

Investigation of the intramolecular structure of styrene-ethylmethacrylate copolymers by ^1H - and ^{13}C -NMR : reassignment of H-NMR spectra

Citation for published version (APA):

Tacx, J. C. J. F., Velden, van der, G. P. M., & German, A. L. (1988). Investigation of the intramolecular structure of styrene-ethylmethacrylate copolymers by ^1H - and ^{13}C -NMR : reassignment of H-NMR spectra. *Journal of Polymer Science, Part A: Polymer Chemistry*, 26(5), 1439-1456. <https://doi.org/10.1002/pola.1988.080260516>

DOI:

[10.1002/pola.1988.080260516](https://doi.org/10.1002/pola.1988.080260516)

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Investigation of the Intramolecular Structure of Styrene–Ethylmethacrylate Copolymers by ^1H - and ^{13}C -NMR: Reassignment of ^1H -NMR Spectra

J. C. J. F. TACX,* *Eindhoven University of Technology, Laboratory of Polymer Chemistry, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*, and G. P. M. VAN DER VELDEN, *DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands*, and A. L. GERMAN, *Eindhoven University of Technology, Laboratory of Polymer Chemistry, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

Synopsis

The compositions and sequence distributions of homogeneous styrene (S)–ethyl methacrylate (E) copolymers, obtained by low conversion solution polymerization have been studied by ^1H - and ^{13}C -NMR. A new set of peak triad assignments was proposed for the δ 2.1–4.2 ppm region in the ^1H -NMR spectrum, whereby the reactivity ratios of $r_{\text{S}} = 0.59$ and $r_{\text{E}} = 0.50$ were used to establish this new assignment. The EEE and SSS blocks, present in these copolymers, have a high degree of syndiotacticity ($\sigma_{\text{EE}} = 0.23$, $\sigma_{\text{SS}} = 0.39$), whereas the ESE units are exhibiting a slight tendency toward isotacticity ($\sigma_{\text{ES}} = 0.66$).

INTRODUCTION

Copolymer molecular structure is a very complicated matter, since on the one hand the molecules may differ in chain length and composition (intermolecular structure), while on the other hand, monomer sequencing and tacticity in the chains may also differ (intramolecular structure). The intramolecular structure of copolymers may supply information about the process of addition of monomers, during a radical copolymerization and also about the preference of monomers to add in a (co)iso- or (co)syndiotactic configuration. In addition, the intramolecular structure may strongly affect the physical and mechanical properties of the copolymers.^{1–3} This explains the still increasing need to reveal molecular structures.

One of the advanced methods of determining the intramolecular structure of copolymers is NMR. ^1H -NMR has been used extensively to study the microstructure of styrene–methacrylate copolymers, especially styrene–methyl methacrylate (STY–MMA). In various earlier studies,^{4–9} spectra have been shown (40–100 MHz ^1H -NMR), displaying three major groups of peaks, representing the oxymethylene region. This fine structure was attributed to the differences in shielding effects of the styrene monomer. It was shown that

* Present address: DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands.

the coisotacticity parameter (σ) of styrene and methyl methacrylate and the number fraction of M-centered triads could be estimated from these relatively simple ^1H -spectra.

However, spectra of styrene-methacrylate copolymers recorded at higher field strengths (270 and 600 MHz) display significantly more fine structure than reported in the earlier work.^{8,10,11} Five peaks could be distinguished in the oxymethylene region. From these recent publications it becomes clear that the original assignments were not correct. For instance, the spectra of STY-MMA, originally assigned by Bovey and Ito⁴⁻⁹ and *p*-tert-butylstyrene-methyl-methacrylate were successfully reassigned by Uebel and Dinan.^{10,11}

Recently, we have studied the copolymerization behavior of styrene and ethyl methacrylate in batch solution processes and the inter- and intramolecular structure of the resulting copolymers. From this study¹²⁻¹⁵ it appeared that the copolymerization behavior in solution processes could successfully be described by the classical Alfrey-Mayo (AM) model, even at high conversions (96%). The intermolecular structure [chemical composition distribution (CCD)] of copolymers, obtained at low and very high conversions, could also be predicted by models, based on the classical AM model.

As an important result, we found that the assignments by Bovey and Ito for styrene-methyl methacrylate copolymers in ^1H -NMR spectra certainly do not hold for styrene-ethyl methacrylate copolymers also. Despite the improvements recently proposed by Uebel,¹¹ his improved assignment appeared not to hold either. The possibility of the application of an invalid model or incorrect *r*-values must be ruled out, since the model and parameters obtained from low conversion kinetic data, could predict high conversion copolymerization behavior and copolymer intermolecular structure very accurately. In order to correlate the observed resonance pattern with structural features we reassigned the ^1H -NMR spectra for STY-EMA copolymers. The reassignment was confirmed by data obtained from ^{13}C -NMR.

EXPERIMENTAL

Purification of Chemicals

The monomers styrene and ethyl methacrylate (Merck) were distilled at reduced pressure under nitrogen. The middle fraction of the distillate was collected and used. In all cases the distillate was found to be > 99.5% pure by GLC analysis. The free radical initiator AIBN (Fluka p.a.) was recrystallized once from methanol. The solvent toluene (Merck p.a.) was dried over sodium, degassed, and distilled under helium.

Preparation of Copolymers

The copolymers were prepared under high pressure (118 MPa) in a stainless steel autoclave (Autoclave Engineers) as described in detail elsewhere.¹⁶ The total monomer concentration was 1 mol dm^{-3} in toluene; the initiator concentration was 5 mmol dm^{-3} .

Both conversion and feed ratio were calculated from quantitatively monitoring the entire course of the reaction. Samples of $2 \mu\text{L}$ were injected by means of a special sampling disk valve described previously.¹⁷ The GLC

conditions were: stationary phase, carbowax 400 on poracil S 100–120 mesh (Waters Associates Inc.); column length 1.20 m and column temperature 388 K; detector temperature 423 K; injection port temperature: 393 K; total monomer conversions were generally less than 12%.

All copolymers were isolated and purified by pouring out in cold hexane. The final products were dried at 328 K in a vacuum stove for 6 h at 10^{-1} torr and finally for 8 h at 10^{-5} torr. The products contained less than 0.1% monomer or non-solvent as confirmed by GPC analysis.

Experimental Conditions for Recording ^1H - and ^{13}C -NMR Spectra

^1H -NMR spectra were measured with 200 MHz (Varian XL-200) and 300 MHz (Bruker CXP-300) spectrometers at 298 K, using CDCl_3 (200 MHz) and CCl_4 (300 MHz) as solvents and $(\text{CD}_3)_2\text{CO}$ as internal locking agent.

