

## Proton and Carbon NMR Spectra of Alternating and Statistical Styrene–Methyl Methacrylate Copolymers Revisited

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**ABSTRACT:** The  $\alpha$ -methyl proton NMR resonances of the three different configurational methyl methacrylate centered triad sequences of alternating styrene–methyl methacrylate (SMMA) copolymers have been reassigned. Literature assignments are inconsistent with data and each other. Selective decoupling experiments were carried out in the present study to assign the carbon NMR resonances of the  $\alpha$ -methyl groups of alternating styrene–methyl methacrylate copolymers. Subsequently, the carbon resonances of the aromatic C1 and  $\alpha$ -methyl literature assignments of the statistical SMMA copolymers have been reconsidered and reassigned in terms of configurational triad sequences.

## Introduction

Determination of the intramolecular (sequence distribution and tacticity) and intermolecular (chemical composition and molar mass distribution) chain structure of copolymers is of great importance because it supplies information regarding the polymerization processes.<sup>1–3</sup> Further, the molecular microstructure may supply information about the monomer addition process, e.g., about the preference of monomers to add in coiso- or cosyndiotactic configurations. One of the techniques which has been very effective in the determination of the average copolymer composition and of the intramolecular microstructure of copolymers is high-resolution nuclear magnetic resonance (NMR). One of the most important systems of interest in copolymerization studies is the styrene–methyl methacrylate (SMMA) copolymer. These copolymers have been extensively studied by proton NMR (see ref 3 and references cited therein). The result of these studies is that the analysis of sequence distribution is possible, although rather complicated due to sensitivity toward pentad sequences in the methoxy region. Another possibility for analyzing sequence distributions is carbon-13 NMR. The carbon NMR spectra of statistical copolymers of styrene–methyl methacrylate were investigated by Katritzky et al.<sup>4</sup> in 1974 and by Kato et al.<sup>5</sup> in 1975. It was shown that in carbon NMR a splitting not only occurs in the carbonyl, quaternary, methoxy, and  $\alpha$ -methyl carbons in the MMA-centered unit, but also in the aromatic C1 and methine carbons in the S-centered unit. Therefore, carbon NMR made it possible to determine simultaneously MMA-centered and S-centered stereosequences.<sup>4–6</sup> Katritzky and Kato independently developed an assignment for the aromatic C1 resonance and the  $\alpha$ -methyl main-chain carbon resonance.<sup>4,5</sup> The assignments of the aromatic C1 and  $\alpha$ -methyl carbon resonances by Katritzky<sup>4</sup> and Kato<sup>5</sup> are, however, reversed. Hirai et al.<sup>7</sup> pointed out this problem and confirmed that the Kato assignment (e.g., of the aromatic C1) is the correct one. Hirai showed that the assignments pertaining to the alternating structural parts in the carbon NMR spectra of the statistical SMMA copolymers<sup>5</sup> are in agreement with the carbon NMR spectra of fully alternating SMMA copolymers. The triplet peaks in the NMR spectra of the alternating copolymer of the SMS (methoxy protons) or MSM (C1 carbon) triads

were assigned as cosyndiotactic, coheterotactic, and coisotactic configuration in order of increasing shielding. This assignment was substantiated by comparison of the NMR peak areas of several carbons with the peak areas of the methoxy proton NMR signals of several alternating copolymers made with different kinds of Lewis acids<sup>7,8</sup> and by the combined use of partly relaxed NMR signals and selective decoupling NMR techniques. Another ambiguity also exists in the literature: the tacticity splitting of the SMS triad of the  $\alpha$ -methyl carbon resonance in the alternating SMMA copolymer seems to have the same order of shielding as the aromatic C1,<sup>9</sup> but in the proton NMR assignment the reverse situation has been suggested.<sup>10</sup> Although these assignments in the proton NMR spectra are seemingly confirmed by calculations,<sup>10</sup> the 2D NOESY (two-dimensional nuclear Overhauser effect spectroscopy) experiments of Heffner<sup>11</sup> showed that this is impossible: a cross peak exists between the  $\alpha$ -methyl and the aromatic proton signals at lower field. Notwithstanding these contradictions in the assignments, up to now the assignments and the conclusions of Katritzky et al.<sup>4</sup> and of Hirai et al.<sup>7</sup> are both used in the literature indiscriminately.<sup>9,12</sup>

In this paper the following topics are discussed. First, the  $\alpha$ -methyl resonances in both the proton and carbon NMR spectra of the *alternating* copolymers are discussed, and secondly, the carbon resonances of the aromatic C1 and  $\alpha$ -methyl carbon of the *statistical* copolymers are discussed.

## Experimental Section

**Materials.** The monomers styrene (S) and methyl methacrylate (MMA) (Merck) were distilled at reduced pressure under nitrogen. The middle fraction of the distillate was collected and used. 2,2'-Azobis(isobutyronitrile) (AIBN) p.a. purchased from Fluka was recrystallized once from methanol.

**Alternating Copolymer.** The preparation of the alternating copolymer has been described elsewhere.<sup>3</sup>

**Statistical Copolymers.** The SMMA copolymers were synthesized in bulk at 40 °C in a 100-mL glass vessel. The solution was degassed and the polymerization was carried out under a nitrogen atmosphere. The initiator (AIBN) concentration was approximately  $2 \times 10^{-2}$  mol/L. To isolate and purify the copolymer, the reaction mixture was poured into a 10-fold excess of cold heptane. The total conversion was determined by means of solid weight and was always less than 3%.

