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Characterization of Intramolecular Microstructure of Styrene–Methyl Methacrylate Copolymers: New ^{1}H NMR Assignments Supported by 2D-NOESY NMR

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ABSTRACT: The methoxy ^{1}H NMR signals in the δ 2.10–3.70 region for statistical styrene–methyl methacrylate copolymers have been reassigned for several methyl methacrylate centered triad/pentad resonances. Former literature assignments for statistical copolymers were inconsistent with experimental results. New peak assignments are completely based on pentad sequence distributions. Supporting evidence for these reassignments is 2-fold: First, comparison of theoretically calculated and experimentally observed peak areas, and the use of various independent procedures for the determination of the coisotacticity parameter σ, yields consistent results ($\sigma = 0.44$). Second, 2D-NOESY (Nuclear Overhauser effect spectroscopy) NMR experiments were carried out for alternating as well as for statistical copolymers. The results supported the proposed reassignments.

Introduction

High-resolution nuclear magnetic resonance (NMR) spectroscopy has been particularly effective in the determination of the intramolecular chain structure of polymers. The intramolecular (sequence distribution and tacticity) and intermolecular (chemical composition molar mass distribution) copolymer microstructure is important, because it may supply information about the monomer addition process, e.g., about the preference of monomers to add in the (co)iso- or cosyndiotactic configuration.[1-3] Moreover, knowledge about the inter- and intramolecular structure is of paramount importance for the understanding of relations between molecular structure and polymer properties.[4]

In our laboratories much attention has been paid to low- and high-conversion solution and high-conversion emulsion S–EMA[5] (styrene–ethyl methacrylate) and S–MA[6] (styrene–methyl acrylate) copolymers. Modeling of high-conversion solution and emulsion copolymers requires experimental data on sequences and sometimes tacticities to confirm the correctness of the model. Also, for S–MMA (styrene–methyl methacrylate copolymers) an unambiguous assignment of proton NMR spectra is a prerequisite for comparing the experimental results with our kinetic model, used in the modeling of several polymerization processes.

Several groups have (re)investigated the ^{1}H NMR spectra of statistical S–MMA copolymers, i.e., the groups of Ito/Yamashita,[7-10] Bovey[11] and Harwood/Ritchey,[3,12] and San Roman et al.,[13] and the Eastman Kodak group (Uebel/Dinan).[14,15] Alternating S–MMA copolymers have been recently analyzed by the groups of Hirai/Koinuma/Tanabe,[16,17] Niknam/Harwood,[18] and Heffner/Bovey.[19] In early studies,[3,7-12] the 40–60-MHz proton NMR spectra of statistical copolymers were found to exhibit a multiplicity in the δ 2.1–3.7 region characteristic of methoxy protons. The methoxy region was broken into three composite peak groupings, designated X, Y, and Z, respectively. The improved resolution of the methoxy region in ^{1}H NMR spectra recorded at higher magnetic fields[13-15] leads to significantly more observable fine structure. The complex peak envelopes have been reinterpreted in terms of six major peak groupings (contrary to the earlier observed three peak groupings), each of which is attributed to an individual M-centered triad or to groups of M-centered triads.

Subsequently, San Roman et al.[13] and Uebel[14] have partly reassigned resonances (270 MHz) in the oxymethylene region of the M-centered triads and pentads. Unfortunately, the improvements of Uebel, valid for S–MMA copolymers, appeared to be inapplicable to S–EMA copolymers,[5] and a new set of peak triad/pentad assignments was proposed, confirmed by data from ^{13}C NMR. A reinvestigation of the S–MMA proton NMR spectra of Uebel[14] at 400 MHz has been performed by a joined effort of the groups of Kale/O'Driscoll and Uebel/Dinan.[15] The spectra of the previous series of statistical nondeuterated copolymers[14] and a series of deuterated copolymers of styrene-d_8 and MMA were analyzed quantitatively.[15] In the Z peak region (Ito notation) a methine–methoxy overlap has been proven to exist (already pointed out by Harwood[3]). As a result the peak areas reported earlier by Uebel[14] have been remeasured.[15] Kale et al.[15] have also suggested a minor correction in the assignments; moreover, a different method has been used to estimate the coisotacticity parameter σ in comparison to the method put forward in ref 14. This leads to a value different from Uebel's earlier proposal ($\sigma = 0.63$[14] and $\sigma = 0.44$[15]).

The theoretical triads and pentads have been calculated by using the ultimate model (i.e., Alfrey/Mayo kinetics).[1] The copolymer composition could be described successfully with the ultimate model. However, Fukuda[20] and O'Driscoll[21] have shown that, on the contrary, this model is apparently incapable of describing the kinetic process (i.e., the propagation rate k_p). From this we conclude that, besides the copolymer composition, the sequences can also be readily described by the ultimate model.