The 200 MHz ^1H -NMR spectra were obtained using a spectral width of 2600 Hz, acquisition time of 3 s, a flip angle of 35° , and a pulse delay of 10 s. Spectra were generally obtained after accumulating 64 scans, using a sample concentration of 1% (w/v). The digital resolution amounted to 0.17 Hz, corresponding to a data length of 16 K. Similar conditions were employed in recording 300 MHz ^1H -NMR spectra, except a larger flip angle (75°) and a smaller pulse delay (5 s) were used.

The 50 MHz ^{13}C -NMR spectra were obtained with a Varian XL-200 spectrometer, equipped with a V77-200 Sperry Univac computer. The sample concentration was 9% (w/v) in CDCl_3 . Using 10 mm tubes, ^{13}C -NMR spectra were recorded at 298 K. The pulse width (10 μs) corresponds to a flip angle of 77° , and a pulse delay of 4 s was found to be necessary. Spectra were generally obtained after the accumulation of 10000 FID's, where the digital resolution amounted to 0.687 Hz, corresponding to a spectral width and a data length of 16 K. Peak areas were determined via planimeter or electronic integration methods. Monomer sequence distribution and configurational sequence arrangements were determined by comparing relative peak areas of the protons or carbons involved. In performing quantitative NMR measurements, it is necessary to take differences in spin-lattice relaxation times (T_1) into account. During the investigation, no proton or carbon T_1 's have been measured. Only for the calculation of the composition of the copolymers, areas belonging to different types of protons were measured. The delay time (10 s) was considered to be adequate for quantitative purposes.

Irrespective of this effect, no differential T_1 's have been considered to occur for the OCH_2 resonances. Within these limits relative peak areas are proportional to the number of protons involved. Similar arguments hold for the ^{13}C -NMR data, where it has been assumed that no different spin-lattice relaxation times or NOE's were present for different stereo isomeric or compositional sequences.

RESULTS AND DISCUSSION

^1H -NMR Spectra: Determination of Copolymer Composition

Figure 1 depicts the 200 MHz ^1H -NMR spectra of two STY-EMA copolymers, dissolved in CDCl_3 at 25°C , whereas in Figure 2 expanded 300 MHz

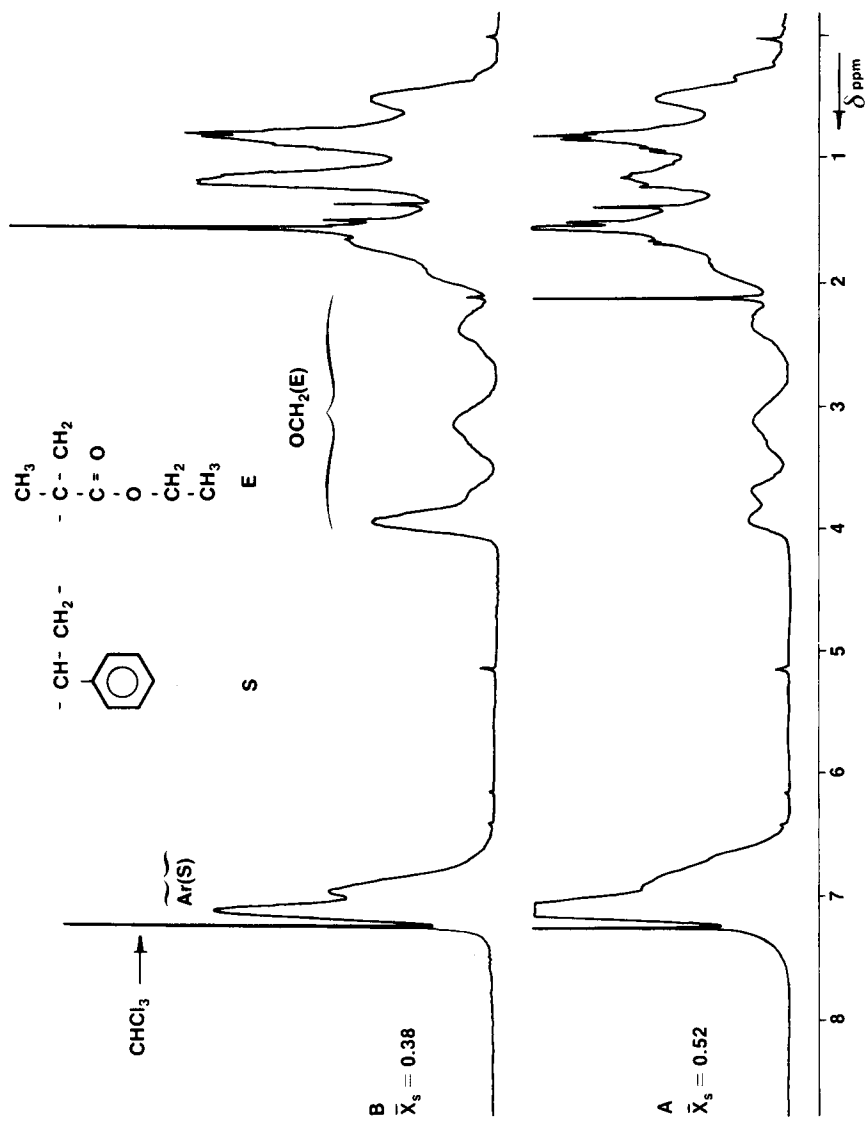


Fig. 1. 200 MHz ^1H -NMR spectra of styrene (S)-ethyl methacrylate (E) copolymers in CDCl_3 at 25°C . The mole fraction STY is indicated on the left.

