^1H and ^{13}C NMR Investigation of the Intramolecular Structure of Solution and Emulsion Styrene–Methyl Acrylate Copolymers

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ABSTRACT: The intramolecular structure (triad distribution and tacticity parameter, σ_{SM}) of homogenous styrene (S)–methyl acrylate (M) copolymers, obtained by low-conversion solution polymerization, has been studied by ^1H and ^{13}C NMR. With the set of reactivity ratios $r_S = 0.73$ and $r_M = 0.19$ and classical formulas, based on Alfrey–Mayo (AM) kinetics, it was possible to verify the experimentally observed triad distributions. For the methoxy proton region in the ^1H NMR spectra it is difficult to make a correct peak assignment. Two different assignments can fit the observed data on triad level. The well-known Ito–Yamashita (I–Y) assignment leads for the random copolymers to a high degree of coisotacticity ($\sigma_{MS} = 0.9$), contrary to the value obtained for alternating copolymers ($\sigma_{MS} = 0.5$). An alternative assignment is possible, which results in $\sigma_{MS} = 0.3$. In order to discriminate between the two assignments, three 2D NMR COLOC experiments were carried out in an attempt to establish the connectivity over three bonds of the carbonyl C=O resonances and the protons of the OCH_3 resonances. However, the correctness of neither of the two ^1H assignments of the methoxy resonances could be rigorously proved by means of the 2D NMR COLOC experiments. The cumulative triad fractions and the molar composition of copolymers, obtained up to very high conversion by means of both solution and emulsion batch processes, could be adequately described by models, on the basis of instantaneous distributions according to AM kinetics. In the case of the emulsion copolymerization it is shown that the model for predicting the sequence distribution should account for the monomer partitioning between the oil and water phases. The agreement found between predicted and observed triad distributions was quite satisfactory for both polymerization processes. It was shown that (statistical) emulsion copolymers have the same degree of coisotacticity as the statistical solution copolymers, regardless of whether or not the I–Y assignment is used for the alternative assignment.

Introduction

Determination of the intramolecular (triad distribution, tacticity) and intermolecular (chemical composition and molar mass distribution) copolymer microstructure is generally recognized as a prerequisite, since revealing the molecular microstructure may supply information about the monomer addition process, e.g., about the preference of monomers to add in a (co)iso- or cosyndiotactic configuration.[1-3] Moreover, knowledge about the inter- and intramolecular structures is of paramount importance for the understanding of relations between molecular structure and polymer properties.[4-6] Furthermore, the microstructure depends upon the polymerization process and provides information on the reaction mechanisms occurring during polymerization.[7,8] NMR methods provide information on the average copolymer composition as well as on the intramolecular structure.[1,3] However, the majority of publications concerning the elucidation of intramolecular microstructure of copolymers deal with well-defined low-conversion (<15%) bulk or solution copolymers. Several examples in the field of styrene–(meth)acrylate copolymers can be found in the literature.[9-13] Far less attention has been paid to the determination of the microstructure of copolymers obtained by high-conversion solution processes[14,15] or high-conversion emulsion processes,[16-19] even though high conversion is of great technological importance. In the case of high-conversion solution copolymerization of styrene (S) and methyl methacrylate (MMA), it has also been shown that the inter- and intramolecular structure could be successfully predicted, on the basis of the integrated Alfrey–Mayo (AM) model, by using kinetic parameters obtained for low-conversion data.[14,20,21] Similar results were obtained by our group on the styrene (S)–ethyl methacrylate (EMA) system.[13,15] However, due to the overlap of OCH_3 or OCH_2 resonances (in the S–MMA and S–EMA systems, respectively) and the methine main-chain backbone resonances in the ^1H NMR spectra of the above-mentioned systems,[11,13] as already put forward by Harwood,[3] still problems may occur with the correct quantitative analysis of the sequence assignment of the acrylate-centered triads; see, e.g., a recent publication of Kale et al. on the S–MMA system.[22] Therefore, we have studied the styrene–(S) methyl acrylate (M) system, because (i) no overlap occurs between the OCH_3 resonances and the other main-chain resonances,[23] (ii) mixed configurational and compositional sequence effects are reported to occur for the OCH_3 ^1H NMR resonances,[23-25] and (iii) the polymer statistics can be rigorously tested via an analysis of the ^{13}C carbonyl carbons.[26-28] Contrary to S–MMA or S–EMA systems,[13] the ^{13}C chemical shifts of these carbons in the S–M system are only influenced by compositional sequence effects.[28] For low-conversion (<20%) solution S–M copolymers we have measured the reactivity ratios, and the set of r values, together with the assumed AM model, has been used to test the validity of this model (via an interpretation of the ^{13}C NMR data). Moreover, we have tried to distinguish between on the one hand Ito's earlier peak assignment[23] (tentatively based on the same assignment order for S–MMA copolymers[9]), which results in an extremely high coisotacticity (σ_{MS} = 0.8–0.9), and on the other hand an alternative assignment[29] apparently resulting in a much lower σ_{MS}. In an attempt