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Although Kale et al.[15] have achieved a better agreement between the experimentally observed peak areas and those predicted by theory, an inconsistency remains in some parts of their assignments. Different estimation procedures for the coisotacticity parameter σ lead to widely differing σ_{SM} values, as will be shown in this paper. This coisotacticity parameter σ_{SM} ($=\sigma$) is defined as a measure of the probability that alternating S- and MMA-centered triads adopt a coisotactic configuration. In order to explain these discrepancies in peak areas and σ values, we propose a new M-centered mixed configurational triad, compositional pentad sequence assignment, based on a comparison of experimentally observed and theoretically predicted peak areas for a series of low-conversion solution copolymers and supported by 2D-NOESY data on both statistical and alternating S–MMA copolymers. 2D-NOESY is an NMR technique, specifically tailored to detect spatial relations over short distances (generally <5 Å). By this technique, the close proximity of styrene units to the methoxy group can directly be shown through nuclear Overhauser effects. A recent 2D-NOESY study on an alternating S–MMA copolymer has been published by Heffner et al.[19] Up to now the NOESY spectra of statistical copolymers have not been published to the best of our knowledge, possibly due to the complexity in the OCH_3 region. The present paper shows that, in spite of the complex grouping, additional information can be obtained. More cross peaks were observed than would be possible according to the earlier proposed assignments of iso- and heterotactic S–MMA triads, which justifies a reassignment in pentads.

Experimental Section

The monomers styrene and methyl methacrylate (Merck) were distilled at reduced pressure under nitrogen. The middle fraction of the distillate was collected and used. The free-radical initiator AIBN (Fluka p.a.) was recrystallized once from methanol. The solution-synthesized copolymers were prepared in a 100-mL glass vessel, thermostated at 323 K. The total monomer concentration was 3 mol/L in toluene. The total conversion was determined by means of solid weight and amounted to 5 wt %. The initiator concentration was 8 mmol/L. To isolate and purify the copolymer, the reaction mixture was poured into a 10-fold excess of cold hexane. The final product was dried at 328 K in a vacuum oven for at least 16 h at 10^{-5} Torr.

The alternating copolymer was prepared as published by Tanabe,[22] employing zinc chloride initiator, in the dark at 278 K. The alternating structure is confirmed by proton NMR.

^1H NMR spectra were recorded with a 400-MHz (Bruker AM 400) spectrometer at 298 K, using $CDCl_3$ as a solvent and locking agent. Generally, the spectra were obtained by using a spectral width of 6024 Hz, an acquisition time of 2.7 s, a flip angle of 45°, and a pulse delay of 5 s. Spectra were obtained after accumulating 64 scans, using a sample concentration of 1% (w/v). The digital resolution amounted to 0.38 Hz, corresponding to a data length of 32 K. In performing quantitative NMR measurements via compositional sequence placements, one must take into account differences in spin–lattice relaxation times (T_1). The T_1's were measured by inversion recovery.

The phase-sensitive 2D-NOESY[23] experiment employed a $\pi/2$–t_1–$\pi/2$–τ_m–$\pi/2$–t_2 pulse sequence[24,25] and has been used for the observation of dipole–dipole interactions between neighboring S and MMA units. The 2D-NOESY experiments were recorded on a Bruker AM 600 spectrometer. The polymer solutions were prepared in hexachlorobutadiene with 10% benzene-d_6 as lock. The concentrations were 2% (w/v). The spectra were recorded at a temperature of 353 K. The process data matrix consisted of 512 × 512 points covering 5882 Hz in both dimensions. The repetition time was 2 s with 16 scans collected for each of the 256 spectra. Repetition times of up to 5 s did not lead to different cross-peak patterns. The phase-sensitive spectra were processed with window multiplication of sine bell squared with a shift of 2 in the F2 direction and a shift of 4 in the F1 direction.

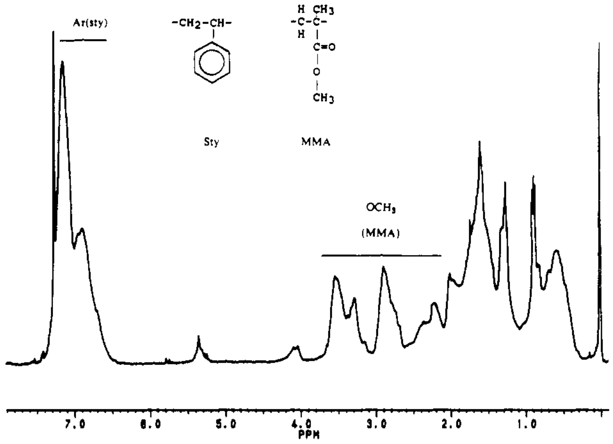


Figure 1. 400-MHz ^1H NMR spectrum of a low-conversion solution styrene–methyl methacrylate copolymer (f_M = 0.47) in $CDCl_3$ at 298 K.

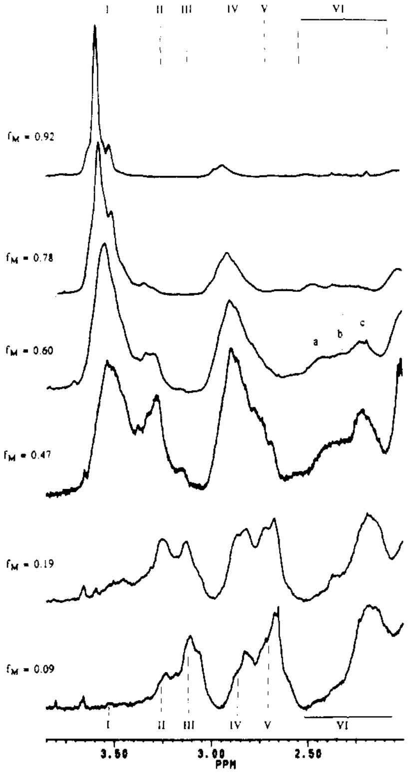


Figure 2. Expanded 400-MHz ^1H NMR spectra of low-conversion solution S–MMA copolymers, showing the methoxy region only. Spectra were recorded in $CDCl_3$ at 298 K. Molar feed compositions (f_M) are indicated for each copolymer on the left-hand side.