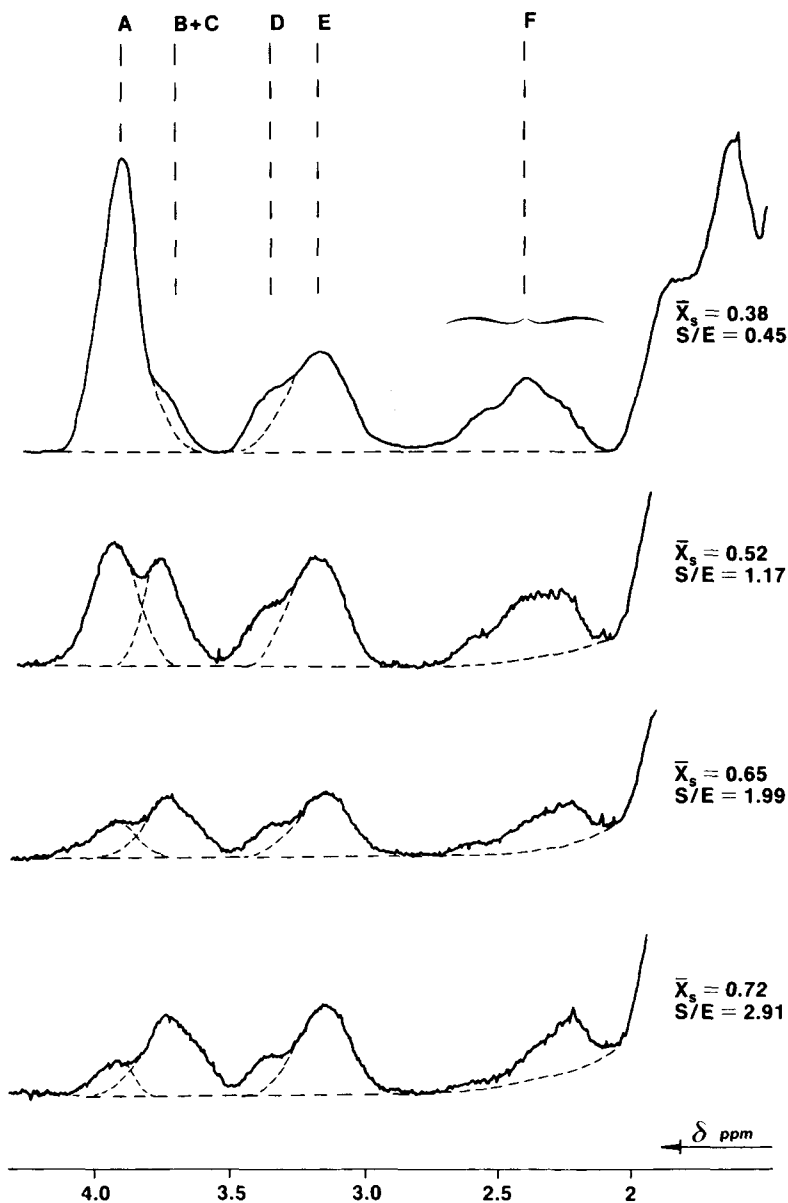


Fig. 2. Expanded 300 MHz $^1\text{H-NMR}$ spectra of S-E copolymers, showing the oxymethylene region only. Spectra were recorded in CCl_4 at 25°C . Copolymer compositions and molar feed ratios are indicated on the right. Area measurements have been performed for the regions A-F using the dotted areas.

spectra are shown for four copolymers, recorded in CCl_4 at 25°C . These 300 MHz $^1\text{H-NMR}$ spectra only show the oxymethylene region, since this region in particular displays additional fine splittings due to combined configurational and compositional sequence effects.

The average copolymer composition [mole fraction styrene (\bar{X}_{STY})]

TABLE I
Initial Feed Composition and Final Copolymer Composition (Mole Fraction Styrene)

Feed composition		Copolymer composition
$q_0 = [\text{STY}]/[\text{EMA}]$	$[\text{STY}]/([\text{STY}] + [\text{EMA}])$	$[\text{STY}]/([\text{STY}] + [\text{EMA}])$
2.91	0.74	0.72
2.80	0.74	0.69
1.99	0.67	0.65
1.46	0.59	0.58
1.17	0.54	0.52
0.66	0.40	0.42
0.45	0.31	0.38

can be readily obtained, using

$$\bar{X}_{\text{STY}} = \frac{10A_1}{7A_1 + 5A_2} \quad (1)$$

where A_1 and A_2 represent the total peak areas of the aromatic and aliphatic proton resonances, respectively. The initial feed ratio and copolymer compositions are summarized in Table I.

Determination of r -Values

It should be emphasized that r -values are extremely important parameters in the prediction of the intramolecular structure. As a consequence, accurate and precise determination of both r -values is a prerequisite. There are a number of methods reported in literature¹⁸⁻²⁴ to estimate the reactivity ratios. The methods can be roughly divided into two classes. On one hand, there are methods based on the differential Alfrey-Mayo (AM) model which require copolymer and initial feed compositional data. Such approximation methods have been proposed by Fineman and Ross,²¹ and Kelen et al.^{22,23} On the other hand, there are some very sophisticated methods, e.g., improved curve fitting I-procedure (ICFIP), based on the integral AM model, using GLC data. GLC analysis of the reaction mixture throughout a copolymerization reaction in conjunction with the so-called ICFIP, which accounts for measurement errors in both variables, has been found to lead to a reliable estimation of monomer reactivity ratios.^{17-20,25}

In this study, we compared three well-known calculation methods. Two methods [Kelen and Tüdös low conversion (KETL) and Fineman and Ross

TABLE II
Results of Estimation of r -Values by Means of Different Calculation Methods¹⁷⁻²¹:
Styrene (S) and Ethyl Methacrylate (E) in Toluene (62°C and 118 MPa)

Method	r_S	r_E
FR ²¹	0.58 ± 0.09	0.41 ± 0.2
KETL ^{22,23}	0.62 ± 0.06	0.51 ± 0.1
ICFIP ²⁵	0.59 ± 0.03	0.50 ± 0.02

(FR)] are based on the differential AM model, using copolymer compositional data. The third one (ICFIP) is based on the integral AM model. The results of the estimations are summarized in Table II.

From this table it appears that the r -values, estimated by two significantly differing methods (viz., KETL and ICFIP) are in very good agreement. However, the results of the FR method are somewhat different. From an extensive study on the comparison of various estimation procedures,¹⁸⁻²⁰ it appears that, the FR method, although very rapid, lacks precision as compared with the ICFIP and KETL, under the present conditions.

In a separate study,¹⁴ we have found that the intermolecular structure (CCD) as well as the high conversion copolymerization behavior could be predicted very accurately by means of the r -values obtained from low conversion data. From these results, it might be inferred that the copolymerization kinetics can be successfully described by the first order AM model. The r -values as obtained by ICFIP^{17, 18, 25} were applied for model calculations.

Correlation between Resonance Pattern and Structural Features

Concentrating on the oxymethylene region (2-4.2 ppm), these resonances display considerable fine structure, similar to the pattern observed in spectra of STY-MMA copolymers.¹¹ In comparison with recently published ¹H-NMR spectra of STY-EMA copolymers, recorded at 60²⁶ and 100 MHz²⁷ respectively, our spectra display at least five peaks, therefore displaying a more fine structure.

The 10 theoretically possible EMA-centered triads are not resolved in distinct resonances, and up to now^{26, 27} the three peaks in spectra of STY-EMA copolymers have been analyzed in terms of Bovey and Ito's approach for STY-MMA copolymers, breaking the oxymethylene region in three composite groupings.