**NMR.** Proton NMR spectra were recorded with a 400-MHz (Bruker AM 400) spectrometer at 298 K, using CDCl<sub>3</sub> as solvent and locking agent. The spectra were obtained using a spectral width of 6024 Hz, an acquisition time of 2.7 s, a flip angle of 45°,

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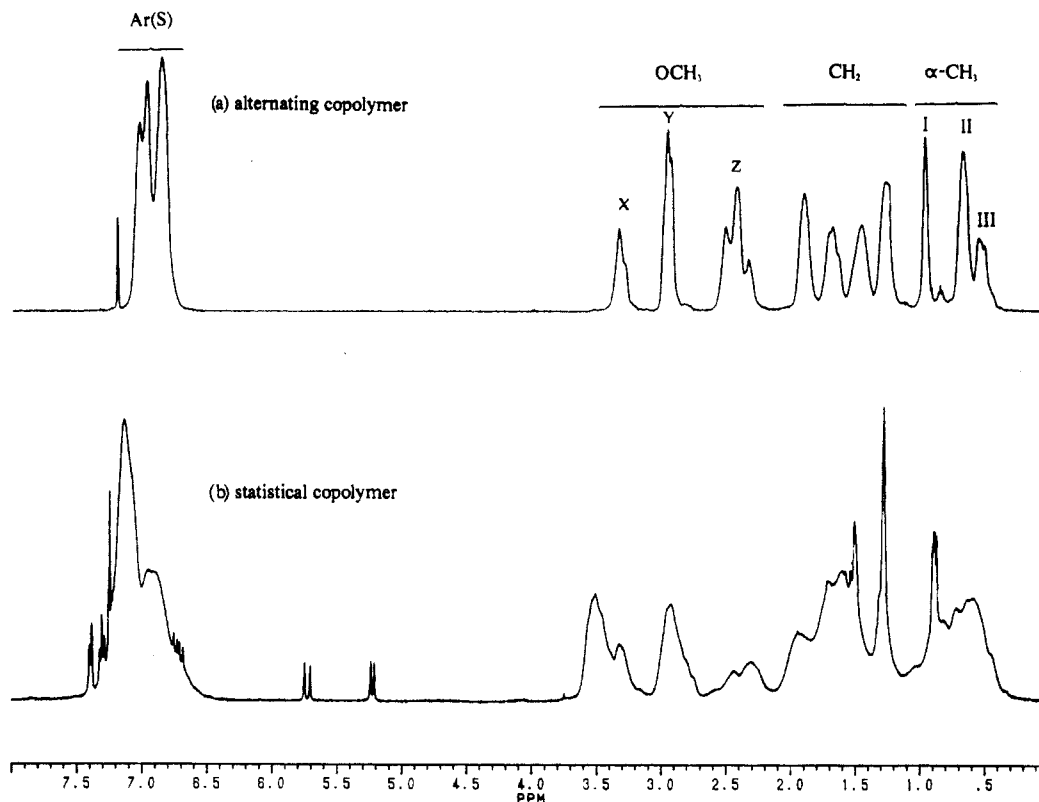


Figure 1. (a) 400-MHz proton NMR spectrum of an alternating SMMA copolymer in hexachloro-1,3-butadiene at 353 K. (b) 400-MHz proton NMR spectrum of a low-conversion bulk SMMA copolymer (molar feed composition styrene = 0.458) in  $\text{CDCl}_3$  at 298 K.

Table I  
Proton Methoxy and  $\alpha$ -Methyl Assignments of Alternating SMMA Copolymers<sup>a</sup>

	OCH <sub>3</sub>			$\alpha$ -CH <sub>3</sub>		
	X 3.5–3.2 ppm	Y 3.0–2.8 ppm	Z 2.7–2.2 ppm	I 1.0–0.85 ppm	II 0.8–0.65 ppm	III 0.6–0.5 ppm
literature <sup>11</sup>	$(1 - \sigma)^2 F_{\text{sms}}$	$2\sigma(1 - \sigma) F_{\text{sms}}$	$\sigma^2 F_{\text{sms}}$	$\sigma^2 F_{\text{sms}}$	$2\sigma(1 - \sigma) F_{\text{sms}}$	$(1 - \sigma)^2 F_{\text{sms}}$
this work				$(1 - \sigma)^2 F_{\text{sms}}$	$2\sigma(1 - \sigma) F_{\text{sms}}$	$\sigma^2 F_{\text{sms}}$

<sup>a</sup>  $\sigma = \sigma_{\text{sm}}$  = coisotacticity parameter.

and a pulse delay of 5 s. Spectra were obtained after accumulating 32 scans. The digital resolution amounted to 0.38 Hz, corresponding to a data length of 32K.

The carbon NMR spectra were recorded at 100 MHz with the same spectrometer. The sample concentration was 10% (w/v) in  $\text{CDCl}_3$ . The spectra were obtained accumulating 8000 scans with a digital resolution of 1.526 Hz/point, corresponding to a spectral width of 25 000 Hz and a data length of 32K. The flip angle and the pulse delay were 45° and 4 s, respectively.

The alternating copolymer was dissolved in hexachloro-1,3-butadiene and benzene- $d_6$  as lock at 353 K. With this solvent a better resolution was achieved in the proton NMR spectra, in contrast to the carbon NMR spectra. (Figure 2 and cf. Figures 5a and 6a).

Selective proton decoupling was used to correlate the proton NMR signals of the  $\alpha$ -methyl groups with the corresponding carbon NMR signals. Typical spectra are shown in Figure 5. Typically, 15 000 scans were accumulated (pulse interval time 4 s) for three different values of the proton irradiation frequencies (with reduced power by a factor of ca. 3 with respect to the broadband decoupled case). The irradiation frequencies are given in the text (section 1.2.b) and in the figure caption of Figure 5.