Results and Discussion

Figure 1 depicts a typical 400-MHz ^1H NMR spectrum of a statistical S–MMA copolymer, whereas in Figure 2 expanded 400-MHz spectra are presented, showing only the methoxy region for a series of low-conversion solution copolymers with various S–MMA feed ratios. At a higher magnetic field strength, i.e., 600 MHz, no additional resolution enhancement can be achieved in the methoxy region (Figure 3b). The impurities at 5.3 and 4.1 ppm are resonances of unknown compounds. In Figure 2 the peak areas are designated I–VI; these are due to combined compositional (=sequence) and configurational (=tacticity) effects. The areas are assigned to specific M-centered triad and pentad sequences. Earlier assignments are

Table I
Literature and New Assignments of Methoxy Resonances for Statistical S-MMA Copolymers

	peak					
	I	II	III	IV	V	VI
chemical shift region, ppm	3.70–3.40	3.40–3.17	3.17–2.95	2.95–2.78	2.78–2.50	2.50–2.10
Ito/Bovey[7-11]	MMM	$(1-\sigma)$MMS $(1-\sigma)^2$SMS		σMMS	$2\sigma(1-\sigma)$SMS	σ^2SMS
Uebel/Dinan[14]	MMM $(1-\sigma)$MMS	$(1-\sigma)^2$MSMSM $(1-\sigma)^2$SSMSM	$(1-\sigma)^2$SSMSS	σMMS	$2\sigma(1-\sigma)$SMS	σ^2SMS
Kale/O'Driscoll[15]	MMM $(1-\sigma)$MMS	$(1-\sigma)^2$MSMSM $(1-\sigma)^2$SSMSM	$(1-\sigma)^2$SSMSS	σMMS + $2\sigma(1-\sigma)$MSMSM	$2\sigma(1-\sigma)$SMS − $2\sigma(1-\sigma)$MSMSM	σ^2SMS
this work	MMMMM 2MMMMS SMMMS $(1-\sigma)$MSMMM $(1-\sigma)$MSMMS $(1-\sigma)^2$MSMSM	σSSMMM σSSMMS $(1-\sigma)$SSMMM $(1-\sigma)^2$SSMSM	$(1-\sigma)^2$SSMSS	σMSMMM σMSMMS $2\sigma(1-\sigma)$MSMSM $2\sigma(1-\sigma)$SSMSM	$(1-\sigma)$SSMMS $2\sigma(1-\sigma)$SSMSS	σ^2MSMSM $2\sigma^2$SSMSM σ^2SSMSS

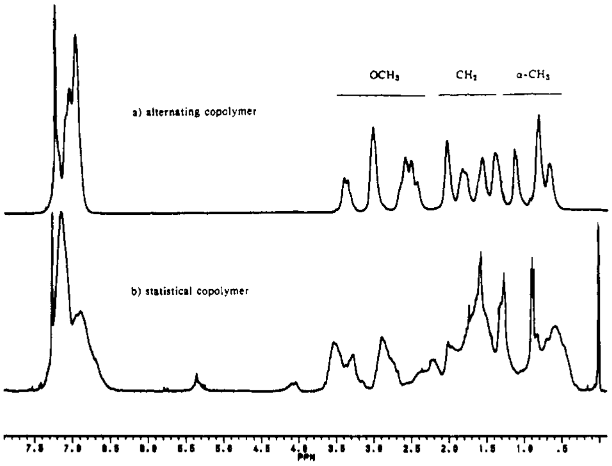


Figure 3. (a) 600-MHz ^{1}H NMR spectrum of an alternating S-MMA copolymer in hexachlorobutadiene at 298 K. (b) 600-MHz ^{1}H NMR spectrum of a low-conversion statistical S-MMA copolymer in $CDCl_3$ at 298 K.

summarized in Table I. In Table II, the molar feed ratio q, the experimentally corrected observed peak areas, and the peak areas calculated according to intrinsically related peak assignments are given. Overlapping of the OCH_3 Z peak with the methine proton of styrene can be seen in Figure 1. To circumvent this problem in an attempt to measure quantitatively the peak areas I-VI, Gotoh[17] et al. have suggested the use of eqs 1-4 where A_1 and A_2 represent

$$\text{area } OCH_3 = {}^3/_8(\text{area } A_2 - ({}^3/_5)\text{area } A_1) \quad (1)$$

$$\text{peak } X = \text{I} + \text{II} + \text{III} \qquad f_X = X/\text{area } OCH_3 \quad (2)$$

$$\text{peak } Y = \text{IV} + \text{V} \qquad f_Y = Y/\text{area } OCH_3 \quad (3)$$

$$\text{peak } Z = \text{VI} \qquad f_Z = 1 - f_X - f_Y \quad (4)$$

the total peak areas of the aromatic and aliphatic proton resonances, respectively. The theoretical relative methoxy peak areas have been calculated by using the theoretical triads and pentads and a coisotacticity parameter $\sigma = 0.63$ (Uebel[14]) and $\sigma = 0.44$ (Kale[15]). The triads and pentads can be calculated using Alfrey/Mayo (AM) kinetics (=first-order Markov statistics),[1] assuming this model to be valid at any moment of the reaction for low-conversion solution copolymers with reactivity ratios $r_m = 0.45$ and $r_s = 0.50$ (Kelen/Tüdös[26]). The following equations apply to M-centered triads or pentads where F represents the number fraction of triads and pentads normalized to unity and $P(M_1/M_2)$ is the probability of an M_2-type growing chain end to react with monomer M_1. In addition, $P(M/M) = (r_M/q)/(1 + (r_M/q))$, $P(S/M) = 1/(1 + (r_M/q))$, $P(S/S) = (r_Sq)/(1 + (r_Sq))$, $P(M/S) = 1/(1 + (r_sq))$, and q = S/MMA, the molar feed ratio. The