However, with the work of San Roman²⁸ and Uebel¹¹ a reassignment can be given for the resonances in STY-EMA copolymers. In Table III the assignments of Ito,⁴⁻⁹ Uebel,^{10, 11} and our final tentative assignments are summarized. The symbols A-F refer to Figure 2 and are similar to I-VI used for STY-MMA copolymers.¹¹

TABLE III
Literature and New Assignments of Triads for STY-EMA Copolymers

	Peak number				
	A	B + C	D	E	F
Chemical shift region (ppm)	4.2-3.85	3.85-3.5	3.5-3.3	3.3-3.0	2.7-2.1
Ito/Bovey ⁴⁻⁹	EEE	(1 - σ)EES (1 - σ) ² SES	σ EES	2 σ (1 - σ)SES	σ ² SES
Uebel/Dinan ^{10, 11}	EEE (1 - σ)EES	(1 - σ) ² SES	σ EES	2 σ (1 - σ)SES	σ ² SES
This work	EEE (1 - σ)EES	2 σ (1 - σ)SES	(1 - σ) ² SES	σ EES	σ ² SES

In Table III, the parameter σ_{SE} ($= \sigma$ in shorthand notation) is defined as a measure of the probability that alternating EMA and STY units adopt a coisotactic configuration⁵ and EEE, EES and SES denote the three different kinds of compositionally EMA centered triads. More details can be found in earlier work.⁴⁻¹¹

Table IV summarizes the normalized peak areas experimentally determined for each of the seven STY-EMA copolymers, together with the copolymer and initial feed composition data. It should be realized that methine protons (ca. 2.1 ppm) may contribute to the area representing peak F, especially in spectra of copolymers, having a relatively high styrene content. In order to cope with this difficulty, appropriate smooth baseline corrections were made as indicated in Figure 2. Implicitly it has been assumed, that spin-spin coupling effects only contribute to the linewidth of the various peaks. This has been verified for the homopolymer poly(ethyl methacrylate) (PEMA).

Assuming the AM model to be valid at any moment of reaction, the number fraction (F) of EMA (E) and STY (S) centered triads can be predicted.²⁸⁻³¹

TABLE IV
Normalized Peak Areas (A-F) of the Oxymethylene Resonances of Seven S-E Copolymers,
Feed Ratio ($q_0 = [\text{STY}]/[\text{EMA}]$), Copolymer Composition (mole fraction styrene).
The Predicted Peak Areas are Calculated, Using $r_S = 0.59$, $r_E = 0.50$, $\sigma_{SE} = 0.66$

Feed ratio q_0	Copolymer composition \bar{X}_{STY}	Normalized peak area					Assignment
		A	B + C	D	E	F	
2.91	0.72	0.05	0.31	0.07	0.35	0.22	Observed
		0.02	0.17	0.16	0.34	0.31	Ito
		0.10	0.09	0.16	0.34	0.31	Uebel
		0.10	0.34	0.09	0.16	0.31	Current
2.80	0.69	0.08	0.23	0.08	0.29	0.32	Observed
		0.02	0.17	0.17	0.32	0.32	Ito
		0.11	0.08	0.17	0.32	0.32	Uebel
		0.11	0.32	0.08	0.17	0.32	Current
1.99	0.65	0.13	0.25	0.06	0.30	0.28	Observed
		0.04	0.20	0.20	0.29	0.27	Ito
		0.15	0.09	0.20	0.29	0.27	Uebel
		0.15	0.29	0.09	0.20	0.27	Current
1.46	0.58	0.19	0.26	0.10	0.26	0.19	Observed
		0.07	0.19	0.25	0.24	0.24	Ito
		0.20	0.06	0.25	0.24	0.24	Uebel
		0.20	0.24	0.06	0.25	0.24	Current
1.17	0.52	0.24	0.18	0.07	0.27	0.24	Observed
		0.09	0.21	0.27	0.23	0.20	Ito
		0.24	0.06	0.27	0.23	0.20	Uebel
		0.24	0.23	0.06	0.27	0.20	Current
0.66	0.42	0.36	0.08	0.05	0.25	0.27	Observed
		0.21	0.20	0.31	0.15	0.14	Ito
		0.37	0.04	0.31	0.15	0.14	Uebel
		0.37	0.15	0.04	0.31	0.14	Current
0.45	0.38	0.48	0.03	0.04	0.25	0.20	Observed
		0.28	0.20	0.32	0.09	0.11	Ito
		0.46	0.03	0.32	0.09	0.11	Uebel
		0.46	0.09	0.03	0.32	0.11	Current

The relation between intramolecular structure (number fraction of triads) and reaction kinetics is given by the set of eqs. (2):

$$\begin{aligned}
 F_{EEE} &= P(E) * P(E/E) * P(E/EE)/P(E) = P^2(E/E) = (1 - P(S/E))^2 \\
 F_{EES} &= 2P(S/E) * (1 - P(S/E)) \\
 F_{SES} &= P^2(S/E) \\
 F_{SSS} &= (1 - P(E/S))^2 \\
 F_{SSE} &= 2P(E/S) * (1 - P(E/S)) \\
 F_{ESE} &= P^2(E/S)
 \end{aligned}
 \tag{2}$$

where $P(S/E) = (1 + r_2/q)^{-1}$, $P(E/S) = (1 + r_1q)^{-1}$, and $q (= [STY]/[EMA])$ is the instantaneous feed ratio. Here F is the normalized number fraction of triads, $P(M_1/M_2)$ the probability of a growing chain, having an M_2 -type chain-end, to add monomer M_1 .

All these triad fractions are predicted, using the initial feed ratios (q_0 , see Table I) and r -values (see Table II), estimated by means of ICFIP. The results are summarized in Table V.

In order to predict the relative intensities of each peak, with the appropriate assignment, it is necessary to estimate the values of the coisotactic parameter σ_{SE} . Three different sets of assignments have been investigated: Ito's approach,⁴⁻⁹ Uebel's,¹¹ and our tentative assignments to be discussed in detail shortly.

The theoretically calculated values, using the triad fraction (Table V) and the different models (Table III) are tabulated in Table IV. By comparing the experimental results with the results of the first model (Bovey and Ito), it is immediately clear that in this model, the area A (i.e., only EEE triad) is severely underestimated, irrespective of the value of the parameter σ_{SE} . This leads to a similar conclusion for our STY-EMA as compared with the STY-MMA copolymers, i.e., the earlier assignments have to be reconsidered. According to Uebel's assignment and ours, the relative intensity of peak A is

TABLE V
Normalized EMA (E) and STY (S) Centered Triad Fractions, Calculated with Alfrey-Mayo Kinetics, Reactivity Ratios $r_S = 0.59$ and $r_E = 0.50$, and Initial Feed Ratios ($q_0 = [STY]/[EMA]$)

q_0	\bar{X}_{STY}	F_{EEE}	F_{EES}	F_{SES}	F_{SSS}	F_{SSE}	F_{ESE}
2.91	0.72	0.02	0.25	0.73	0.40	0.46	0.14
2.80	0.69	0.02	0.26	0.72	0.39	0.47	0.14
1.99	0.65	0.04	0.32	0.64	0.29	0.50	0.21
1.46	0.58	0.07	0.38	0.55	0.21	0.50	0.29
1.17	0.52	0.09	0.42	0.49	0.17	0.48	0.35
0.66	0.42	0.19	0.49	0.32	0.08	0.40	0.52
0.45	0.38	0.28	0.50	0.22	0.04	0.33	0.63

TABLE VI
 Predicted Fraction F_{EEE} and F_{EES} Triads, Initial Feed Ratio ($q_0 = [\text{STY}]/[\text{EMA}]$),
 and Calculated σ_{SE}

q_0	Area A	F_{EEE}	F_{EES}	σ_{SE}
2.91	0.05	0.02	0.25	0.88
2.80	0.08	0.02	0.26	0.76
1.99	0.13	0.04	0.32	0.72
1.46	0.19	0.07	0.38	0.68
1.17	0.24	0.09	0.42	0.65
0.66	0.36	0.21	0.47	0.68
0.45	0.48	0.28	0.50	0.60

assumed to be caused by the EEE and $(1 - \sigma_{SE})EES$ configurations. The values of σ_{SE} is now easily estimated, using eq. (3) (σ_{SE} is truncated as σ)

$$\text{Area A} = F_{EEE} + (1 - \sigma)F_{EES} \quad (3)$$

Both triad fractions can be predicted by the differential AM model, using r -values obtained from highly accurate and independent measurements. The area of peak A is obtained from experimental data. The parameter σ_{SE} now can be easily estimated.

