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Microstructure of *trans*-4-acryloyloxyazobenzene/methyl methacrylate copolymers by n.m.r. spectroscopy

A.S. Brar* and M. Thiyagarajan
Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India
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Trans-4-Acryloyloxyazobenzene/methyl methacrylate (A/M) copolymers were prepared by free-radical solution polymerization in DMF using AIBN as initiator. The copolymer compositions were obtained from ^{1}H n.m.r. spectroscopy. The reactivity ratios for the copolymerization of A with M were calculated using the Kelen-Tudos (KT) and non-linear error in variables model (EVM) methods. The reactivity ratios obtained from the KT and EVM methods are $r_A = 0.6 \pm 0.1$ and $r_M = 1.2 \pm 0.1$, and $r_A = 0.6 \pm 0.1$ and $r_M = 1.2 \pm 0.1$, respectively. The A- and M-centered triad concentrations were calculated from ^{13}C{^{1}H} n.m.r. spectra of copolymers and correlated with those calculated from Harwood's program using the terminal model reactivity ratios determined by EVM method. A ^{13}C DEPT (distortionless enhancement by polarization transfer) spectrum was used to differentiate the resonance signals for methine and methylene carbons in the copolymer. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: microstructure; n.m.r. spectroscopy; copolymer)

INTRODUCTION

The photochemical and photoviscosity effects and the pH control system of photoresponsive polymers are used in constructing photoactive devices in several fields, such as printing, photocopying, photolithography and photosensors[1]. The photo and thermal isomerization of optically active polymers containing side chain photochromic groups has been the subject of thorough investigation aimed at establishing useful correlation between photochromic properties and structural parameters. A photoresponsive synthetic polymer is a speciality polymer having photoreceptor chromophores, which can transfer light energy into a change in the conformation of the polymer. The basic idea for controlling properties of polymers by photoirradiation is to use photoresponsive trigger molecules[2]. Blair *et al.*[3] described photoresponsive effects on photochromic polyamides in which every monomer unit contains an azo group. It is well known that n.m.r. spectroscopy is probably the most effective method for characterizing the configurational and compositional sequences of the polymers[4,5]. DEPT is used extensively for the analysis of the overlapping carbon resonances in the ^{13}C n.m.r. spectra[6,7]. O'Donnell and co-workers[8] used DEPT for the assignment of broad and overlapping aliphatic carbon resonances. Borbely *et al.*[9] were able to assign the aliphatic carbon resonance to dyad, triad and tetrad level.

To the best of our knowledge the microstructure of *trans*-4-acryloyloxyazobenzene/methyl methacrylate (A/M) copolymer has not been reported in the literature. In our earlier publication we have reported the synthesis and microstructure of poly(*trans*-4-acryloyloxyazobenzene)[10]. In continuation of our earlier investigation we report, in this paper, the reactivity ratios obtained from the Kelen-Tudos (KT) method[11], the non-linear error in variables model (EVM)[12] method using the RREVM[13] program, and ^{13}C{^{1}H} n.m.r. spectra of the copolymers. The microstructure was obtained in terms of A- and M-centered triad sequences distribution from ^{13}C{^{1}H} n.m.r. spectra and compared with a first-order Markov statistical model. The resonance signals of methine and methylene carbons in the copolymers were resolved by C-13 DEPT n.m.r. spectroscopy.

