

Microstructure Determination of the Acrylonitrile–Styrene–Methyl Methacrylate Terpolymers by NMR Spectroscopy

A. S. BRAR, S. K. HEKMATYAR

Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

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ABSTRACT: Acrylonitrile–styrene–methyl methacrylate (A–S–M) terpolymers were prepared by photopolymerization using uranyl nitrate ions as photo initiators, which were analyzed by NMR spectroscopy. The terpolymer compositions were determined by Goldfinger's equation using comonomer reactivity ratios: $r_{as} = 0.04$; $r_{sa} = 0.31$; $r_{am} = 0.17$, $r_{ma} = 1.45$; $r_{sm} = 0.52$; $r_{ms} = 0.47$. The terpolymer compositions were also determined from the quantitative $^{13}\text{C}(^1\text{H})$ -NMR spectroscopy. The sequence distribution of the acrylonitrile-, styrene-, and methyl methacrylate-centered triads were determined from the $^{13}\text{C}(^1\text{H})$ -NMR spectra of the terpolymers and are in good agreement with triad concentrations calculated from the statistical model. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3026–3032, 1999

Key words: acrylonitrile–styrene–methyl methacrylate terpolymer; carbon-13 NMR; sequence distribution; microstructure; multicomponent

INTRODUCTION

The addition of the third component to a binary copolymer system can give desirable chemical, physical, and mechanical properties that differs from those of the copolymers. Therefore, the interest in multicomponent polymerization in industry and academia is increasing.¹ However, the properties of a copolymer depends upon its microstructure.² The study of the microstructure of terpolymers requires prior knowledge about comonomer sequences in the binary copolymer system of the constituents.

The microstructure of the acrylonitrile–styrene (A–S) copolymer has been reported.³ The comonomer sequences and cotacticity in the acrylonitrile–methyl methacrylate (A–M) have been published.^{4–10}

In this publication we report the sequence distribution of the acrylonitrile–styrene–methyl methacrylate (A–S–M) terpolymer prepared by

photopolymerization using uranyl ions as photo initiators. The monomer composition and triads sequences distribution obtained from the $^{13}\text{C}(^1\text{H})$ -NMR spectra are compared with those calculated from the statistical model, using reactivity ratios determined from the EVM program. The triads concentrations calculated from $^{13}\text{C}(^1\text{H})$ -NMR are in good agreement with those determined from the statistical model.

EXPERIMENTAL SECTION

Acrylonitrile (Merk, Germany), Styrene (Commercial, India) and methyl methacrylate (BDH, England) monomers were vacuum-distilled under reduced pressure and stored below 5°C. Acrylonitrile–styrene–methyl methacrylate terpolymers were prepared by photopolymerization using a uranyl ion as initiator. The percent conversion was kept below 10% by precipitating the terpolymers in methanol. The terpolymers were further purified by dissolving in chloroform and reprecipitated in methanol. The terpolymer compositions were determined experimentally by quantitative

Correspondence to: A. S. Brar.

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Table I Terpolymer Compositions for Acrylonitrile–Styrene–Methyl Methacrylate Terpolymers (A/S/M)

No.	Monomer	Feedmole Fraction	Mole Fraction in Terpolymer		$M_w \times 10^{-5}$ (g/mol)
			a	b	
1	A	0.63	0.46	0.44	1.07
	S	0.22	0.40	0.41	
	M	0.15	0.14	0.15	
2	A	0.42	0.37	0.35	0.71
	S	0.36	0.46	0.46	
	M	0.22	0.17	0.19	
3	A	0.23	0.27	0.25	0.72
	S	0.53	0.53	0.53	
	M	0.24	0.20	0.22	
4	A	0.41	0.32	0.31	1.28
	S	0.16	0.29	0.29	
	M	0.43	0.39	0.40	
5	A	0.29	0.22	0.22	1.43
	S	0.08	0.15	0.16	
	M	0.63	0.63	0.62	
6	A	0.29	0.30	0.28	0.35
	S	0.44	0.48	0.48	
	M	0.27	0.22	0.24	

a, terpolymer composition using quantitative ^{13}C -NMR spectroscopy; b, terpolymer composition using statistical model using Alfrey–Goldfinger's equations. M_w is weight average molecular weights.