In general, this calculation procedure can be applied to more equations. However, application to other triad combinations represented by various peaks is limited, since those peaks are not highly resolved and don't cover such a wide range of values as compared with peak A. In addition, the baseline belonging to peak A is assumed to be straight without interference by various types of protons. Uebel's assignment and ours are in agreement when considering peak A. As a consequence, σ_{SE} is obtained as accurate as possible and has the same value in both Uebel's and our assignments. The results of the calculations are tabulated in Table VI.

The σ_{SE} values obtained for $q_0 = 2.91$ and 2.80 are probably the least reliable ones, owing to the difficulty of measuring accurately the small areas (cf., Fig. 2). These values are omitted in the calculation of the average σ_{SE} value, the result being $\sigma_{SE} = 0.66 \pm 0.05$. This value is in very good agreement with the value obtained for STY-MMA copolymers ($\sigma_{SM} = 0.65$).

Considering the assignments of Uebel^{10,11} in greater detail now, serious discrepancies show up between predicted and observed areas of peaks B + C, D, and E. The values for areas A and F are in reasonable agreement. The discrepancies can be easily verified comparing Figure 2 of Reference 11 with our Figure 2 (or alternatively Table 2 of Reference 11 with our Table IV). Although the absolute values of peak areas I (A) and VI (F) agree reasonably well for copolymers having approximately the same composition, this does not hold for the respective areas II (B)-V (E).

Via visual inspection of Table IV one easily verifies that a cyclic permutation of the values for peak areas B + C, D and E of the model of Uebel¹¹ leads to significantly better results. Comparison of our new assignment with the one of Uebel leads to the conclusions that the $2\sigma(1 - \sigma)SES$ triad apparently resonates at 3.5-3.8 ppm, whereas the $(1 - \sigma)^2SES$ and σEES triads only

shift to slightly higher field. Accidentally in our model the predicted areas B + C and F (see Table IV) are approximately equal irrespective of the copolymer composition, using $\sigma = 0.66$. Comparing experimentally determined and theoretically calculated values for the peak areas B + C and F, this appears to be true, except for the two copolymers with $\bar{X}_s = 0.38$ and $\bar{X}_s = 0.42$. However in both cases the discrimination between the large peak area A and the small peak area B + C is arbitrary (see Fig. 2, $\bar{X}_s = 0.38$) leading to large inaccuracies. Possibly in these cases the experimentally determined peak areas B + C in relation to peak area A have been underestimated slightly. However, within experimental accuracy limits (± 0.06), these areas hardly change, neither leading to a significantly better fit (still a discrepancy occurs between the experimentally determined peak areas B + C and F for the polymers with $\bar{X}_s = 0.38$ and $\bar{X}_s = 0.42$) nor to a large change of the average σ value (0.69 vs. 0.66, see Table VI). Because no theoretical explanation can be offered for the cyclic permutation of the peak areas B + C, D and E in our model in respect to the model of Uebel,¹¹ and because of the above mentioned minor anomalies, several other possibilities have been considered, e.g.:

Partial overlap of the resonances of the σ^2 SES triad and styrene methine protons;

Differences in measurement circumstances;

Other triad reshufflings;

Pentad analysis; and

Anomalous AM propagation kinetics.

The first probability is not likely, because the overlap of the σ^2 SES triad and the styrene methine centered resonances, would only result in a decrease of the σ^2 SES triad and an increase of all other triads, without affecting the values mutually. Differences of inaccuracies of measurement conditions must be ruled out, since the results of 200 and 300 MHz ¹H-NMR spectra, recorded on different spectrometers and under different conditions are almost identical.

All other triad reshufflings have been investigated extensively. In addition, an extension to pentad analysis has been tried, however both methods failed to give better results.

Finally a non-AM model, e.g., Coleman-Fox³¹ is not considered to occur, since the low and high conversion copolymerization behavior and the intermolecular structure of the resulting copolymers, could successfully be described by means of the classical AM model.

Hence, we believe that for the system under consideration, i.e. STY-EMA, the new assignment is the correct one, but it should be emphasized that the calculation of the value of σ_{SE} is independent of the assignment (Uebel's or ours) and that the earlier model might still be valid for STY-MMA copolymers.

¹³C-NMR Spectra: Determination of Copolymer Composition

Figure 3 shows the 50 MHz ¹³C-NMR spectra of the homopolymer poly(ethyl methacrylate) (PEMA) and two copolymers with significantly differing styrene content. The assignments of all resonances have been depicted in the same