## Results and Discussion

This section is divided into two major parts; part 1 concerns the proton and carbon NMR spectra of the alternating copolymers, and part 2 concerns the proton and carbon NMR spectra of the statistical copolymers. Note that the terminologies (between parentheses) of the peak signals are mostly taken from the literature and are

as follows, where in some cases the terminologies were slightly adapted (X' for X) to avoid the use of one symbol for more than one purpose. For the alternating copolymers there are the methoxy protons (X, Y, Z), the  $\alpha$ -methyl protons (I, II, and III), the C1 carbon (X', Y', Z'), and the  $\alpha$ -methyl carbon (I', II', III'). For the statistical copolymers there are the C1 carbon (X'', Y'', Z'') and the  $\alpha$ -methyl carbon (A, B, C, D).

**1. Alternating Copolymers.** In the next paragraphs we discuss first the proton NMR spectra of the alternating copolymers (methoxy protons and  $\alpha$ -methyl protons) and subsequently their carbon NMR spectra. Only the aromatic C1 and the  $\alpha$ -methyl carbon resonances are described because these resonances are the most interesting ones in the statistical SMMA copolymers, since they can be assigned to a combination of comonomer sequence distributions and different configurational situations.

**1.1. Proton NMR.** The proton NMR spectra of alternating copolymers have been investigated by several groups,<sup>7,9–11</sup> in particular with respect to the methoxy protons (summarized in section 1.1.a) and the  $\alpha$ -methyl protons (discussed in section 1.1.b).

**(a) Methoxy Protons.** It is clearly shown in the literature that the methoxy proton NMR signals are split into three peaks ( $\delta = 3.5$ –2.2 ppm), designated X, Y, and Z, where X corresponds to the syndiotactic, Y to the heterotactic, and Z to the isotactic configuration<sup>7,9–11</sup> (Figure 1a and Table I). That this assignment is correct

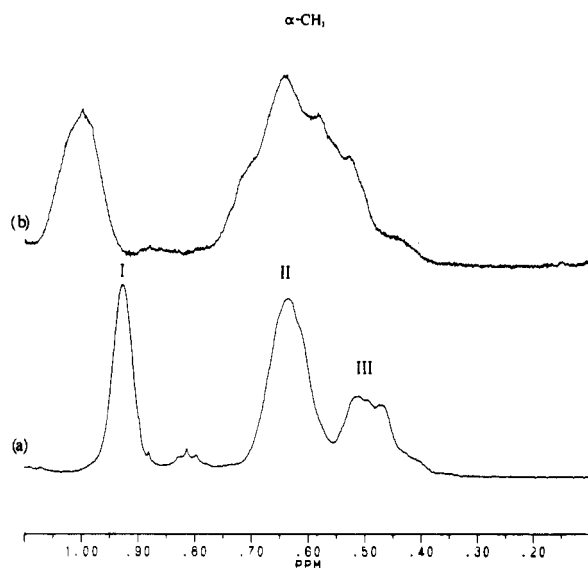


Figure 2. Expanded proton NMR spectra of the  $\alpha$ -methyl resonances of the alternating copolymer (a) in hexachloro-1,3-butadiene and (b) in  $\text{CDCl}_3$ .

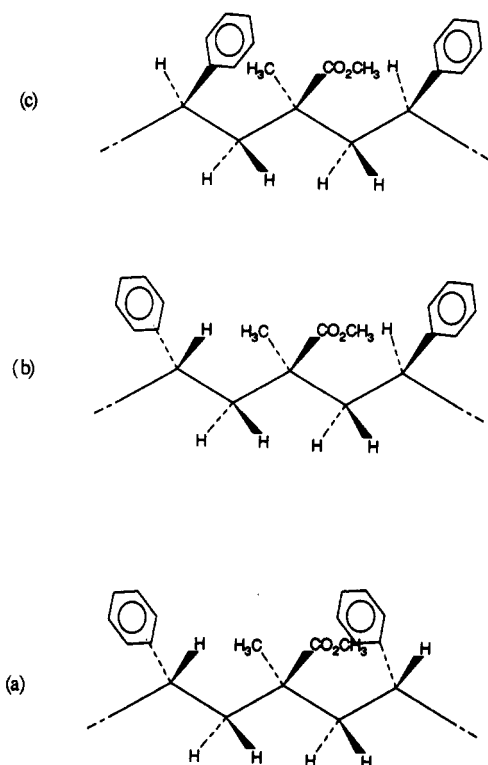


Figure 3. Various configurations of the SMS triad: (a) syndiotactic; (b) heterotactic; (c) isotactic.

is clearly demonstrated by Heffner et al.<sup>11</sup> by 2D NOESY NMR spectra where dipole-dipole interactions between methoxy protons and phenyl protons result in a cross peak. Peak Y yields a weak cross peak (heterotactic) and peak Z yields a strong cross peak (isotactic). In Figure 3, the three different configurations of the SMS triad are shown. Because of the shielding effects by the aromatic ring, the methoxy protons in the meso configuration are shifted to higher field.

**(b)  $\alpha$ -Methyl Protons.** The assignments of the  $\alpha$ -methyl proton resonances are also given in the literature;<sup>7,10,11</sup> the three peaks, in order of increasing shielding, are assigned to isotactic, heterotactic, and syndiotactic sequences (I ( $\delta = 0.95$ ), II ( $\delta = 0.65$ ), and III ( $\delta = 0.5$ ), respectively, Table I). The assignments are based on the