EXPERIMENTAL

Trans-4-Acryloyloxyazobenzene/methyl methacrylate (A/M) copolymer samples were prepared by solution polymerization using AIBN (0.5%) as initiator in DMF at 65°C for 5 h under nitrogen atmosphere in a sealed tube. The copolymers were reprecipitated using $CHCl_3$/CH_3OH solvent system and were dried in vacuum. The percent conversion was kept below 10%. The average molecular weights of the copolymers were determined from gel permeation chromatography (g.p.c.) using polystyrene as narrow standard. The copolymer compositions were determined from ^{1}H n.m.r. spectra. The ^{1}H and ^{13}C{^{1}H} n.m.r. spectra were recorded in $CDCl_3$ on a Bruker DPX-300 MHz spectrometer operating at a frequency of 300.13 and 75.5 MHz for ^{1}H and ^{13}C nuclei, respectively. DEPT measurements were carried in $CDCl_3$ using the standard pulse sequence with a modulation time J of 3.7 s ($J_{CH} = 135$ Hz) with a 2 s delay time. The details of the Lorentzian shape curve fitting have been described elsewhere[14]. All regressions converged to $\chi^2 < 1$.

RESULTS AND DISCUSSION

Determination of reactivity ratios

The ^{1}H n.m.r. spectrum of the *trans*-4-acryloyloxyazobenzene/methyl methacrylate (A/M) copolymers (A, 46 mol.% in the copolymer) along with the assignment of

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* To whom correspondence should be addressed

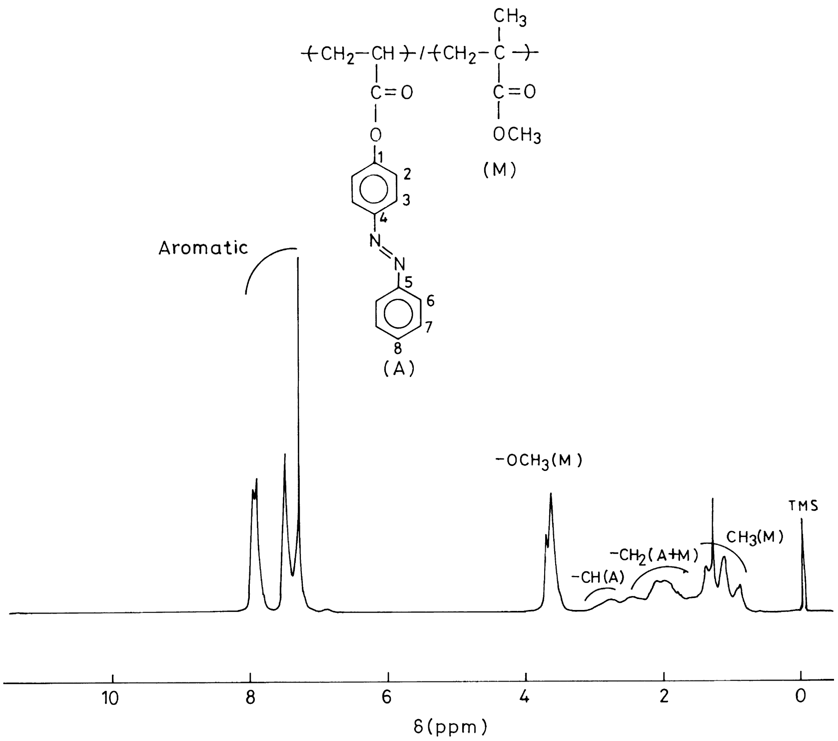

Figure 1 300 MHz ^{1}H n.m.r. spectrum of *trans*-4-acryloyloxyazobenzene/methyl methacrylate (A/M) copolymer in $CDCl_3$. (A, 46 mol.% in the copolymer) at room temperature

Table 1 Copolymer composition data and molecular weight of the copolymers by GPC measurements

Sample	f_A	f_M	F_A	F_M	$\bar{M}_w$ ($\times 10^{-4}$ g/mol)	$\bar{M}_n$ ($\times 10^{-4}$ g/mol)	Poly-dispersity
AM1	0.30	0.70	0.26	0.74	3.6	2.2	1.68
AM2	0.35	0.65	0.30	0.70	3.5	2.3	1.52
AM3	0.45	0.55	0.38	0.62	2.8	2.4	1.16
AM4	0.55	0.45	0.46	0.54	2.4	1.5	1.57
AM5	0.65	0.35	0.51	0.49	2.7	1.2	2.17
AM6	0.75	0.25	0.66	0.34	2.5	1.7	1.42

f_A and f_M are the mole fractions of A and M comonomers, respectively, in feed

F_A and F_M are the mole fractions of A and M comonomers, respectively, in the copolymer