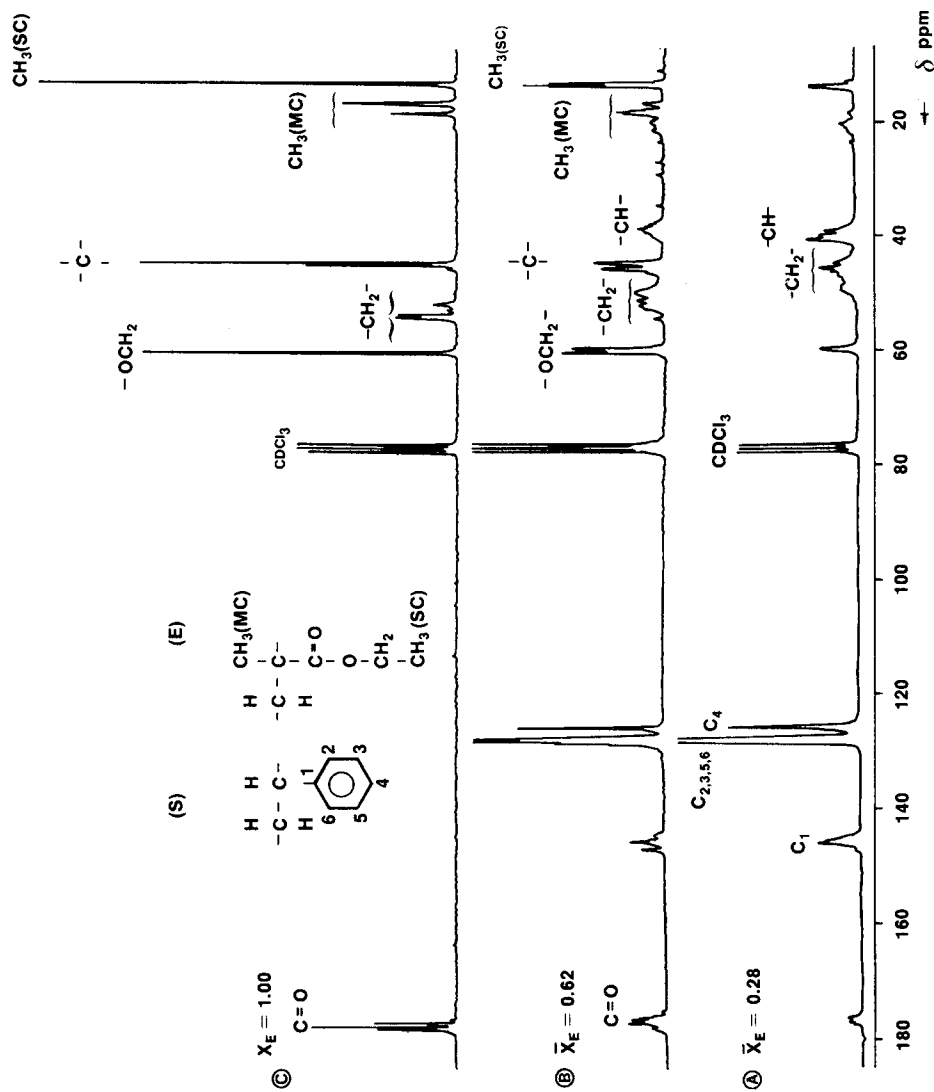


Fig. 3. 50 MHz ¹³C-NMR spectra of poly(ethyl methacrylate) (C) and two S-E copolymers (A, B) recorded in CDCl₃ at 25°C. Assignments are discussed in the text.

figure. For assignment purposes, we have applied shift additivity rules,³² earlier results reported on related STY-MMA copolymers,³³ and ¹³C-NMR spectra of various polymethacrylates and polystyrenes.³⁴

The copolymer composition can be determined readily using eq. (4)

$$\bar{X}_{\text{STY}} = \frac{A_{\text{CH}}}{A_{\text{CH}} + A_{\text{OCH}_2}} \quad (4)$$

where A_{CH} represents the total peak area of the styrene methine resonances and A_{OCH_2} the total peak area of the oxymethylene carbon resonance.

The results for the two depicted copolymers are $\bar{X}_{\text{STY}} = 0.40$ and 0.73 , respectively, in favorable agreement with the results determined via ¹H-NMR: $\bar{X}_{\text{STY}} = 0.38$ and 0.72 , respectively.

Sequence Determination: Estimate of σ_{EE} , σ_{SS}

From Figure 3 it appears that the majority of the ¹³C resonances show additional splittings due to configurational effects of comonomer sequence distributions or a combination of both. The ethyl methacrylate centered triad splittings will provide information about the (co-)isotacticity parameters σ_{EE} (not accessible via ¹H-NMR analysis) and σ_{ES} . Styrene centered triads show also splittings for the quarternary aromatic carbon resonances (C_1 , cf. Fig. 3) and the methine carbon resonances, giving information on σ_{SS} and σ_{ES} .

From Figure 3 it appears that the most environmentally sensitive and the best resolved areas are the main-chain CH_3 and the C_1 aromatic resonances. In Figure 4 the expanded ¹³C-NMR spectra are shown for the two copolymers, focusing on the C_1 and CH_3 carbon regions only.

A comparison between experimentally observed and theoretically predicted spectra can now be made if the following prerequisites have been fulfilled:

The assignments of the complex configurations and compositionally induced splitting of these selected resonances have to be known.

The different (co-)isotacticity parameters have to be known;

The propagation statistics can be described by the AM model.

As an hypothesis we apply the same relative assignment order as was used previously by Katritzky and Weiss³³ for the ¹³C-spectra of STY-MMA copolymers. Moreover, we treat the complex configurational and compositional patterns via triad analysis as was also done in the evaluation of ¹H-NMR spectra.

The coisotacticity parameters σ_{ES} and σ_{SE} are assumed to be equal and have already been determined by ¹H-NMR, the value being $\sigma_{\text{ES}} = 0.66$. Both the other isotacticity parameters σ_{SS} and σ_{EE} are assumed to be equal to the corresponding values in the homopolymers, i.e., $\sigma_{\text{SS}} = 0.29$.³⁵ Unfortunately the value σ_{EE} is not known for poly(ethyl methacrylate). Figure 5 shows the ¹³C-NMR spectrum of PEMA. The assignment of all resonances has been depicted in the same figure (cf. Fig. 3). Tacticity effects are observed for various carbon atoms, in a manner duplicating the ¹³C-NMR spectrum of poly(methyl methacrylate).³⁶ The value σ_{EE} can be calculated using the triad splittings of the methyl main chain or quarternary carbons or even the pentad