assumption that if the styrene rings are in the meso conformation with respect to the  $\alpha$ -methyl protons (Figure 3), then the latter group consequently resonates at higher field. The assignment of Koinuma et al.<sup>10</sup> results from a theoretical concept based on simple ring current calculations. However, this assignment has never been proved by experiment. On the other hand, the 2D NOESY experiment published by Heffner et al.<sup>11</sup> (used for assigning the methoxy and methylene protons) can also be used for assigning the  $\alpha$ -methyl protons. In the racemic configuration (denoted as isotactic) of the styrene rings and  $\alpha$ -methyl protons (Figure 3) no cross peaks can occur because there are no measurable dipole-dipole interactions between the protons of the respective groups. A weak and a strong cross peak is expected in the heterotactic and syndiotactic configuration, respectively. As mentioned before, the  $\alpha$ -methyl group is split into three peaks ( $\delta = 0.95, 0.65$ , and  $0.5$  ppm). According to the assignments of Koinuma<sup>10</sup> and Hirai,<sup>7</sup> one would expect cross peaks at higher fields ( $\delta = 0.65$  and  $0.5$  ppm) but not at low field ( $\delta = 0.95$  ppm), which is clearly in contrast with the observations in Figure 3 of ref 11. Therefore, the assignments of the alternating SMS triad in the existing literature<sup>10</sup> are incorrect. This means that the assignment of the  $\alpha$ -methyl protons should be in the reversed order as published in the literature (Table I). The reason for this deshielding effect is already mentioned in the text of Heffner et al.<sup>11</sup> a given proton may be very close to the ring but also on the periphery of the shielding cone or actually in the deshielding region. It can be correctly deduced from the deshielding that the three  $\alpha$ -methyl peaks should be assigned as cosyndiotactic, coheterotactic, and coisotactic in order of increasing shielding. Hence, the new assignments are given in Table I.

**1.2. Carbon NMR.** The carbon NMR spectra of the alternating copolymers have previously been studied.<sup>7,9,11,13</sup> Several carbon NMR resonances of the styrene-centered and of the MMA-centered triads are split due to tacticity effects.<sup>7</sup> Figure 4 shows a 100-MHz carbon NMR spectrum of an alternating copolymer. The carbonyl, quaternary, methoxy, and  $\alpha$ -methyl carbons in MMA and the aromatic C1 and the methine carbons in S show induced splitting because of different tacticities. Here, only the aromatic C1 resonances are summarized and the  $\alpha$ -methyl carbon resonances are discussed.

**(a) C1 Carbon.** The three groups of signals of the C1 carbon in the alternating copolymer are designated X', Y', and Z' ( $\delta = 148$ – $143$  ppm, Figure 4). These peaks are assigned to cosyndiotactic, coheterotactic, and coisotactic configurations, respectively (Table II). Hirai et al.<sup>7</sup> analyzed several alternating copolymers made by using various metal halides as catalysts. The relative signal areas of the three different configurations varied with the metal halides used (see also Introduction). The assignments of the C1 and other carbons (except  $\alpha$ -methyl) are based on comparisons of the relative carbon NMR peak intensities of the C1 carbon with the relative proton NMR signals of the methoxy protons. These assignments of the methoxy carbon NMR signals were justified by the combined use of partly relaxed NMR signals and selective decoupling experiments.<sup>7</sup>

**(b)  $\alpha$ -Methyl Carbon.** In contrast to the carbonyl, quaternary, and methoxy carbons in MMA and the aromatic C1 and methine carbons in S, no obvious assignments of the  $\alpha$ -methyl carbons exist, although a clear peak splitting can be observed at stronger magnetic fields (Figures 4 and 6a, peaks I', II', and III'). There exists an assignment for the  $\alpha$ -methyl group originating from the

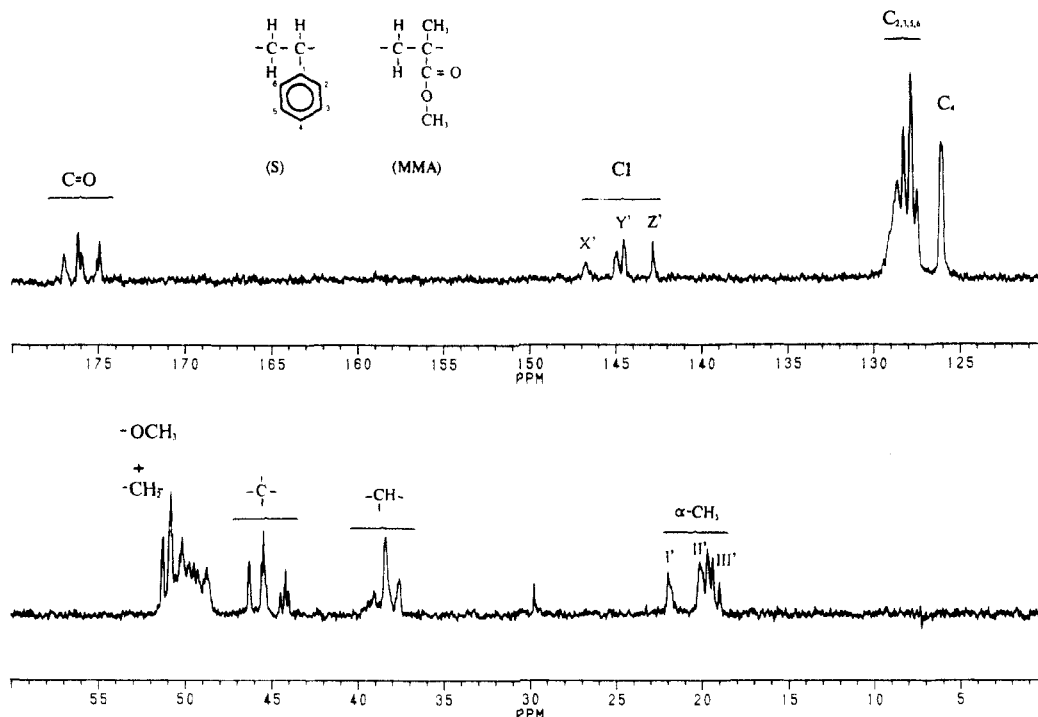


Figure 4. 100-MHz carbon-13 NMR spectrum of an alternating SMMA copolymer in  $\text{CDCl}_3$  at 298 K.