$^{13}\text{C}(^1\text{H})$ -NMR, using the inverse gated-pulse program, where relaxation delay was kept at 10 sec. The average molecular weight (M_n and M_w) of the terpolymers was determined by GPC in THF at $30^\circ \pm 0.1^\circ$, using polystyrene as the narrow standard.

The ^1H - and $^{13}\text{C}(^1\text{H})$ -NMR spectra were recorded in CDCl_3 on a Bruker 300-MHz DPX spectrometer at a frequency of 300.13 MHz and 75.5 MHz, respectively, using TMS as an internal standard. The details of the Lorentzian-shape curve fitting have been described elsewhere.¹¹

RESULTS AND DISCUSSION

The composition of the acrylonitrile–styrene–methyl methacrylate terpolymers were determined from $^{13}\text{C}(^1\text{H})$ -NMR, using a pulse repetition time of 10 sec, which was more than five times the T_1 values of the carbon signals in the A–S–M terpolymer. The terpolymer composition data were calculated employing Goldfinger's equation,¹² using the reactivity ratios of $r_{as} = 0.04$, $r_{sa} = 0.31$, $r_{am} = 0.17$, $r_{ma} = 1.45^4$, $r_{ms} = 0.52$, and $r_{sm} = 0.47$. These compositions were then determined

with those determined experimentally (NMR), as shown in Table I. The A–S, S–M, and A–M copolymer systems were prepared and the reactivity ratios were calculated by Brar et al.⁴ The spin-lattice relaxation time (T_1) was determined using the inversion–recovery method with pulse sequences of $(180-\tau-90-t)_n$. The spin-lattice relaxation time (T_1) of the carbon resonance of the terpolymer in CDCl_3 was measured at 75.5 MHz at 23°C . The T_1 values for the nitrile, quaternary, and carbonyl carbons are 0.54 s, 0.69 s, and 1.82 s, respectively.

^1H -NMR Studies

The ^1H -NMR spectrum of the acrylonitrile–styrene–methyl methacrylate terpolymer (A–S–M) ($A = 0.32$, $S = 0.29$, $M = 0.39$, mol % in the terpolymer) is shown in Figure 1. The resonance signals in the spectrum were assigned by comparing them with the ^1H -NMR spectra of the A–S, S–M, and A–M copolymers. The methylene ($-\text{CH}_2$) and methine ($-\text{CH}$) protons of the terpolymer overlaps in the region δ 1.25–3.20 ppm, whereas the aromatic protons of the styrene resonances as multiplet are around δ 6.4–7.5 ppm.