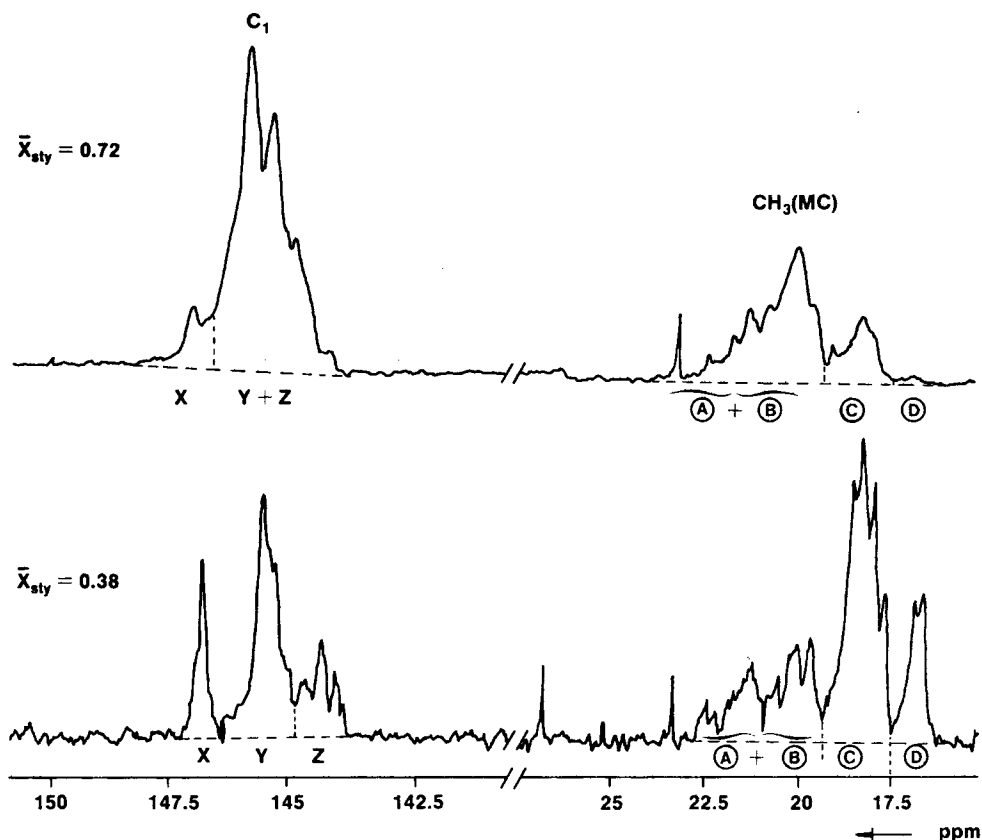


Fig. 4. Expanded 50 MHz ^{13}C -NMR spectra of two S-E copolymers, showing only the CH_3 main chain carbon region (15–23 ppm) and the quaternary aromatic carbon region (142–147 ppm). Spectra were recorded in CDCl_3 at 25°C. Copolymer compositions are indicated on the left. Area measurements have been performed on the indicated regions A–D and X–Z. Assignments for these selected spectral regions are discussed in the text.

resolved carbonyl resonance. The combination of these independent calculations leads to $\sigma_{\text{EE}} = 0.23$, again in good agreement with σ_{MM} for poly(methyl methacrylate), $\sigma_{\text{MM}} = 0.23$.³³

Finally we assume that the propagation reactions can be described by the classical AM model. This assumption has already been verified.^{12–15}

Now, the following set of equations has been used to analyze the C_1 aromatic region:

$$\begin{aligned}
 X &= \sigma_{\text{ES}}^2 F_{\text{ESE}} \\
 Y &= \sigma_{\text{SS}}^2 F_{\text{SSS}} + 2\sigma_{\text{SS}}(1 - \sigma_{\text{SS}})F_{\text{SSS}} + (\sigma_{\text{SS}}\sigma_{\text{ES}})F_{\text{SSE}} + (1 - \sigma_{\text{SS}})\sigma_{\text{ES}} \\
 &\quad \cdot F_{\text{SSE}} + 2\sigma_{\text{ES}}(1 - \sigma_{\text{ES}})F_{\text{ESE}} \\
 Z &= (1 - \sigma_{\text{SS}})^2 F_{\text{SSS}} + \sigma_{\text{SS}}(1 - \sigma_{\text{ES}})F_{\text{SSE}} \\
 &\quad + (1 - \sigma_{\text{ES}})(1 - \sigma_{\text{SS}})F_{\text{SSE}} + (1 - \sigma_{\text{ES}})^2 F_{\text{ESE}}
 \end{aligned} \tag{5}$$

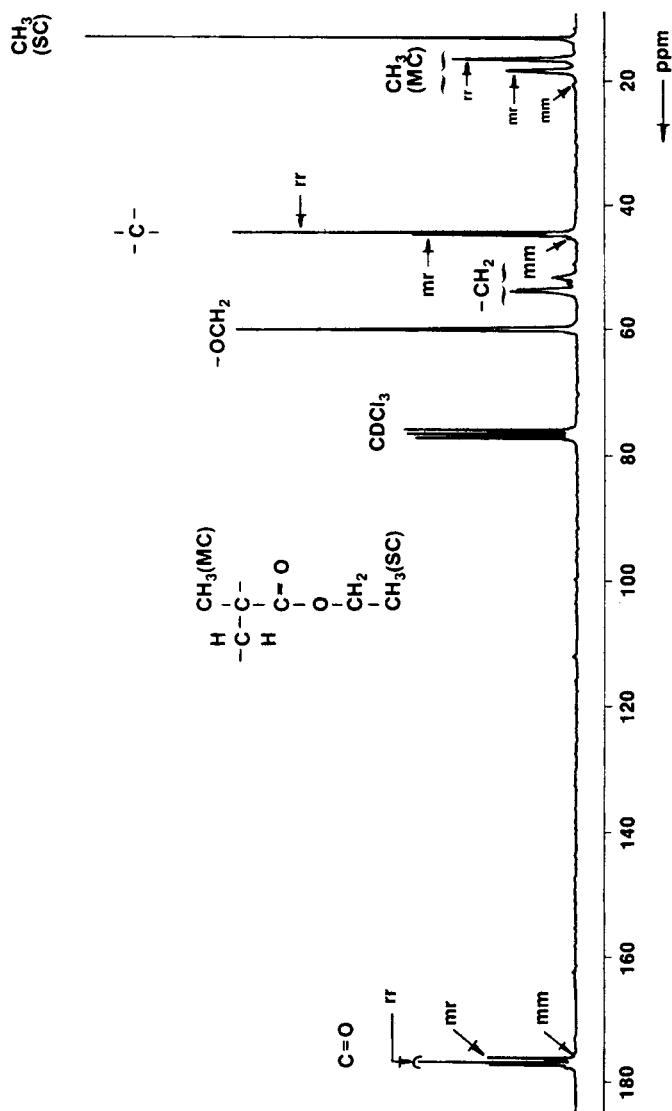


Fig. 5. 50 MHz ^{13}C -NMR spectrum of poly(ethyl methacrylate), recorded in CDCl_3 at 25°C. Tacticity induced splittings have been assigned.

TABLE VII
Observed and Predicted Triad Distribution Reflected on the
Values X-Z and A-D for Two S-E Copolymers with Different Compositions

Molar composition (via ¹ H-NMR)	Resonance area C ₁			Resonance area CH ₃				Predicted/observed
	X	Y	Z	A	B	C	D	
	$\bar{X}_{\text{STY}} = 0.72$	6 10	57 90	37	6 70	64	29 30	
$\bar{X}_{\text{STY}} = 0.38$	27 25	51 50	22 25	11	20 33	52 50	17 17	Predicted Observed

where X, Y, and Z denote the normalized relative peak areas between the respective chemical shifts: 147.2–146.2, 146.2–144.8, and 144.8–143.4 ppm (Figure 4). A similar set of equations can be derived from the results for STY-MMA copolymers to be valid for the EMA centered main chain CH₃ resonance:

$$\begin{aligned}
 A &= \sigma_{\text{EE}}(1 - \sigma_{\text{SE}})F_{\text{EES}} + \sigma_{\text{EE}}\sigma_{\text{ES}}F_{\text{EES}} \\
 B &= \sigma_{\text{EE}}^2F_{\text{EEE}} + \sigma_{\text{ES}}^2F_{\text{SES}} + 2\sigma_{\text{ES}}(1 - \sigma_{\text{ES}})F_{\text{SES}} \\
 C &= 2\sigma_{\text{EE}}(1 - \sigma_{\text{EE}})F_{\text{EEE}} + \sigma_{\text{SE}}(1 - \sigma_{\text{EE}})F_{\text{EES}} + (1 - \sigma_{\text{ES}})^2F_{\text{SES}} \\
 &\quad + (1 - \sigma_{\text{EE}})(1 - \sigma_{\text{SE}})F_{\text{EES}} \\
 D &= (1 - \sigma_{\text{EE}})^2F_{\text{EEE}}
 \end{aligned} \quad (6)$$

where A, B, C, and D are the normalized relative peak areas between the respective chemical shifts: 23.2–20.8, 20.8–19.4, 19.4–17.5, and 17.5–15.5 ppm.