Table II  
Carbon C1 and  $\alpha$ -Methyl Assignments of Alternating SMMA Copolymers<sup>a</sup>

	C1			$\alpha$ -CH <sub>3</sub>		
	X'	Y'	Z'	I'	II'	III'
	148.0–147.0 ppm	145.5–144.5 ppm	144.0–143.0 ppm	22.8–22.0 ppm	21.0–20.2 ppm	20.2–19.8 ppm
Hirai <sup>7</sup>	$(1 - \sigma)^2 F_{\text{msm}}$	$2\sigma(1 - \sigma) F_{\text{msm}}$	$\sigma^2 F_{\text{msm}}$			
Niknam <sup>9</sup>	$(1 - \sigma)^2 F_{\text{msm}}$	$2\sigma(1 - \sigma) F_{\text{msm}}$	$\sigma^2 F_{\text{msm}}$	$(1 - \sigma)^2 F_{\text{sms}}$	$2\sigma(1 - \sigma) F_{\text{sms}}$	$\sigma^2 F_{\text{sms}}$
this work				$\sigma^2 F_{\text{sms}}$	$2\sigma(1 - \sigma) F_{\text{sms}}$	$(1 - \sigma)^2 F_{\text{sms}}$

<sup>a</sup>  $\sigma = \sigma_{\text{sm}}$  = coisotacticity parameter.

thesis of Niknam,<sup>9</sup> albeit without any justification (see Table II). As is apparent from section 1.1.a, which describes the correct assignment for the  $\alpha$ -methyl protons, justification of the assignments of the  $\alpha$ -methyl carbon can be achieved by selective decoupling experiments. These experiments were carried out in the present investigation and are shown in Figure 5. Figure 5a is a broad-band decoupled carbon NMR spectrum of an alternating SMMA copolymer in hexachloro-1,3-butadiene at 353 K. A comparison of Figures 5a and 6a shows that there exists a strong solvent effect: the induced splitting in hexachloro-1,3-butadiene is not as clear as in chloroform. We assume that the order of the peaks is the same for both solvents. The solvent hexachloro-1,3-butadiene is preferred because a better splitting in the  $\alpha$ -methyl proton NMR signals is obtained (Figure 2). In experiment 5d (Figure 5) the protons of peak I ( $\delta = 0.95$  ppm) are irradiated, resulting in a narrowing of the carbon-13 NMR shoulder at  $\delta = 20.8$  ppm and the signal peak at  $\delta = 20.4$  ppm. In experiment 5c the protons of peak II ( $\delta = 0.65$  ppm) and in experiment 5b the protons of peak III ( $\delta = 0.5$  ppm) are irradiated. Summarizing, the experiments in Figure 5 thus showed that the order in which the carbon-13 signals appear is the converse of that for the proton signals (Table II).

At this stage we know the assignments of the carbon NMR resonances of the aromatic C1 (MSM triads) and of the  $\alpha$ -methyl (SMS triads) in alternating copolymers, which is a prerequisite for assigning the carbon resonances of the statistical SMMA copolymers.

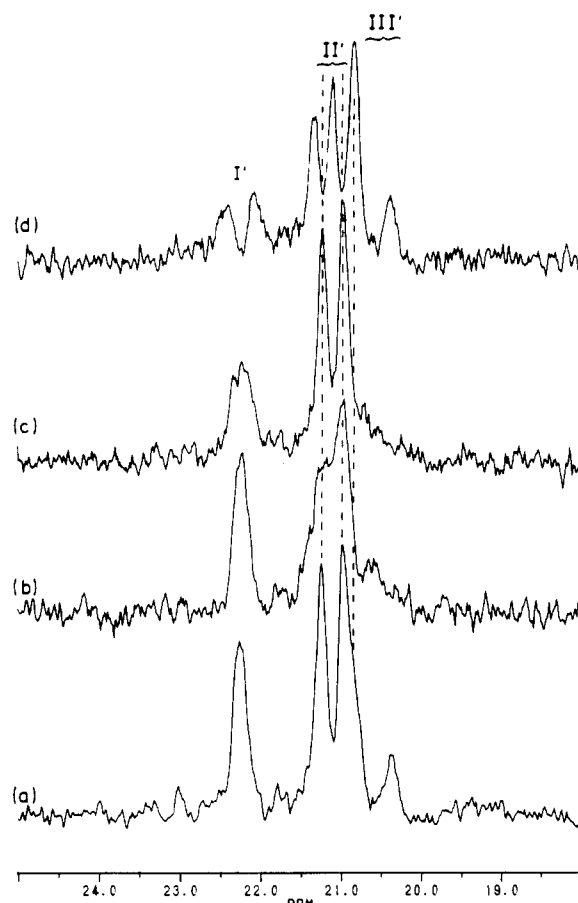
**2. Statistical SMMA Copolymers.** In the alternating SMMA copolymers, there exist only three different

configurations of the SMS triad and three different configurations of the MSM triad. The number of sequences in statistical SMMA copolymers clearly exceeds that in alternating copolymers. For this reason and because of the indiscriminate use of contradicting assignments (see Introduction), the following discussion is necessary rather than elaborate.