$$F_{MMM} = (1 - P(S/M))^2$$

$$F_{MMS} = 2P(S/M)(1 - P(S/M))$$

$$F_{SMS} = P(S/M)^2$$

$$F_{MMMMM} = F_{MMM}P(M/M)^2$$

$$F_{SMMMM} = 2F_{MMM}P(S/M)P(M/M)$$

$$F_{SMMMS} = F_{MMM}P(S/M)^2$$

$$F_{MSMMM} = F_{SMM}P(M/S)P(M/M)$$

$$F_{SSMMM} = F_{SMM}P(S/S)P(M/M)$$

$$F_{MSMMS} = F_{SMM}P(M/S)P(S/M)$$

$$F_{SSMMS} = F_{SMM}P(S/S)P(S/M)$$

$$F_{MSMSM} = F_{SMS}P(M/S)^2$$

$$F_{SSMSM} = 2F_{SMS}P(S/S)P(M/S)$$

$$F_{SSMSS} = F_{SMS}P(S/S)^2 \quad (5)$$

numerical values of the theoretical number fractions of M-centered triads and pentads are summarized in Table III. If we compare the experimental results with the theoretical relative peak areas calculated according to the various assignments, none of the earlier published assignments yields a satisfactory agreement (Table II). The results of Uebel's assignment and $\sigma = 0.63$ yield widely differing relative peak areas for all copolymer compositions. The improvements made by Kale et al.[15] are clearly observable. However, some discrepancies still remain. For the copolymer feed compositions f_M = 0.47–0.09 the predicted peak areas of peak II have too small values, and at higher styrene content of the copolymer, peak I is too high. For the same copolymers the predicted peak areas of peak IV are much too small and of peak V too high.[15]

Table II
Normalized Peak Areas of the Oxymethylene Resonances of the S–MMA Copolymers Obtained by Low-Conversion Batch Solution Processes[a]

initial feed ratio, q_0	f_M	rel intens I	II	III	IV	V	VI	assignt
0.09	0.92	0.84	0.01	0.00	0.14	0.00	0.01	obsv
		0.80	0.00	0.00	0.18	0.00	0.01	Uebel
		0.85	0.01	0.00	0.13	0.00	0.01	Kale
		0.86	0.01	0.00	0.13	0.00	0.01	this work
0.29	0.78	0.66	0.05	0.01	0.20	0.03	0.06	obsv
		0.55	0.02	0.00	0.35	0.02	0.06	Uebel
		0.64	0.05	0.00	0.27	0.02	0.03	Kale
		0.65	0.06	0.00	0.25	0.01	0.03	this work
0.66	0.60	0.43	0.13	0.01	0.30	0.06	0.08	obsv
		0.34	0.05	0.00	0.30	0.17	0.14	Uebel
		0.43	0.11	0.01	0.31	0.08	0.07	Kale
		0.42	0.12	0.01	0.32	0.05	0.07	this work
1.15	0.47	0.30	0.17	0.02	0.33	0.09	0.09	obsv
		0.23	0.06	0.01	0.35	0.14	0.20	Uebel
		0.31	0.14	0.02	0.28	0.15	0.10	Kale
		0.30	0.16	0.02	0.33	0.09	0.10	this work
4.26	0.19	0.07	0.20	0.12	0.21	0.21	0.18	obsv
		0.07	0.06	0.04	0.15	0.34	0.33	Uebel
		0.11	0.14	0.12	0.13	0.36	0.16	Kale
		0.07	0.17	0.12	0.24	0.25	0.16	this work
9.72	0.09	0.02	0.13	0.21	0.16	0.32	0.16	obsv
		0.03	0.04	0.07	0.06	0.42	0.36	Uebel
		0.09	0.05	0.20	0.05	0.43	0.18	Kale
		0.02	0.11	0.20	0.14	0.35	0.18	this work

[a] Predicted relative areas calculated using the model valid for low-conversion polymers, and $r_s = 0.50$, $r_M = 0.45$, $\sigma_{SM} = 0.63$ (Uebel[14]), $\sigma = 0.44$ (Kale[15]), and the appropriate assignment with $\sigma = 0.44$ (this work) for various initial feed ratios $q_0 = [S]/[MMA]$.