$\bar{M}_w$ and $\bar{M}_n$ are the weight and number average molecular weights of the copolymers, respectively

various resonance signals is shown in *Figure 1*. The copolymer compositions were calculated from the relative intensities of the phenyl proton signals of the A-unit and methoxy proton signals of the M-unit in the ^{1}H n.m.r. using the following expression

$$F_M = \frac{[3I(OCH_3)_M]}{[I(-\phi_2)_A + 3I(OCH_3)_M]}$$

where F_M is the mole fraction of methyl methacrylate in the copolymer, $I(\text{-}OCH_3)_M$ and I(-phenyl)$_A$ are the intensities of the methoxy (M-unit) and phenyl (A-unit) proton resonances in the copolymer, respectively. *Table 1* shows the copolymer composition and the molecular weight distribution of various A/M copolymers. The copolymer composition data were used to calculate the terminal model reactivity ratios by the KT method. The reactivity ratios obtained from the KT method were taken as initial estimates for the reactivity ratios calculated from the EVM method using the RREVM program. The reactivity ratios obtained are $r_A = 0.6 \pm 0.1$ and $r_M = 1.2 \pm 0.1$ (KT) and $r_A = 0.6 \pm 0.1$ and $r_M = 1.2 \pm 0.1$ (RREVM program). The theoretical composition curve obtained from the copolymer composition equation using terminal model reactivity ratios ($r_A = 0.6 \pm 0.1$ and $r_M = 1.2 \pm 0.1$) along with the experimental points are shown in *Figure 2*. The experimental points are in good agreement with the theoretical one, and indicate that the values of reactivity ratios obtained from the copolymer composition data are more reliable.

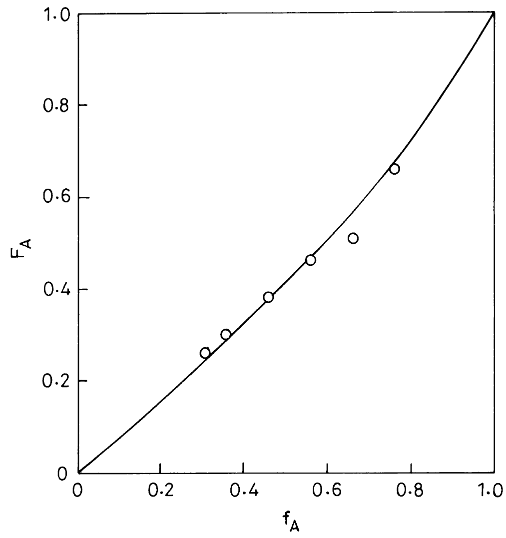

Figure 2 The theoretical composition curve (——) obtained from copolymer composition equation using terminal model reactivity ratios ($r_A = 0.6 \pm 0.1$, $r_M = 1.2 \pm 0.1$) along with experimental points (○)

Carbon-13 n.m.r. studies

Figure 3 shows $^{13}C\{^1H\}$ n.m.r. spectrum of the A/M copolymer (A, 46 mol.% in the copolymer) along with