In statistical copolymers a total of 20 configurational sequences occur; i.e., for the MMA-centered triads the 10 following tacticity coefficients and sequences are possible:  $\sigma_{\text{mm}}^2 F_{\text{mmm}}$ ,  $2\sigma_{\text{mm}}(1 - \sigma_{\text{mm}}) F_{\text{mmm}}$ , and  $(1 - \sigma_{\text{mm}})^2 F_{\text{mmm}}$  for the MMM sequence,  $\sigma_{\text{mm}}\sigma_{\text{ms}} F_{\text{mms}}$ ,  $(1 - \sigma_{\text{mm}})\sigma_{\text{sm}} F_{\text{mms}}$ ,  $\sigma_{\text{mm}}(1 - \sigma_{\text{sm}}) F_{\text{mms}}$ , and  $(1 - \sigma_{\text{mm}})(1 - \sigma_{\text{sm}}) F_{\text{mms}}$  for the MMS or SMS sequences, and  $\sigma_{\text{sm}}^2 F_{\text{sms}}$ ,  $2\sigma_{\text{sm}}(1 - \sigma_{\text{sm}}) F_{\text{sms}}$ , and  $(1 - \sigma_{\text{sm}})^2 F_{\text{sms}}$  for the SMS sequences.

Here  $\sigma$  is the probability that two adjacent monomeric units have a meso configuration (isotactic). Similar configurational sequences are present for the S-centered triads. The coisotacticity  $\sigma_{\text{sm}}$  is calculated from the methoxy region in the proton NMR spectrum to be 0.44.<sup>3,14</sup> The other tacticities  $\sigma_{\text{mm}}$  and  $\sigma_{\text{ss}}$  are taken from the carbon NMR spectra of the homopolymers: 0.23<sup>15</sup> and 0.29,<sup>16</sup> respectively.

**2.1. Proton NMR.** The proton NMR spectra of statistical SMMA copolymers are well resolved for the methoxy protons;<sup>3,14</sup> the complex peak grouping in the methoxy region is sensitive to M-centered pentad sequence distributions and cotacticity on the triad level.<sup>3</sup> The  $\alpha$ -methyl proton region could not be assigned to sequence distributions and tacticities because of the unresolved peaks (Figure 1b).



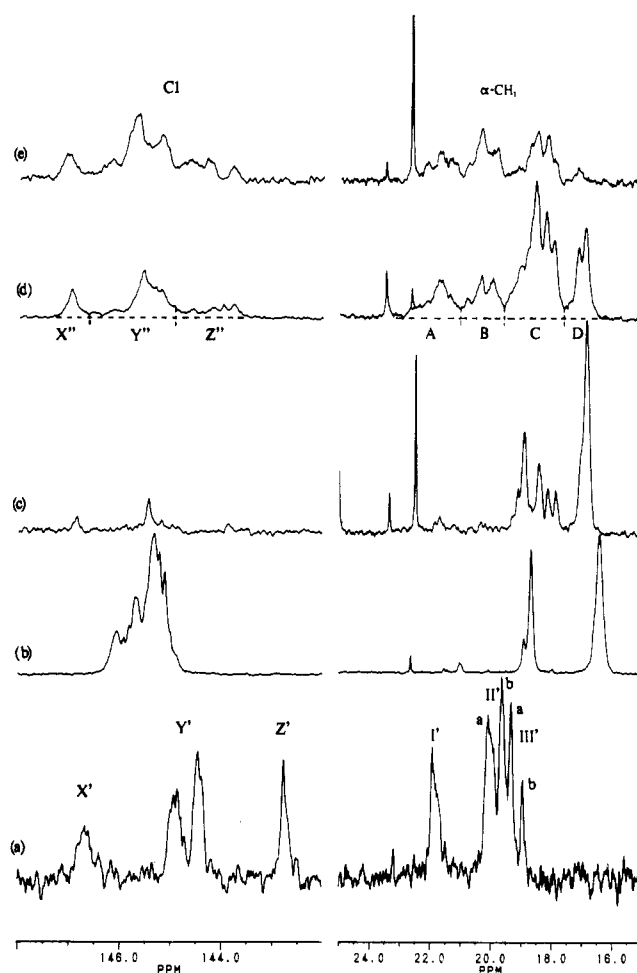
**Figure 5.** Expanded 100-MHz carbon-13 NMR spectra of an alternating SMMA copolymer in hexachloro-1,3-butadiene at 353 K: (a) broad-band decoupled; (b) selective irradiation of peak III ( $\delta = 0.5$ , Figure 2); (c) selective irradiation of peak II ( $\delta = 0.65$ , Figure 2); (d) selective irradiation of peak I ( $\delta = 0.95$ , Figure 2).

In what follows we examine the carbon NMR spectra of the statistical copolymers, using the assignments of the alternating SMMA copolymers and both homopolymers polystyrene and poly(methyl methacrylate). The aim of this work is to overcome some of the limitations described above for proton NMR, namely, to develop a method whereby triad sequence distributions can be experimentally determined for SMMA copolymers utilizing carbon NMR.

**2.2. Carbon NMR.** Figure 6c–e shows typical 100-MHz carbon NMR spectra of statistical SMMA copolymers of different copolymer composition of the aromatic C1 region ( $\delta = 148$ –143 ppm) and the  $\alpha$ -methyl region ( $\delta = 25$ –15 ppm). It appears from Figure 6a–e that the carbon resonances of statistical SMMA show additional splittings due to comonomer sequence distributions and configurational effects.<sup>4,5</sup>

**(a) C1 Carbon.** The C1 carbon resonances in statistical SMMA copolymers can be divided into three peaks, X'', Y'', Z''. The assignments of the aromatic C1 resonance of Katritzky<sup>4</sup> and of Kato<sup>5</sup> are given in Table III. From this table it is clear that the two assignments are in contradiction. As described in the section of this paper dealing with alternating copolymers, Hirai<sup>7</sup> mentioned that the assignment of Kato should be used for the statistical SMMA copolymers as far as the C1 resonance is concerned, because the isotactic MSM triad resonates at higher field. In the process of evaluation of this assignment, we will reconsider all 10 different S-centered sequences.