A disagreement also occurs in the calculation of the coisotacticity parameter σ from experimental results (Table IV), using different sets of equations (see later this section). Uebel[14] has suggested the calculation of $\sigma(=\sigma(a))$ from the ratio of the areas $(1-\sigma)$MMS and σMMS. According to Uebel's assignment, peak I is assumed to consist of approximately coinciding twin resonances of MMM and heterotactic MMS triads, and peak IV is exclusively attributed to the resonance of isotactic MMS. With use of the calculated number fraction of MMM triads and the experimentally observed peak areas I and IV, the coisotacticity parameter σ according to Uebel[14] can be calculated:

$$f_\Delta = \text{area I} - F_{MMM} = (1-\sigma)F_{MMS} \quad (6)$$

$$f_{IV} = \text{area IV} = \sigma F_{MMS} \quad (7)$$

$$\sigma(a) = f_{IV}/(f_\Delta + F_{IV}) \quad (8)$$

The results of $\sigma(a)$ are collected in Table IV for the series of copolymers. The average $\sigma(a)$ value, considering all the copolymer compositions, except the $\sigma(a)$ value for $q_0 = 4.26$ and $q_0 = 9.72$, is 0.47 ± 0.06. The average σ value of the uncorrected peak areas as published in ref 14 is $\sigma = 0.63$, which is also somewhat higher than the values published by other groups.[15,18,27] Using other peak combinations, for example, using the SMS triad resonances (Table I), one arrives at

$$\text{area (II + III)} = (1-\sigma)^2 F_{SMS} \quad (9)$$

$$\text{area V} = 2\sigma(1-\sigma)F_{SMS} \quad (10)$$

$$\text{area VI} = \sigma^2 F_{SMS} \quad (11)$$

in which F_{SMS} is the normalized number fraction of SMS triads, and the areas (II + III), V, and VI are experimentally observed. The following set of equations is valid:

$$\text{area VI/area V} = \sigma^2/2\sigma(1-\sigma) \rightarrow \sigma(b) \quad (12)$$

$$\text{area (II + III)/area V} = (1-\sigma)^2/2\sigma(1-\sigma) \rightarrow \sigma(c) \quad (13)$$

$$\text{area (II + III)/area VI} = (1-\sigma)^2/\sigma^2 \rightarrow \sigma(d) \quad (14)$$

All σ values are summarized in Table IV. Actually, σ should be constant over one copolymer using several calculation procedures. It is obvious from Table IV that the four estimated σ values vary largely over the entire series of copolymers. This cannot only be due to the low accuracy of measuring the very small peak areas (error <5%). When the slightly modified assignments of Kale et al.[15] are used, it can be shown that the set of eqs 12–14 passes into

$$\text{area VI/(area (IV + V) - MMS} + f_\Delta) = \sigma^2/2\sigma(1-\sigma) \rightarrow \sigma(e) \quad (15)$$

$$\text{area (II + III)/(area (IV + V) - MMS} + f_\Delta) = (1-\sigma)^2/2\sigma(1-\sigma) \rightarrow \sigma(f) \quad (16)$$

$$\text{area (II + III)/area VI} = (1-\sigma)^2/\sigma^2 \rightarrow \sigma(d) \quad (17)$$

Equation 17 is identical with eq 14 and therefore also designated as $\sigma(d)$ and tabulated in Table IV together with $\sigma(e)$ and $\sigma(f)$. Kale et al.[15] have also introduced an alternative method for the calculation of the coisotacticity parameter σ

$$\text{area peak } X/\text{area peak } Y = (1 - \sigma P(S/M))^2/(2P(S/M))\sigma(1 - \sigma P(S/M)) = (1/2\sigma P(S/M)) - 1/2 \quad (18)$$

wherein $P(S/M) = 1/(1 + (r_M/q))$. The series averaged σ value $\langle\sigma\rangle = \sigma(g) = 0.41$. From Tables II and IV ($\sigma(a) - \sigma(d)$) and ($\sigma(d) - \sigma(g)$), we may conclude that both the assignments made by Uebel/Dinan[14] and by Kale/O'Driscoll[15] are not completely correct. Apparently, the assignments of the resonances in the methoxy region are more complicated than suggested by the above results, possibly as a consequence of the influence of the next neighbor styrene unit on the MMA in the center of the sequence. Therefore, we have performed 2D NOESY NMR on statistical copolymers to analyze in greater detail the pentad sequences, assuming coisotacticity to be present on a triad level.

In the literature[7-15] several assumptions have been made about the assignments in the methoxy region. In order of decreasing importance we mention the following:

(1) Chemical shift differences are due to directly neighboring styrene units (=α) in an M-centered sequence. Styrene rings at a larger distance (i.e., next neighbor) (=β) contribute considerably less. The coisotactic phenyl rings are assumed to have a greater shielding effect than non-coisotactic rings.

(2) Styrene rings with different conformations with respect to the backbone may induce shielding differences.

The first assumption was confirmed by Heffner et al.[19] for an alternating S–MMA copolymer. From 2D-NOESY experiments it has been shown that the assignments made for the 1D spectrum were consistent with the cross peaks

Table III
Predicted Number Fraction of MMA-Centered Triads and Pentads, Using Initial Feed Ratios q_0, r_S = 0.50, r_M = 0.45, and Alfrey/Mayo Kinetics

q_0	f_M	F_{MMM}	F_{MMS}	F_{SMS}	F_{MMMMM}	F_{MMMMS} + F_{SMMMM}	F_{SMMMS}	F_{MSMMM}	F_{SSMMM}	F_{MSMMS}	F_{SSMMS}	F_{MSMSM}	F_{MSMSS} + F_{SSMSM}	F_{SSMSS}
0.09	0.92	0.70	0.27	0.03	0.49	0.19	0.02	0.22	0.01	0.04	0.00	0.02	0.00	0.00
0.29	0.78	0.38	0.47	0.15	0.14	0.18	0.06	0.26	0.04	0.16	0.02	0.11	0.03	0.00
0.66	0.60	0.16	0.48	0.36	0.03	0.08	0.06	0.15	0.05	0.21	0.07	0.20	0.14	0.02
1.15	0.47	0.08	0.41	0.51	0.01	0.03	0.04	0.07	0.04	0.19	0.11	0.21	0.24	0.07
4.26	0.19	0.01	0.17	0.82	0.00	0.00	0.01	0.01	0.01	0.05	0.11	0.08	0.36	0.38
9.72	0.09	0.00	0.08	0.92	0.00	0.00	0.00	0.00	0.00	0.01	0.07	0.03	0.25	0.64

