signal shows splitting mostly due to the tacticity of the SMS triad.³

NMR of Copolymers Stabilized with Ferric Chloride

The addition of ferric chloride during the copolymerization favors the homopolymerization of styrene. This may be due to the interactions of outer most vacant orbitals of Fe^{3+} species with the delocalized electrons of

the phenyl ring of styrene moiety, leading to weakening of the olefinic bond in styrene thereby favoring the homopolymerization of styrene. This fact has been verified by NMR spectroscopy.

^{13}C NMR spectra of copolymers prepared

Table III. Observed triad concentrations using ^{13}C NMR

Mol% styrene	Sequence					
	SSS	MSS	MSM	MMM	MMS	SMS
60	0.29	0.55	0.16	—	—	—
50	0.26	0.51	0.23	0.18	0.49	0.33
45	0.22	0.53	0.25	0.28	0.47	0.25
40	0.24	0.54	0.22	—	—	—

Table IV. TGA data of methyl methacrylate-styrene copolymers

Mol% styrene	IDT	FDT	$T_{\max}$
	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$
10	297.3	413.0	382.7
40	391.9	435.3	417.6
45	366.8	434.5	409.5
50	346.9	422.3	402.6
55	334.6	399.8	377.4
60	386.6	431.4	413.5

Figure 4. Initial decomposition temperature (IDT) and temperature of maximum decomposition ($T_{\max}$) vs. styrene in copolymers.

with 2% ferric chloride shows the absence of resonance signals due to methyl methacrylate unit. Characteristic resonance signals due to α -methyl, methoxy and carbonyl groups are missing. This shows that ferric chloride which was added as a stabilizer, affects the reactivity ratios of the monomers to such an extent that only polystyrene is formed as a block polymer. The compositions of copolymers in the presence of ferric chloride entirely differ from the copolymers without ferric chloride. Therefore, it was difficult to observe the effects of ferric chloride on the thermal stability of copolymers.

TGA Studies

Initial decomposition temperature (IDT) and temperature of maximum decomposition ($T_{\max}$) for the copolymers are included in the Table IV. TGA studies reveals that the IDT and $T_{\max}$ are lowest in the case of a copolymer with 45% MMA and increase on both sides of the concentration (Figure 4). The concentration of SSM/SMM triad calculated from NMR using Bovey's statistics is maximum for 50% MMA copolymer. This shows as the concentration of this triad decreases, the IDT and $T_{\max}$ increases. From these observations,

the conclusion can be drawn that the concentration of SSM/SMM triad plays an important role in the thermal stability of the copolymers, since the molecular weights of the copolymers are of the same order.

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