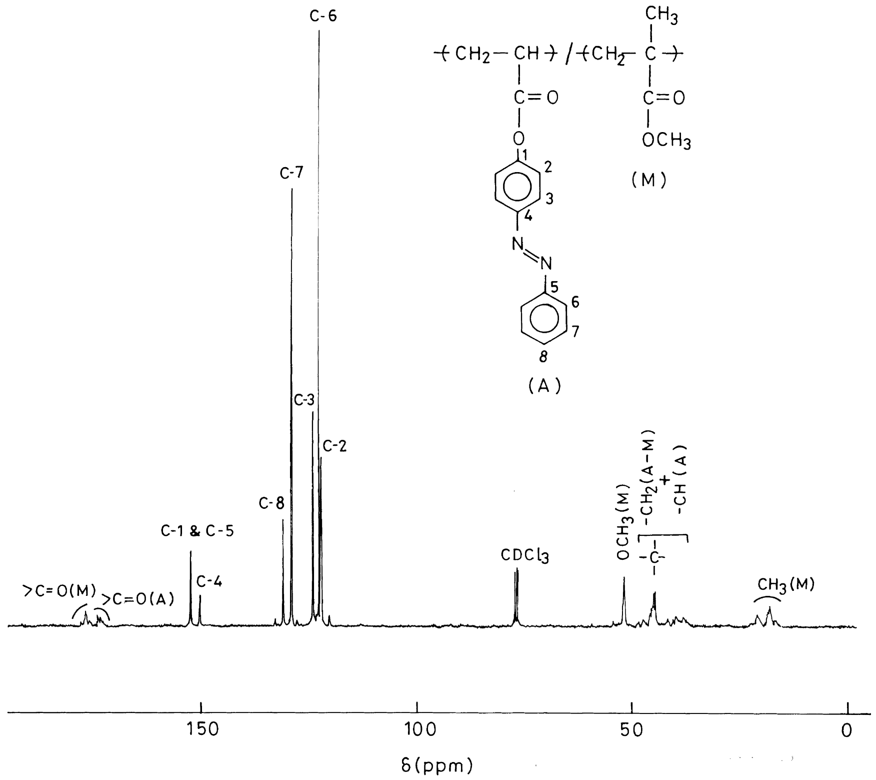

Figure 3 $^{13}C\{^1H\}$ n.m.r. spectrum (75 MHz) of A/M copolymer (A, 46 mol.% in the copolymer) in $CDCl_3$ at room temperature

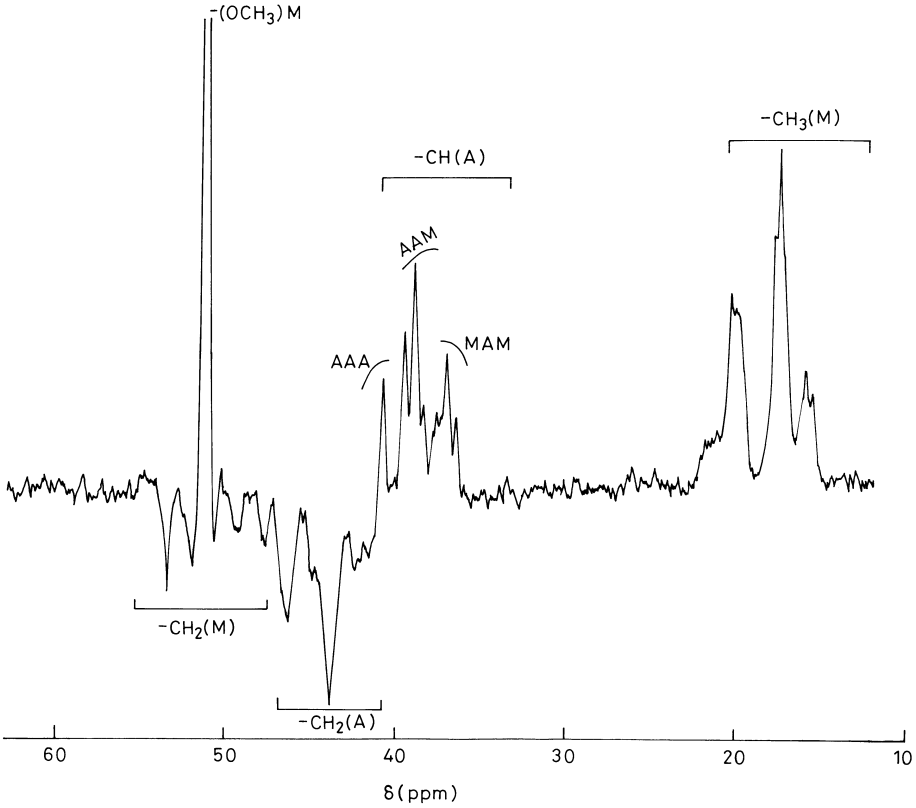

Figure 4 The DEPT-135 spectrum of A/M copolymer (A, 46 mol.% in the copolymer) in $CDCl_3$