Table IV
Various Calculated σ_{SM}[a]

		assignt Uebel				assignt Kale			new assignt:
q_0	f_M	σ(a)	σ(b)	σ(c)	σ(d)	σ(e)	σ(f)	σ(g)	σ(h)
0.09	0.92	0.50				0.74	0.26	0.46	0.45
0.29	0.78	0.42	0.80	0.23	0.52	0.76	0.28	0.35	0.41
0.66	0.60	0.44	0.67	0.19	0.41	0.52	0.35	0.40	0.44
1.15	0.47	0.53	0.63	0.25	0.43	0.54	0.32	0.42	0.45
4.26	0.19	0.77	0.63	0.32	0.43	0.54	0.32	0.39	0.44
9.72	0.09	0.88	0.50	0.24	0.41	0.43	0.38	0.42	0.42

[a] σ(a) was calculated from eq 8, σ(b), σ(c), and σ(d) were calculated from eqs 12–14, respectively, according to Uebel's assignment. σ(d), σ(e), σ(f), and σ(g) were calculated from eqs 14–16 and 18, respectively, according to the assignment of Kale.[15] σ(h) was calculated using a nonlinear least-squares procedure based on current assignment.

observed between aliphatic and aromatic parts of the spectrum. In the methoxy region, the upfield resonances (2.2–2.7 ppm), which are assigned to coiso SMS triads, indeed give strong cross peaks. The central resonance (2.8–3.10 ppm), assigned to cohetero SMS triads, give weak cross peaks. The low-field resonances (3.2–3.5 ppm) have no cross peaks at all; therefore, these are assigned to the cosyndio configuration of the SMS triads. According to the second assumption, Heffner et al.[19] invoked noncomplete staggering of the backbone to explain their results with dihedral angles of −20° and +100°. According to the assignment of Kale et al.,[15] in a 2D-NOESY spectrum of a statistical S–MMA copolymer, one would expect three cross peaks between the styrene and the methoxy regions:

$$2.10\text{–}2.50\ \text{ppm} \rightarrow \text{coisotactic SMS triad (strong)}$$

$$2.50\text{–}2.78\ \text{ppm} \rightarrow \text{coheterotactic SMS triad (weak)}$$

$$2.78\text{–}2.95\ \text{ppm} \rightarrow \text{coisotactic SMM triad (weak)}$$

Prior to recording the 600-MHz 2D-NOESY spectrum of the statistical S–MMA copolymer, we reproduced the 2D-NOESY spectrum of alternating S–MMA as published by Heffner[19] to make sure that the differences in recording conditions between our spectra and those of Heffner et al.[19] do not interfere with the interpretation of the results of the statistical copolymer. The spectra were recorded under the same conditions as in ref 19 apart from the field strength and sample concentration (see the Experimental Section). Lower sample concentrations were used in order to diminish the intermolecular interactions, which could lead to too many cross peaks in the NOESY spectrum, but sample concentrations of 10% and 2% give identical results. As expected, the spectra of the alternating copolymer recorded with a mixing time of τ_m = 300 ms do not show all of the NOE interactions (Figure 4a). This could be due to differences in T_1 between our sample and Heffner's. Also different contour levels show no more cross peaks. The T_1 values of several peak groupings were measured and are tabulated in Table V. From this table it appears that with a mixing time of 300 ms only the aliphatic CH_3 and CH_2 protons could have optimal NOE contacts (Figure 4a). For the methoxy region, with T_1's of about 800–900 ms, a mixing time of at least 1 s is necessary. This can be seen in Figure 4b, where the NOE contacts of the methoxy protons with the aromatic protons are optimal and those of the CH_3 and CH_2 protons are losing intensity. The diagonal of the 2D spectrum