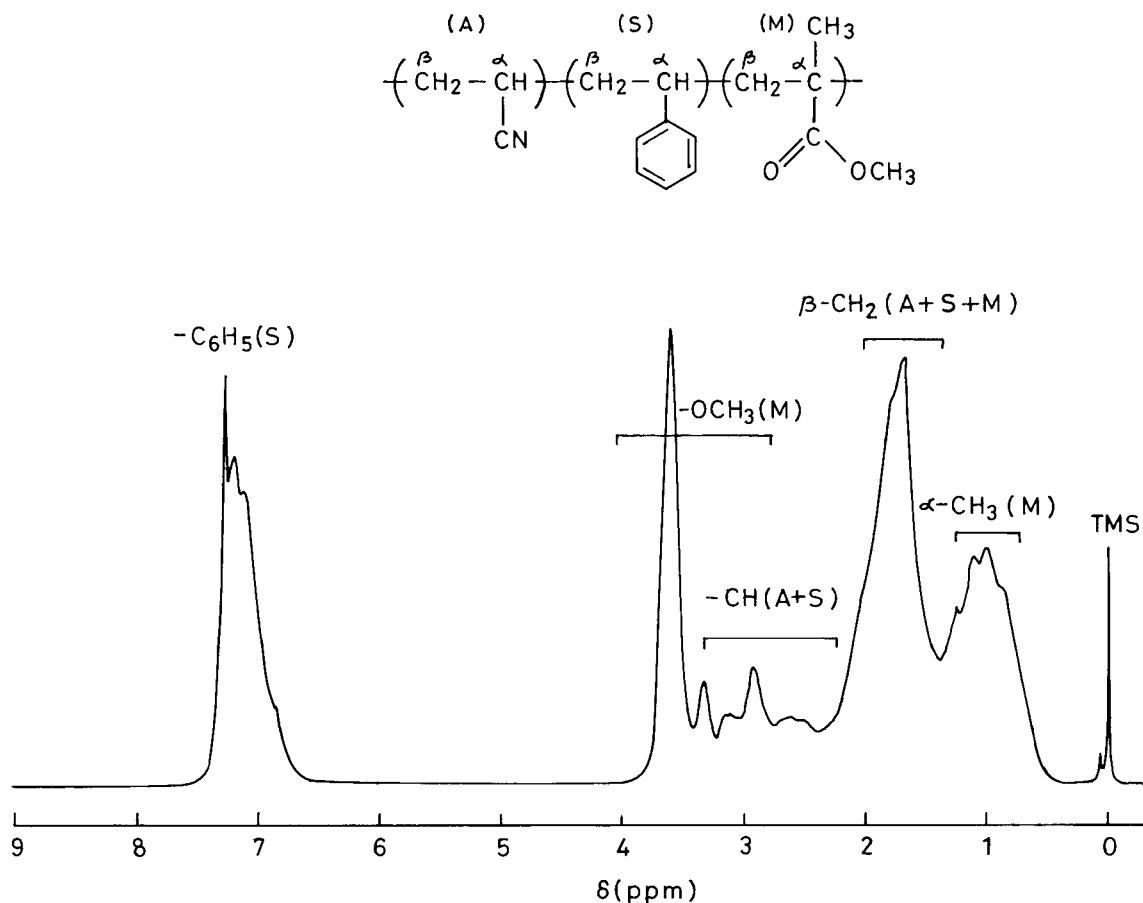


Figure 1 The ^1H -NMR spectrum of the acrylonitrile–styrene–methyl methacrylate terpolymer (A–S–M) ($A = 0.32$, $S = 0.29$, $M = 0.39$, mol % in the terpolymers) in CDCl_3 .

The α -methyl protons are assigned around δ 0.6–1.4 ppm, whereas the methoxy protons ($-\text{OCH}_3$)_M protons show a multiplet around δ 2.8–3.8 ppm.

^{13}C -NMR Studies

The $^{13}\text{C}(^1\text{H})$ -NMR spectra of the A–S–M ($A = 0.32$, $S = 0.29$, $M = 0.39$, mol % in the terpolymer) terpolymer in CDCl_3 is shown in Figure 2. The resonance signals were assigned by comparing the $^{13}\text{C}(^1\text{H})$ -NMR spectra of the A–S, S–M, and A–M copolymers.

The resonance signal at δ 17.5–24.4 ppm is that of α -methyl carbon of the M-unit. This signal is observed in terpolymer spectra with very large M-content. The methine carbon of the A-unit appears as multiplet at δ 24.4–28.0 ppm, which overlaps with the methyl carbon of the M-unit in the $^{13}\text{C}(^1\text{H})$ -NMR spectra. The methylene carbons of the A-, S-, and M-units resonate in the region of δ 36.0–53.0 ppm, which are overlapped by the qua-

ternary carbon resonance (δ 42.3–45.5 ppm) of the M-unit and the methine carbon of the S-unit (δ 36.0–42.0 ppm). The splitting of the methine carbon of the A-unit is due to compositional triads sequences. The methoxy carbon ($-\text{OCH}_3$) of the M-unit appears as a multiplet and is assigned around δ 45.0–53.0 ppm.

The nitrile carbon ($-\text{CN}$) resonance shows signals around δ 118.0–124.0 ppm, which are sensitive to the distribution of the respective A-centered monomers sequences. The multiplets around δ 138.0–146.5 ppm are assigned to quaternary carbon ($=\text{C}=\text{C}=\text{C}$) resonances in the phenyl group of the S-unit. The carbonyl carbon ($=\text{C}=\text{O}$) resonance shows multiplet around δ 173.0–178.5 ppm, indicating that they are also sensitive to compositional sequences. The expanded $^{13}\text{C}(^1\text{H})$ -NMR spectra of the nitrile, quaternary, and carbonyl resonance of the A–S–M terpolymer is shown in Figure 3(a–c).