signal assignments. The assignments of aromatic carbon resonances of the A-monomeric unit have been reported by Solaro *et al.*[15] for poly(*trans*-4-methacryloyloxyazobenzene/methyl methacrylate). *Figure 4* shows the DEPT-135 spectra of the A/M copolymers. In the DEPT-135 spectrum, the methyl and methine carbon resonances have positive phase, and methylene carbon resonances have negative phase. The methyl and methine carbon resonances range from $\delta = 15.0–22.5$ and 35.7–41.2 ppm, respectively. The methylene carbon signals resonance around $\delta = 41.2–55.8$ ppm. The signals around $\delta = 41.2–47.3$ and 47.3–55.8 ppm are assigned to methylene carbon resonances of

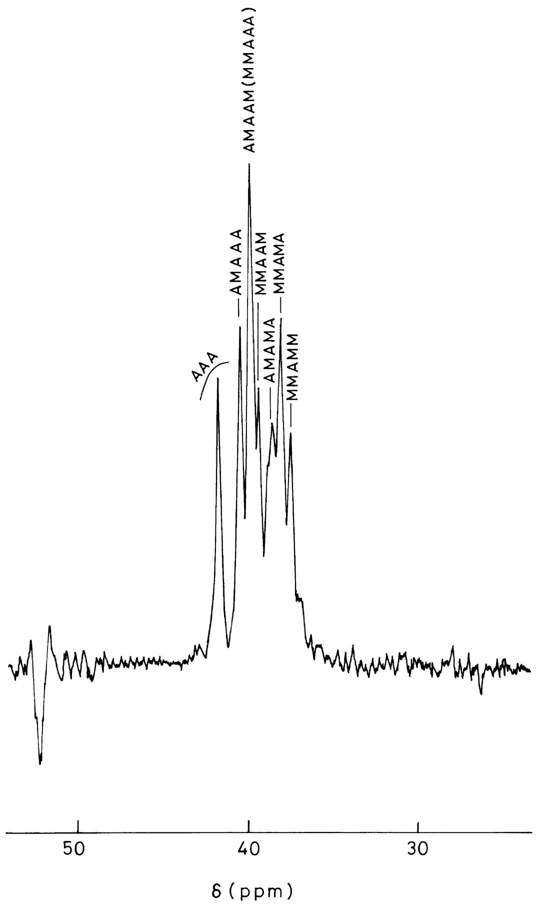

Figure 5 The DEPT-90 spectrum showing the methine carbon signals of A/M copolymer (A, 46 mol.% in the copolymer) in $CDCl_3$

A- and M-monomeric units, respectively, on the basis of the variation of the signals with copolymer composition. The methoxy carbon resonance appears at $\delta = 51.0$ ppm.

Figure 5 shows the DEPT-90 spectrum of the A/M copolymer, where only methine carbon resonances are detected. The methine carbon region can be split into three envelopes. These three envelopes vary with the change in the copolymer composition and can be assigned to AAA ($\delta = 41.7$ ppm) AAM(MAA) ($\delta = 39.2$–41.0 ppm) and MAM ($\delta = 36.5$–39.2 ppm) triad sequences. In the AAM(MAA) triad fraction, further splittings are assigned to pentad sequences on the basis of compositional variation. Therefore, the methine carbon signals at $\delta = 39.4$, 39.9 and 40.5 ppm are assigned to MMAAM, AMAAM(MMAAA) and AMAAA, respectively. The MAM triad fractions is more sensitive to compositional sequences. There are three clear regions, which show variation with composition, and are assigned to pentad sequences. The methine carbon signals at $\delta = 37.4$, 38.0 and 38.6 ppm are assigned to MMAMM, MMAMA and AMAMA, respectively.