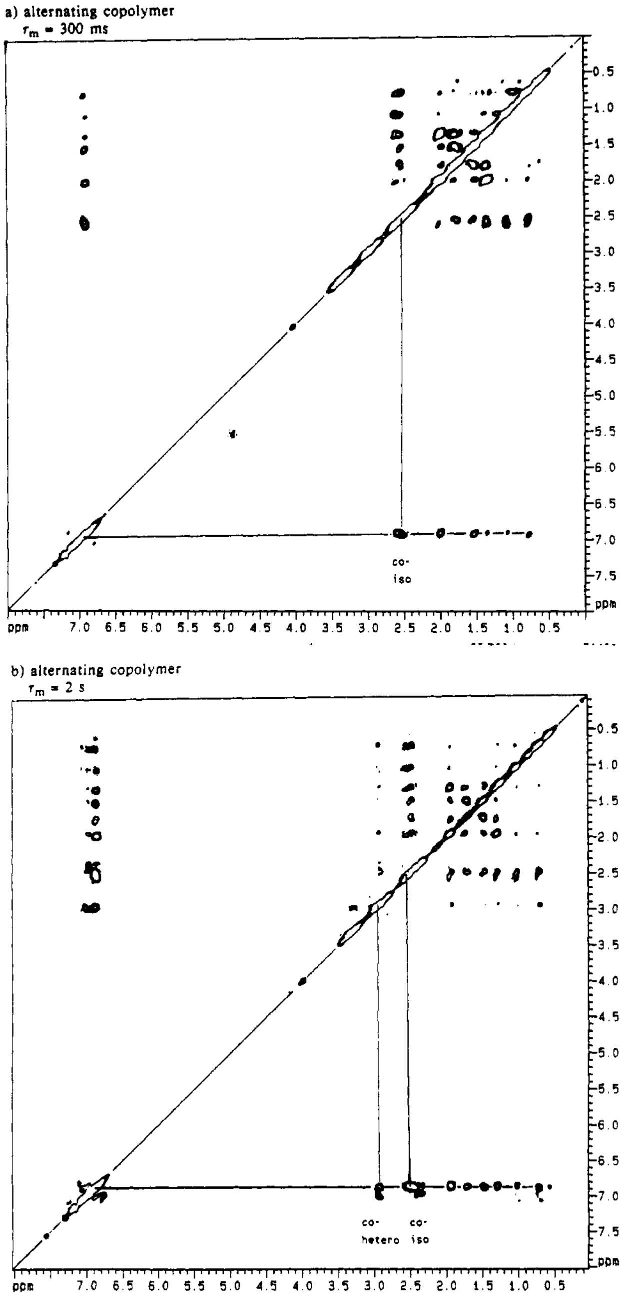


Figure 4. Contour plot of two NOESY experiments (600 MHz) of the alternating S–MMA copolymer using mixing times of (a) 300 ms and (b) 2 s.

Table V
Spin-Lattice Relaxation Time T_1 (ms) of Alternating (50/50) and Statistical (f_M = 0.47) Copolymers, for Several Proton Regions[a]

region (ppm)	T_1 alt S-MMA, ms	T_1 stat S-MMA, ms
aromatic protons (±7)	±900	900–1100
OCH_3		
X (2.95–3.70)	700	800–900
Y (2.50–2.95)	700	900
Z (2.10–2.50)	600	600
CH_2 (1.20–2.10)	325	325
CH_3 (0.50–1.20)	350	300

[a] The 600-MHz ^1H NMR spectra were recorded at 353 K, and sample concentration was 2% (w/v) in hexachlorobutadiene.

corresponds with the 1D spectrum as shown in Figure 3a.

For the statistical S-MMA copolymer almost the same T_1 values are observed (Table V). At present, it is not completely clear what causes the difference in relaxation behavior between our samples and that of Heffner. An explanation could be that our polymers have larger molecular weights. This would result in a decreased overall mobility for a given concentration and thus in larger T_1 values. With our polymers we have to perform at least two experiments with different mixing times to see all NOE contacts for one copolymer. Parts a and b of Figure 5 show the phase-sensitive NOESY spectra of a statistical S-MMA (f_M = 0.47) copolymer with mixing times of 300 ms and 2 s, respectively. Instead of the expected three cross peaks between the OCH_3 and styrene resonances, we now observe *five* cross peaks:

(5) 2.20–2.45 ppm → strong (σ^2 SMS)

(4) 2.70–2.78 ppm → weak ($2\sigma(1-\sigma)$SSMSS)

(3) 2.78–2.95 ppm → medium (σ(MSMMM + MSMMS) + $2\sigma(1-\sigma)$(MSMSM + SSMSM))

(2) 3.15–3.25 ppm → very weak (σSSMMM)

(1) 3.30–3.40 ppm → very weak (σSSMMS)

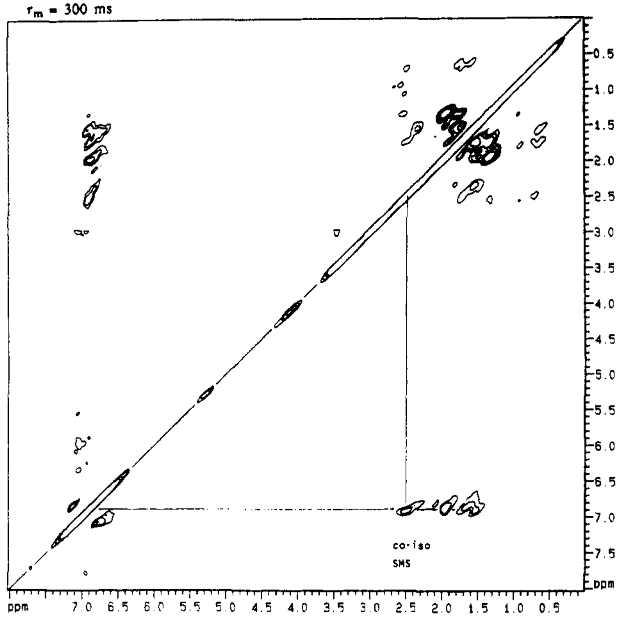
This is only compatible with several pentads rather than triads having different chemical shifts induced by phenyl rings in the next neighbor position (β). Along these lines we can conclude that several pentad resonances have to be reassigned. The new mixed assignment of compositional pentad sequences and configurational sequence placement (on a triad level) tacticity is given in Table I. This new assignment is based on several observations:

(1) MMM resonates at 3.6 ppm and depicts no tacticity splitting. Pentads such as SMMMM or SMMMS may resonate slightly upfield with regard to MMM because of shielding by aromatic rings, but these sequences are still assumed to resonate at peak I.