The expansion of nitrile carbon resonance of the A–S–M terpolymer is shown in Figure 3(a).

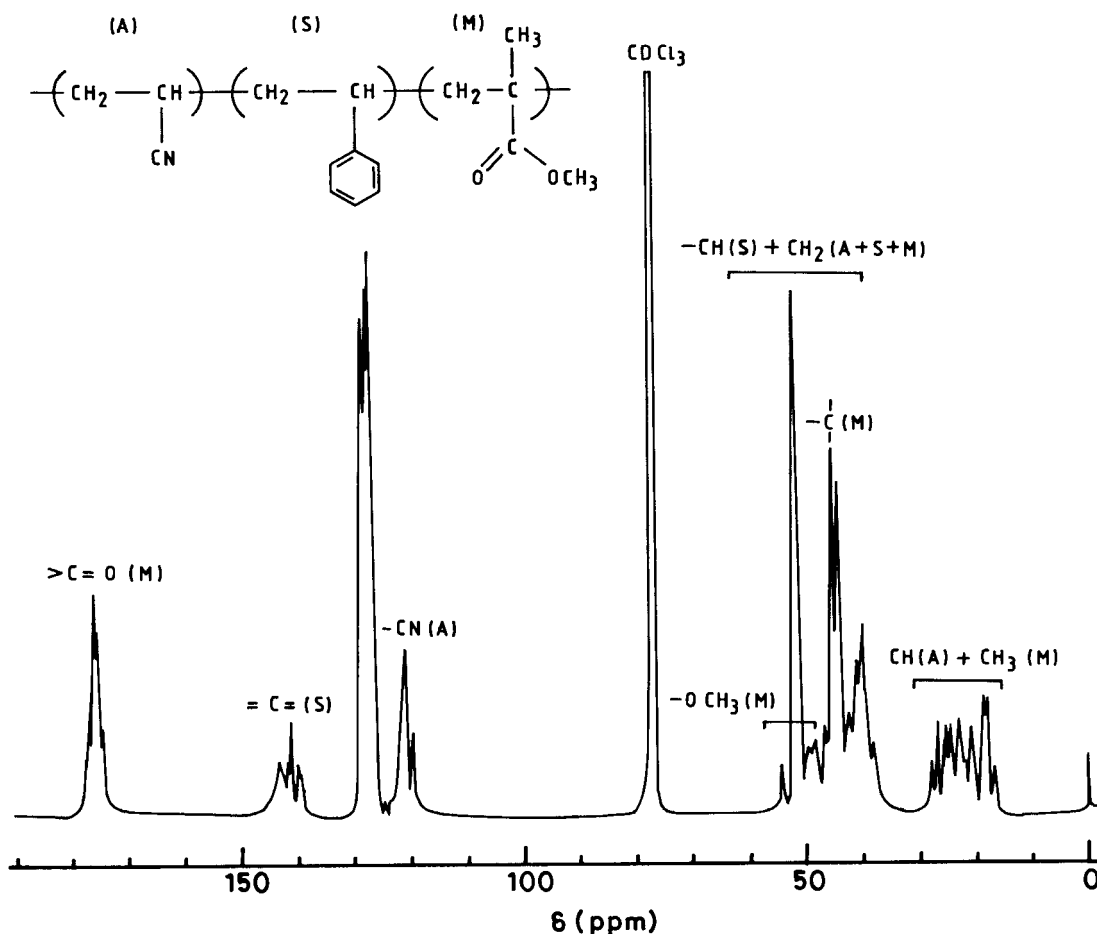


Figure 2 The $^{13}\text{C}(^1\text{H})$ -NMR spectra of the acrylonitrile-styrene-methyl methacrylate terpolymer (A-S-M) ($A = 0.32$, $S = 0.29$, $M = 0.39$, mol % in the terpolymers) in CDCl_3 .