By substituting the various parameters of σ_{SE} , σ_{SS} , and σ_{EE} and using the values for the EMA and STY centered triads, calculating via the AM model (see Table V) the X-Z and A-D values can be predicted. In Table VII the observed and predicted values are shown. From Table VII it may be inferred that predicted and observed values for X-Z, A-D are in very good agreement, indicating the reliability of the parameters σ_{EE} , σ_{SS} , σ_{SE} , r_{S} , and r_{E} .

CONCLUSIONS

The copolymerization behavior of styrene (S) and ethyl methacrylate (E) could successfully be described by the classical AM model. The r -values have been evaluated by three different methods: FR, KETL, and ICFIP. The r -values determined by the method leading to the more reliable estimation, i.e., ICFIP, appeared to be $r_{\text{S}} = 0.59$ and $r_{\text{E}} = 0.50$.

By correlating the observed resonance patterns of homogeneous STY-EMA copolymers, exhibiting AM kinetics and predicted structural features, it appeared to be feasible to assign the ¹H-NMR spectra in terms of triads.

The ^1H - and ^{13}C -NMR spectra of STY-EMA copolymers show that the comonomer sequence placements can be described via the first-order Alfrey-Mayo model. The copolymers contain EEE and SSS blocks exhibiting a high degree of syndiotacticity, whereas the ESE unit exhibits a tendency toward isotacticity.

In view of explaining differences in physical behavior between copolymers, having heterogeneous or anomalous intramolecular structure due to high conversion or emulsion kinetics, it is of paramount importance to apply the appropriate assignment.

The authors wish to acknowledge Dr. J. de Haan for his advice support and Mr. L. van der Ven for recording the 300 MHz, and Mr. J. Beulen (DSM Research) for recording the 200 MHz spectra. This investigation was partially supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (ZWO).

References

1. C. Pichot, M. F. Llauro, and Q. T. Pham, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 2619 (1981).
2. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Dekker, New York, 1980.
3. V. B. F. Mathot and M. F. J. Pijpers, *Polym. Bull.*, **11**, 297 (1984).
4. K. Ito and Y. Yamashita, *J. Polym. Sci. B*, **3**, 625 (1965).
5. K. Ito, S. Iwase, K. Umehara, and Y. Yamashita, *J. Macromol. Sci.*, **A1**, 891 (1967).
6. K. Ito and Y. Yamashita, *J. Polym. Sci.*, **6**, 227 (1968).
7. Y. Yamashita and K. Ito, *Appl. Polym. Symp.*, **8**, 245 (1969).
8. H. J. Harwood, *Problems in Aromatic Copolymer Structure*, in *Natural and Synthetic High Polymers, Volume 4: NMR*, P. Diehl, E. Fluck, and R. Kosfeld, Eds., Springer-Verlag, Berlin, 1970.
9. F. A. Bovey, *J. Polym. Sci.*, **62**, 197 (1962).
10. J. J. Uebel and F. J. Dinan, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 1773 (1983).
11. J. J. Uebel and F. J. Dinan, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2427 (1983).
12. J. C. J. F. Tacx, J. L. Ammerdorffer, and A. L. German, *Polym. Bull.*, **12**, 343 (1984).
13. J. C. J. F. Tacx and A. L. German, *J. Polym. Sci. Polym. Chem. Ed.*, accepted for publication.
14. J. C. J. F. Tacx and A. L. German, *Polymers*, to appear.
15. J. C. J. F. Tacx, J. L. Ammerdorffer, and A. L. German, "Microstructural investigation of copolymers prepared under various process conditions," in *Abstracts of 30th IUPAC International Symposium on Macromolecules*, The Hague, 1985.
16. J. Schrijver, J. L. Ammerdorffer, and A. L. German, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 2696 (1982).
17. R. van der Meer, Ph.D. thesis, Eindhoven University of Technology, 1977.
18. F. L. M. Hautus, A. L. German, and H. N. Linssen, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3487 (1984).
19. F. L. M. Hautus, A. L. German, and H. N. Linssen, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3661 (1984).
20. F. L. M. Hautus, A. L. German, and H. N. Linssen, *J. Polym. Sci. Polym. Lett. Ed.*, **23**, 311 (1985).
21. M. Fineman and S.D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
22. F. Tüdös and T. Kelen, *J. Macromol. Sci. Chem.*, **A1** **10**(8), 1513 (1976).
23. F. Kelen and F. Tüdös, *Polym. Bull.*, **2**, 71 (1980).
24. D. G. Watts, H. N. Linssen, and J. Schrijver, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 1285 (1980).
25. R. van der Meer, H. N. Linssen, and A. L. German, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 2915 (1978).

26. B. C. Simionescu, V. Talmaciu, V. Barboiu, and C. I. Simionescu, *Polym. Bull.*, **10**, 497 (1983).
27. J. Podesva and D. Doskocilova, *Macromol. Chem.*, **178**, 2383 (1977).
28. J. San Roman, E. L. Madriga, and M. A. Del Puerto, *Angew. Makromol. Chem.*, **78**, 129 (1978).
29. H. L. Frich, G. L. Mallows, F. Heatley, and F. A. Bovey, *Macromolecules*, **1**, 533 (1968).
30. G. van der Velden, *Macromolecules*, **16**, 1336 (1983).
31. J. L. Koenig, *Chemical Microstructure of Polymer Chains*, Wiley, New York, 1980.
32. G. C. Levy and G. L. Nelson, *Carbon-13 NMR for Organic Chemists*, Wiley, New York, 1972.
33. A. R. Katritzky, A. Smith, and D. E. Weiss, *J. Chem. Soc. Perkin Trans. 2*, 1547 (1974).
34. Q. T. Pham, R. Pétiard, M. F. Llauro, and H. Waton, *Proton and Carbon NMR Spectra of Polymers*, Vols. 2 and 3, Wiley, New York, 1983, 1984.
35. Y. Inoue, A. Nishioka, and R. Chujo, *Makromol. Chem.*, **156**, 207 (1972).
36. Y. Inoue, A. Nishioka, and R. Chujo, *Polym. J.*, **4**, 535 (1971).

Received January 5, 1987

Accepted May 12, 1987