(2) Alternating pentads will resonate at the same position as the alternating copolymer; i.e., syndiotactic MSMSM coincides with peak I, similarly, heterotactic MSMSM (cross peak 3, Figure 5) with peak IV, and isotactic MSMSM with peak VI.

(3) Phenyl rings in the next neighbor position (β) give significant shielding effects; syndio- and heterotactic SSMSM and SSMSS sequences will resonate at higher field in this order. For example, peak II is assigned to syndiotactic MSMSM and SSMSM sequences and peak III to the syndiotactic SSMSS pentad, according to the assignment of Uebel.[14] Heterotactic SSMSM and MSMSM are assigned to peak IV (cross peak 3, Figure 5), and heterotactic SSMSS is assigned to peak V (cross peak 4, Figure 5).

a) statistical copolymer τ_m = 300 ms



b) statistical copolymer τ_m = 2 s

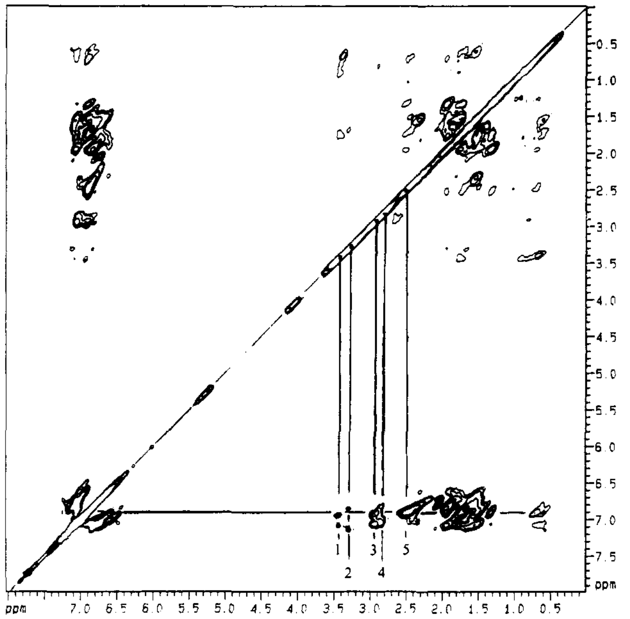


Figure 5. Contour plot of two NOESY experiments (600 MHz) of a statistical low-conversion solution S-MMA copolymer (f_M = 0.47), using mixing times of (a) 300 ms and (b) 2 s. (1) σSSMMS, (2) σSSMMM, (3) σ(MSMMM + MSMMS) + $2\sigma(1-\sigma)$(MSMSM + SSMSM), (4) $2\sigma(1-\sigma)$SSMSS, and (5) σ^2SMS.

(4) The shift effects are not significant for isotactic SSMSM and SSMSS, but in peak VI we can distinguish three parts of isotactic pentads: (a) MSMSM, (b) SSMSM, and (c) SSMSS (Figure 2 and cross peak 5, Figure 5).

(5) Only the two cross peaks at lower field must be due to a coisotactic configuration, which has a deshielding effect; possible triads are isotactic MMS and heterotactic SMS. We assume that isotactic SSMMM and isotactic SSMMS with deshielding effects resonate at 3.20 and 3.35 ppm (cross peaks 2 and 1, Figure 5), respectively. These resonances both appear in peak II.

(6) The remaining pentads have been assigned in the same way following the two assumptions as mentioned

earlier, but the concentrations of some of the pentads are very low, thus somewhat complicating the assignments. Assignments based solely on the agreement between the observed and predicted distributions should be considered tentative because they are not unique.

The results of assigning these pentads are given in Table I. From Table II it can be seen that over the whole range of copolymers, all relative peak areas agree satisfactorily with the experimentally observed peak areas. Even for copolymers with higher styrene contents no discrepancies are observed in peaks I, II, IV, and V.

In order to estimate σ in a reliable manner, the coisotactic tacticity parameter was fitted to the six equations corresponding to the six peak areas, using a nonlinear least-squares procedure, where $\sum((a_{\rm calc}-a_{\rm meas})/a_{\rm meas})^2$ was minimized for each copolymer. In the latter expression $a_{\rm meas}$ is the experimentally observed peak area (Table IV) and $a_{\rm calc}$ is the calculated peak area using the theoretically calculated pentads (Table III) and the current peak assignments. The resulting value, $\sigma(h) = 0.44 \pm 0.03$, predicts all six peak areas based on theoretical pentads within 5% error. The inaccuracy determining the peak areas from the NMR spectra is about 8%. The present results should enable us to analyze ^{1}H NMR spectra of higher conversion solution and emulsion copolymers of styrene and methyl methacrylate.

Conclusion

The 2D-NOESY spectrum of a statistical S-MMA copolymer ($f_M = 0.47$) enables us to draw a number of conclusions regarding the methoxy proton assignments. It shows that the complex peak grouping in the methoxy region is sensitive to pentad sequences rather than triads. The new peak assignments proposed in this paper show a satisfying agreement between experimental and theoretical peak areas over a wide range of copolymer compositions, based on the ultimate copolymerization model and a constant, best fitting average coisotacticity parameter $\sigma = 0.44$.

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Registry No. S-MMA copolymer, 25034-86-0; S-MMA alternating copolymer, 108266-99-5.