In Figure 6b a carbon NMR spectrum of polystyrene is shown (aromatic C1 region only). The shielding differences in the three different SSS triads are very small, and the



**Figure 6.** Expanded 100-MHz carbon-13 NMR spectra showing only the aromatic C1 region ( $\delta = 150$ –142 ppm) and the  $\alpha$ -methyl carbon ( $\delta = 25$ –15 ppm) of (a) alternating SMMA copolymer, (b) a mixture of polystyrene and poly(methyl methacrylate) polymer, (c) statistical SMMA copolymer with a molar feed composition styrene  $f_s = 0.073$ , (d) statistical SMMA copolymer with  $f_s = 0.262$ , and (e) statistical SMMA copolymer with  $f_s = 0.557$ .

meso SS diad is shifted downfield by 0.2 ppm. Because of the small differences in chemical shifts, the iso-, hetero-, and syndiotactic SSS triads are newly assigned to peak Y''. Note that this is not in concurrence with Kato.<sup>5</sup>

In Figure 6a a carbon NMR spectrum of the alternating SMMA copolymer is given, showing only the aromatic C1 region. It is discussed in section 1.2.a that the low-field resonance indicated as X' in Figure 6a corresponds to the syndiotactic MSM triad: this is peak X'' in the statistical SMMA copolymer (see Figure 6d). The isotactic MSM triad resonates at high field (peak Z''; see Figure 6d), so the heterotactic MSM triad is assigned to peak Y''. This all conforms to the work of Kato.<sup>5</sup>

The assignments of the MSS and SSM triads are based on the chemical shift differences in the SSS and MSM triads. For example,  $\sigma_{ss}(1 - \sigma_{sm})$  SSM resonates at lower field than  $(1 - \sigma_{ss})\sigma_{sm}$  SSM, because a meso SS diad is shifted to lower field (+0.2 ppm) and a meso SM diad to higher field (–1.5 ppm). This conforms to the text of Kato,<sup>5</sup> but the published assignments of Kato concerning the SSM triads do not follow this reasoning. In our opinion the  $(1 - \sigma_{ss})(1 - \sigma_{sm})$  SSM (Y''),  $\sigma_{ss}(1 - \sigma_{sm})$  SSM (Y''),  $(1 - \sigma_{ss})\sigma_{sm}$  SSM (Z''), and  $\sigma_{ss}\sigma_{sm}$  SSM (Z'') triads have to be assigned, in the order to signals, from lower to higher magnetic field. Our new assignments are given in Table III.

**(b)  $\alpha$ -Methyl Carbon.** In Figure 6c–e the  $\alpha$ -CH<sub>3</sub> main-chain resonances are shown ( $\delta = 25$ –15 ppm) and are

**Table III**  
**Carbon C1 Assignments of Statistical SMMA Copolymers**

	C1		
	X'' 147.5–146.8 ppm	Y'' 146.8–145.15 ppm	Z'' 145.15–143.5 ppm
Katritzky <sup>4</sup>	$\sigma_{sm}^2 F_{msm}$	$\sigma_{ss}^2 F_{sss}$ $2\sigma_{ss}(1 - \sigma_{ss})F_{sss}$ $\sigma_{ss}\sigma_{sm}F_{ssm}$ $(1 - \sigma_{ss})\sigma_{sm}F_{ssm}$ $2\sigma_{sm}(1 - \sigma_{sm})F_{msm}$	$(1 - \sigma_{ss})^2 F_{sss}$ $\sigma_{ss}(1 - \sigma_{ss})F_{ssm}$ $(1 - \sigma_{sm})(1 - \sigma_{ss})F_{ssm}$ $(1 - \sigma_{sm})^2 F_{msm}$
Kato <sup>5</sup>	$\sigma_{ss}^2 F_{sss}$ $(1 - \sigma_{sm})^2 F_{msm}$	$(1 - \sigma_{ss})^2 F_{sss}$ $2\sigma_{ss}(1 - \sigma_{ss})F_{sss}$ $(1 - \sigma_{ss})(1 - \sigma_{sm})F_{ssm}$ $(1 - \sigma_{ss})\sigma_{sm}F_{ssm}$ $2\sigma_{sm}(1 - \sigma_{sm})F_{msm}$	$\sigma_{ss}(1 - \sigma_{sm})F_{ssm}$ $\sigma_{ss}\sigma_{sm}F_{ssm}$ $\sigma_{sm}^2 F_{msm}$
this work	$(1 - \sigma_{sm})^2 F_{msm}$	$\sigma_{ss}^2 F_{sss}$ $2\sigma_{ss}(1 - \sigma_{ss})F_{sss}$ $(1 - \sigma_{ss})^2 F_{sss}$ $(1 - \sigma_{ss})(1 - \sigma_{sm})F_{ssm}$ $\sigma_{ss}(1 - \sigma_{sm})F_{ssm}$ $2\sigma_{sm}(1 - \sigma_{sm})F_{msm}$	$(1 - \sigma_{ss})\sigma_{sm}F_{ssm}$ $\sigma_{ss}\sigma_{sm}F_{ssm}$ $\sigma_{sm}^2 F_{msm}$