The signals at $\delta 118$ – 119.2 , $\delta 119.2$ – 120.5 , and $\delta 121.6$ – 122.3 ppm increase as the concentration of the A-units in the terpolymer increases and are assigned to acrylonitrile (A)-centered AAA, AAS, and AAM triad sequences, respectively. The resonance signal at $\delta 120.5$ – 121.0 ppm increases in intensity with increase in the concentration of the S-unit and was assigned to the SAS triad. The resonance signal at $\delta 121.0$ – 121.6 ppm was assigned to the SAM triad. The resonance signals in the region $\delta 122.3$ – 124.0 ppm increase in intensity as the concentration of the M-unit content in the terpolymer increases. These resonance signals are assigned to MAM triads.

The quaternary carbon expansion of $^{13}\text{C}(^1\text{H})$ -NMR spectra of the styrene unit of the A-S-M terpolymer is shown in Figure 3(b). The resonance signals in the region at $\delta 137.0$ – 148.0 ppm are assigned to S-centered triads of the quaternary carbon by comparing them with the spectra of the three copolymer systems: A-S, S-M, and

A-M. The resonance signals at $\delta 137.3$ – 140.2 ppm are assigned to the ASA triad as it increases with the concentration of the A-unit. The resonance signals at $\delta 140.2$ – 141.3 and $\delta 144.0$ – 145.4 ppm increase with the increase in the concentration of the S-units in the terpolymer, which were assigned to the SSA and SSM triads, respectively. A sharp broad signal at $\delta 141.3$ – 142.5 ppm was assigned to the ASM triad. The triad at $\delta 142.5$ – 144.3 ppm increases with the increase in the methyl methacrylate content in the terpolymers. This resonance signal was assigned to the MSM triad. The resonance signal at $\delta 145.4$ – 147.7 ppm is assigned to the SSS triads.

The expanded $^{13}\text{C}(^1\text{H})$ -NMR spectra of the A-S-M terpolymer of the carbonyl carbon resonance is shown in Figure 3(c). The resonances around $\delta 173.0$ – 174.8 ppm increase in intensity with the increase in the concentration of the A-unit in the terpolymer and were assigned to the AMA triad sequence. The presence of an S-unit

adjacent to an M-unit could cause a smaller shielding of the central carbonyl carbon (M-unit) than for the adjacent A-unit. Therefore, the reso-