The expanded carbonyl carbon resonance signals of the M-monomeric unit in the A/M copolymer is shown in *Figure 6a*. Since the carbonyl carbon signals in poly(methylmethacrylate) (PMMA) are sensitive to tacticity, the carbonyl carbon signals of A/M copolymers are around $\delta = 175.4$–178.8 ppm, which exhibits configurational as well as compositional sensitivity. The resonance signals around $\delta = 177.4$–178.8 ppm decreases, while the resonance signals around $\delta = 175.4$–176.4 ppm increases in intensity with the decrease in the concentration of the M-unit in the copolymers. Therefore the signals around $\delta = 177.4$–178.8 and 175.4–176.4 ppm are assigned to MMM and AMA triad sequences, respectively. The signals around $\delta = 176.4$–177.4 ppm are assigned to AMM(MMA) triad sequence. The relative fractions of various triads MMM, MMA and AMA were obtained from the resonance signal area measurements.

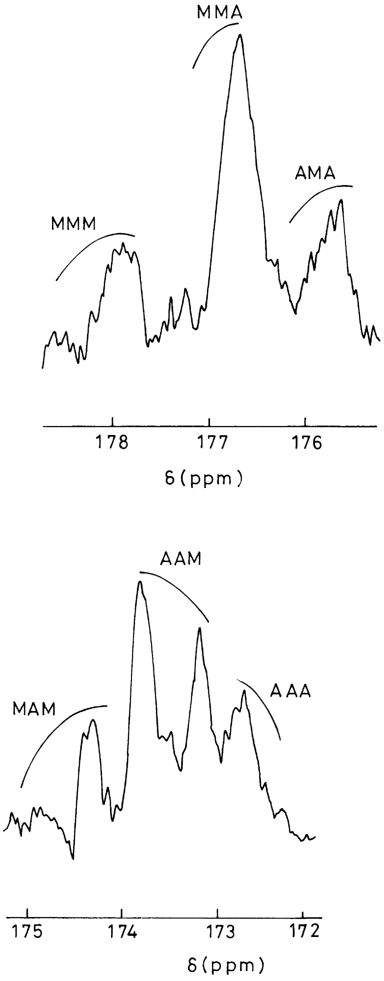

Figure 6 (*a*) Expanded carbonyl carbon resonance of the M-monomeric unit. (*b*) Expanded carbonyl carbon resonance of the A-monomeric unit in (A/M) (A, 46 mol.% in the copolymer) copolymer

The expanded carbonyl carbon resonance of the A-monomeric unit in the A/M copolymer (A, 46 mol.% in the copolymer) is shown in *Figure 6b*. By comparison with poly(*trans*-4-acryloyloxyazobenzene) (PAB), signals in the region of $\delta = 172.3$–172.9 ppm, which increase in intensity with increase in the concentration of the A-unit in the copolymer, are assigned to AAA triad sequences. The signals in the region of $\delta = 174.0$–175.2 ppm, which decrease in intensity with the decrease in the concentration of the M-monomeric unit in the copolymer, are assigned to MAM triad sequences. The signals in the region of $\delta = 172.9$–174.0 ppm are assigned to AAM(MAA) triad sequences. The relative fractions of AAA, AAM(MAA) and MAM triads were obtained by measuring the area of the resonance signal.