**Table IV**  
**Carbon  $\alpha$ -Methyl Assignments of Statistical SMMA Copolymers**

	$\alpha$ -CH <sub>3</sub>			
	A 23.0–21.2 ppm	B 21.2–19.8 ppm	C 19.8–17.8 ppm	D 17.8–16.5 ppm
Katritzky <sup>4</sup>	$\sigma_{mm}(1 - \sigma_{sm})F_{mms}$ $\sigma_{mm}\sigma_{ms}F_{mms}$	$\sigma_{mm}^2 F_{mmm}$ $\sigma_{sm}^2 F_{sms}$ $2\sigma_{sm}(1 - \sigma_{sm})F_{sms}$ $(1 - \sigma_{sm})^2 F_{sms}$	$2\sigma_{mm}(1 - \sigma_{mm})F_{mmm}$ $(1 - \sigma_{mm})\sigma_{sm}F_{mms}$ $(1 - \sigma_{mm})(1 - \sigma_{sm})F_{mms}$	$(1 - \sigma_{mm})^2 F_{mmm}$
Kato <sup>5</sup>	$\sigma_{mm}^2 F_{mmm}$ $\sigma_{mm}(1 - \sigma_{sm})F_{mms}$ $\sigma_{sm}^2 F_{sms}$	$2\sigma_{sm}(1 - \sigma_{sm})F_{sms}$ $(1 - \sigma_{sm})^2 F_{sms}$	$2\sigma_{mm}(1 - \sigma_{mm})F_{mmm}$ $(1 - \sigma_{mm})\sigma_{sm}F_{mms}$ $(1 - \sigma_{mm})(1 - \sigma_{sm})F_{mms}$ $\sigma_{mm}\sigma_{sm}F_{mms}$	$(1 - \sigma_{mm})^2 F_{mmm}$
this work	$\sigma_{mm}^2 F_{mmm}$ $\sigma_{mm}\sigma_{sm}F_{mms}$ $\sigma_{sm}^2 F_{sms}$	$\sigma_{mm}(1 - \sigma_{sm})F_{mms}$ $2\sigma_{sm}(1 - \sigma_{sm})F_{sms}$ $(1 - \sigma_{sm})^2 F_{sms}^a$	$2\sigma_{mm}(1 - \sigma_{mm})F_{mmm}$ $(1 - \sigma_{mm})\sigma_{sm}F_{mms}$ $(1 - \sigma_{mm})(1 - \sigma_{sm})F_{mms}$ $(1 - \sigma_{sm})^2 F_{sms}^a$	$(1 - \sigma_{mm})^2 F_{mmm}$

<sup>a</sup> This peak shows resonance splitting and appears in both the B and C peak areas.

designated as A, B, C, and D. The assignments of these resonances, given by Katritzky<sup>4</sup> and Kato,<sup>5</sup> are summarized in Table IV. There are a few differences between the assignments of Katritzky<sup>4</sup> and Kato.<sup>5</sup> The order of assignment of the configurational MMM triads is the same and in agreement with the literature,<sup>15</sup> and also the order of assignments for the configurational SMS triads are in agreement with the experiments in the present paper (see section 1.2.b). In our view, however, there is a misunderstanding in assigning the MMM and SMS triads to the correct peaks A, B, C, and D, as discussed next.

We agree with the assignments by Kato<sup>5</sup> of the  $\sigma_{mm}^2$  MMM,  $2\sigma_{mm}(1 - \sigma_{mm})$  MMM, and  $(1 - \sigma_{mm})^2$  MMM triads to peaks A, C, and D, respectively (Figure 6d). The SMS triads are also well assigned by Kato,<sup>5</sup> with one exception; there is some doubt that peak IIIb could be assigned to peak C instead of to peak B (cf. Figure 6a,c-e).

The MMS or SMM triads also have to be reconsidered, in the same manner as the SSM triads, and the same reasoning can be used (see section 2.2.a). The meso MM diad resonates at even lower field (+2 ppm) than the meso SM diad. This explanation is again also given by Kato et al.,<sup>5</sup> but there is no reason given for assigning, say  $\sigma_{mm}\sigma_{sm}$  MMS to peak C. This may be one of the reasons why these authors failed to obtain a fit when the experimental peak areas were compared with theoretical predictions.

The following order of MMS configurational triads matches carbon NMR signals with increasing shielding:  $\sigma_{mm}\sigma_{sm}$  MMS (A),  $\sigma_{mm}(1 - \sigma_{sm})$  MMS (B),  $(1 - \sigma_{mm})\sigma_{sm}$

MMS (C), and  $(1 - \sigma_{mm})(1 - \sigma_{sm})$  MMS (C). The complete assignment is given in Table IV.

## Conclusions

It appears that in the proton and carbon NMR spectra of SMMA copolymers (both alternating and statistical) contradicting assignments in the literature have caused confusion. Although some of the original studies containing these assignments are rather ancient, references to these sources are still regularly made in modern studies. This severely hampers the progress in copolymerization studies of SMMA systems.

In the present paper some important rectifications are proposed in the assignments of the  $\alpha$ -methyl protons in the NMR spectra of alternating SMMA copolymers. With this result the  $\alpha$ -methyl carbon NMR resonances can be assigned correctly by means of selective decoupling NMR experiments. With this knowledge and with the assignments for the aromatic C1 and  $\alpha$ -methyl carbon NMR signals of polystyrene, poly(methyl methacrylate), and the alternating SMMA copolymers, it was possible to propose assignments for the statistical copolymers in the aromatic C1 and  $\alpha$ -methyl carbon NMR regions. These new peak assignments were made without comparing experimental and predicted peak areas from any theoretical copolymerization model, because the aim of the accompanying paper<sup>2</sup> is to use the sequence distribution of SMMA copolymers for testing several models for copolymerization. Therefore, sequence distributions should be obtainable from the NMR spectra for lack of alternatives. It is the

aim of the present paper to achieve this goal; see also the Introduction. As shown in the accompanying paper,<sup>2</sup> the MMA-centered triads and the styrene-centered triads can be directly calculated from the  $\alpha$ -CH<sub>3</sub> and C1 peak areas in the carbon NMR spectra. This is contrary to the proton NMR spectra of the SMMA copolymers, where the peak splitting of the methoxy protons is so complicated that the peak areas cannot be translated directly to sequences. It is only possible to theoretically predict M-centered pentads, in which case the peak areas can be calculated and compared with experimental values.

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