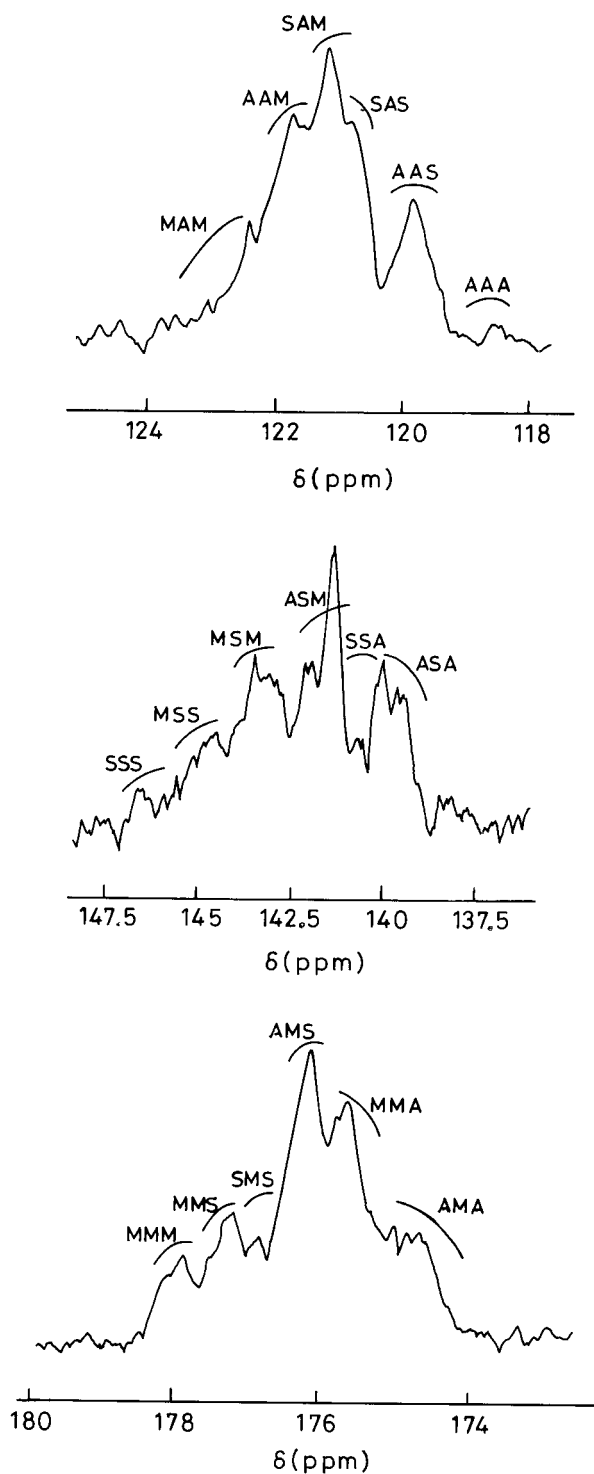


Figure 3 The expansion of the ^{13}C -NMR spectra of the acrylonitrile-styrene-methyl methacrylate terpolymers ($A = 0.32$, $S = 0.29$, $M = 0.39$, mol % in the terpolymers): (a) nitrile region, (b) quaternary region, and (c) carbonyl region.

Table II Calculated and Observed Fractions of A-Centered Triads in Acrylonitrile-Styrene-Methyl Methacrylate Terpolymers

No.	Terpolymer Composition			Triads	Triad Fraction	
					a	b
1	0.46	0.40	0.14	AAA	—	—
				AAS	0.09	0.13
				SAS	0.43	0.45
				SAM	0.34	0.32
				AAM	0.07	0.05
				MAM	0.07	0.05
2	0.27	0.53	0.20	AAA	0.01	—
				AAS	0.05	0.03
				SAS	0.78	0.81
				SAM	0.16	0.16
				AAM	—	—
				MAM	—	—
3	0.32	0.29	0.39	AAA	0.02	0.01
				AAS	0.10	0.08
				SAS	0.24	0.26
				SAM	0.42	0.42
				AAM	0.07	0.06
				MAM	0.15	0.17
4	0.30	0.48	0.22	AAA	0.01	0.01
				AAS	0.06	0.04
				SAS	0.69	0.73
				SAM	0.20	0.22
				AAM	0.01	—
				MAM	0.03	—
5	0.22	0.15	0.63	AAA	—	—
				AAS	0.01	0.02
				SAS	0.04	0.07
				SAM	0.33	0.32
				AAM	0.09	0.09
				MAM	0.53	0.50

Triads fraction determined from (a) quantitative ^{13}C -NMR spectroscopy using nitrile carbon resonance of the A-unit in the terpolymer and (b) from the statistical model using the reactivity ratios $r_{as} = 0.04$, $r_{sa} = 0.31$, $r_{am} = 0.17$, $r_{ma} = 1.45$, $r_{sm} = 0.52$, and $r_{ms} = 0.47$.

nances signals of the MMS and SMS triads have a higher chemical shift compared to those of the AMS and MMA triads, respectively. The signals around δ 174.8–175.7 and δ 177.0–177.6 ppm are assigned to the MMA and MMS triads, respectively, whereas the resonance signals at δ 175.7–176.5 and δ 176.5–177.0 ppm are assigned to the AMS and SMS triads, respectively. The resonance signal in the region at δ 177.6–178.5 ppm increases in intensity with the increase in the concentration of the M-unit in the terpolymer. By comparison with the carbonyl carbon resonances

of the poly(methyl methacrylate) (PMMA), the resonance signal was assigned to the MMM triad sequences in A-S-M terpolymers.

The relative fractions of the A-, S-, and M-centered triads were obtained by measuring the areas under various resonance signals. The experimental values of A-, M-, and S-centered triads were found to be in good agreement with those calculated theoretically using the reactivity ratios of $r_{as} = 0.04$, $r_{sa} = 0.31$, $r_{am} = 0.17$, $r_{ma} = 1.45$, $r_{sm} = 0.52$, and $r_{ms} = 0.47$ in the statistical model^{13,14} as given in the Tables II, III, and IV.