Assuming the Alfrey–Mayo model to be valid for the low-conversion copolymers. The various A- and M-centered triad fractions were calculated using the terminal model reactivity ratios ($r_A = 0.6 \pm 0.1$ and $r_M = 1.2 \pm 0.1$). The relative fraction of A- and M-centered triads determined from the carbonyl carbon signals are in good agreement with those obtained from Harwood's[16] program using the terminal model reactivity ratios (*Table 2*). From

Table 2 The calculated and observed A- and M-centered triad fractions of A/M copolymers

Mole fraction of A in the copolymer	Triads	Triad fractions	
		a	*b*
0.26	AAA	0.05	0.05
	AAM	0.34	0.34
	MAM	0.61	0.62
	MMM	0.55	0.55
	MMA	0.38	0.38
	AMA	0.07	0.07
0.30	AAA	0.08	0.06
	AAM	0.39	0.38
	MAM	0.53	0.56
	MMM	0.48	0.48
	MMA	0.41	0.43
	AMA	0.11	0.09
0.38	AAA	0.13	0.12
	AAM	0.44	0.45
	MAM	0.43	0.43
	MMM	0.34	0.36
	MMA	0.51	0.48
	AMA	0.15	0.16
0.46	AAA	0.19	0.19
	AAM	0.52	0.49
	MAM	0.29	0.32
	MMM	0.23	0.25
	MMA	0.51	0.50
	AMA	0.26	0.25
0.51	AAA	0.29	0.29
	AAM	0.50	0.50
	MAM	0.21	0.21
	MMM	0.14	0.16
	MMA	0.49	0.48
	AMA	0.37	0.37
0.66	AAA	0.45	0.43
	AAM	0.45	0.45
	MAM	0.10	0.12
	MMM	0.08	0.08
	MMA	0.42	0.41
	AMA	0.50	0.51

[a] Triad fractions obtained from ^{13}C n.m.r. spectra of carbonyl carbon resonance signals

[b] Triad fractions calculated using $r_A = 0.6 \pm 0.1$ and $r_M = 1.2 \pm 0.1$ from Harwood's program

Table 3 Copolymerization parameter of A/M copolymers by ^{13}C n.m.r. spectroscopy

Sample	F_A	$P_{A/M}$	$P_{M/A}$	r_A	r_M
AM1	0.26	0.26	0.78	0.66	1.22
AM2	0.30	0.32	0.73	0.70	1.17
AM3	0.38	0.41	0.65	0.66	1.20
AM4	0.46	0.52	0.55	0.67	1.15
AM5	0.51	0.62	0.46	0.63	1.16
AM6	0.66	0.71	0.33	0.69	1.23

$P_{A/M}$, probability of addition of monomeric unit A to a growing chain ending in M; $P_{M/A}$, probability of addition of monomeric unit M to a growing chain ending in A. Average values of reactivity ratios $r_A = 0.6 \pm 0.02$ and $r_M = 1.2 \pm 0.03$ obtained from ^{13}C n.m.r. using Harwood's program

the triad concentration, the conditional probabilities $P_{A/M}$ and $P_{M/A}$ were calculated[17]. Using the $P_{A/M}$ and $P_{M/A}$ conditional probabilities, terminal model reactivity ratios r_A and r_M were calculated. The average value of the reactivity ratios are $r_A = 0.6 \pm 0.02$ and $r_M = 1.2 \pm 0.03$ (*Table 3*). The various A- and M-centered triad concentrations calculated using the terminal model reactivity ratios obtained from the EVM method gave a better correlation with those obtained using the ^{13}C n.m.r. spectrum.

CONCLUSION

The terminal model reactivity ratios were determined from the KT and EVM methods and ^{13}C{^{1}H} n.m.r. spectroscopy and were in good agreement. The microstructure was determined in terms of A- and M-centered triad fractions from the ^{13}C{^{1}H} n.m.r. spectroscopy. There was a good agreement between the triad fractions calculated from the terminal model reactivity ratios and those obtained from n.m.r. spectroscopy. The copolymerization of A and M follows the first-order Markov model. DEPT experiments were used to distinguish the methine and methylene carbon resonance signals which were then assigned to triad and pentad sequences.

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