Table III Calculated and Observed Fractions of S-Centered Triads in Acrylonitrile-Styrene-Methyl Methacrylate Terpolymers

S. No	Terpolymer Composition			Triads	Triad Fraction	
					a	b
1	0.46	0.40	0.14	ASA	0.60	0.65
				ASS	0.07	0.09
				ASM	0.18	0.19
				MSM	0.06	0.04
				MSS	0.06	0.02
2	0.27	0.53	0.20	SSS	0.03	0.01
				ASA	0.15	0.18
				ASS	0.22	0.23
				ASM	0.24	0.23
				MSM	0.09	0.08
3	0.32	0.29	0.39	MSS	0.21	0.19
				MSS	0.21	0.19
				SSS	0.09	0.09
				ASA	0.32	0.34
				ASS	0.07	0.06
4	0.30	0.48	0.22	ASM	0.39	0.42
				MSM	0.15	0.13
				MSS	0.05	0.04
				SSS	0.02	0.01
				ASA	0.21	0.25
5	0.22	0.15	0.63	ASS	0.27	0.22
				ASM	0.23	0.28
				MSM	0.08	0.08
				MSS	0.16	0.12
				SSS	0.05	0.05
	0.22	0.15	0.63	ASA	0.18	0.18
				ASS	0.04	0.02
				ASM	0.43	0.47
				MSM	0.28	0.30
				MSS	0.06	0.03
				SSS	0.01	—

Triads fraction determined from (a) quantitative ¹³C-NMR spectroscopy using quaternary carbon resonance of the S-unit in the terpolymer and (b) from the statistical model using the reactivity ratios $r_{as} = 0.04$, $r_{sa} = 0.31$, $r_{am} = 0.17$, $r_{ma} = 1.45$, $r_{sm} = 0.52$, and $r_{ms} = 0.47$.

Table IV Calculated and Observed Fractions of M-Centered Triads in Acrylonitrile-Styrene-Methyl Methacrylate Terpolymers

No	Terpolymer Compositions			Triads	Triad Fractions	
					a	b
1	0.46	0.40	0.14	AMA	0.20	0.21
				MMA	0.12	0.14
				AMS	0.33	0.36
				SMS	0.18	0.16
				MMS	0.13	0.12
2	0.27	0.53	0.20	MMM	0.04	0.01
				AMA	0.06	0.01
				MMA	0.03	0.04
				AMS	0.14	0.16
				SMS	0.50	0.52
3	0.32	0.29	0.39	MMS	0.25	0.24
				MMM	0.02	0.03
				AMA	0.08	0.08
				MMA	0.25	0.22
				AMS	0.16	0.18
4	0.30	0.48	0.22	SMS	0.10	0.09
				MMS	0.23	0.26
				MMM	0.18	0.17
				AMA	0.05	0.02
				MMA	0.04	0.06
5	0.22	0.15	0.63	AMS	0.23	0.22
				SMS	0.42	0.40
				MMS	0.21	0.26
				MMM	0.05	0.04
				AMA	0.08	0.05
				MMA	0.22	0.26
				AMS	0.08	0.06
				SMS	0.06	0.03
				MMS	0.22	0.20
				MMM	0.34	0.40

Triads fraction determined from (a) quantitative ¹³C-NMR spectroscopy using carbonyl carbon resonance of the M-unit in the terpolymer and (b) from the statistical model using the reactivity ratios $r_{as} = 0.04$, $r_{sa} = 0.31$, $r_{am} = 0.17$, $r_{ma} = 1.45$, $r_{sm} = 0.52$, and $r_{ms} = 0.47$.

CONCLUSIONS

The compositional structure of the acrylonitrile-styrene-methyl methacrylate terpolymers were analyzed by ¹³C(¹H)-NMR spectroscopy. The composition of the terpolymers were obtained by quantitative ¹³C(¹H)-NMR spectroscopy, which were in excellent agreement with those calculated by Goldfinger's equation. The microstructure of the A-S-M terpolymers were obtained from ¹³C(¹H)-NMR spectroscopy only in terms of A-, S-, and M-centered triads. The microstructure was

found to be in good agreement with those calculated from the theoretical model using the reactivity ratios obtained from A-S, S-M, and A-M copolymer systems.

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