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to achieve this goal, 2D NMR COLOC experiments[30] were performed on three well-defined homogeneous low-conversion copolymers, thus trying to correlate the ¹H NMR OCH_3 region and the ¹³C NMR carbonyl region. Related 2D NMR techniques have been performed very recently on the alternating S-MMA system.[31] On the basis of triads only (with the influence of pentads neglected), the quantitative NMR results of the alternating S-MMA copolymers were approximately consistent with the I-Y assignment. However, no expansion was given of the 2D spectrum in the methoxy region of the random copolymer.

We also analyzed the microstructure of some high-conversion solution S-M copolymers and compared it to model calculations using the integrated AM model.[15] Even more challenging is the microstructure of high-conversion emulsion copolymers, because emulsion copolymerization is a heterogeneous process. Therefore, models describing the emulsion copolymer microstructure are necessarily more complex. The model that we use for S-M copolymers takes into account this heterogeneity by calculating the monomer partitioning between the three phases.[17,19,32] With use of the AM equations in combination with local monomer concentrations, together with numerical integration over conversion, the sequence distribution of the emulsion copolymer has been calculated and a comparison is made between the experimentally determined and the calculated triad fractions.

Experimental Section

The monomers styrene and methyl acrylate (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 1-L glass vessel. The total monomer concentration was 3 mol/dm³ in toluene. The conversion of both monomers was determined by means of GLC. The temperature was 335 K, and the initial initiator concentration was 8 mmol/dm³. To isolate and purify the copolymer, samples of the reaction mixture were poured out in a 15-fold excess of cold hexane. The final products were dried at 328 K in a vacuum stove for at least 6 h at 10^{-1} Torr and finally for 8 h at 10^{-5} Torr.

The emulsion copolymers were prepared in a 1-L glass vessel. The monomers (86.3 g of styrene and 214.0 g of methyl acrylate) in which 1.24 g of *n*-dodecyl mercaptan was dissolved were preemulsified by adding them to the soap solution (2.00 g of sodium lauryl sulfate (Fluka) in 580 g of water, distilled twice). Subsequently, the initiator solution (0.201 g of potassium persulfate in 20 g of water) was added to the monomer emulsion, thermostated at 323 ± 0.5 K. The monomer ratio was monitored by means of on-line GLC as described elsewhere.[33] Total weight conversion was determined by solid content analysis. These samples were used for recording the NMR spectra.

¹H NMR spectra were recorded with a 400-MHz (Bruker AM 400) spectrometer at 298 K, by using $CDCl_3$ as the solvent and locking agent. Generally the spectra were obtained by using a spectral width of 6024 Hz, an acquisition time of 1.4 s, a flip angle of 45°, and a pulse delay of 5 s. Spectra were obtained after accumulating 64 scans, by using a sample concentration of 1% (w/v). The digital resolution amounted to 0.18 Hz, corresponding to a data length of 32K. ¹³C NMR were recorded at 100 MHz (Bruker AM 400) at 298 K. The sample concentration was 9% (w/v) $CDCl_3$. Spectra were obtained by using WALTZ-16 decoupling and a pulse delay of 5 s, accumulating 2000 scans with a digital resolution of 0.4 Hz/point, corresponding to a spectral width of 25 000 Hz and a data length of 64K. The flip angle and acquisition time were 90° and 1.3 s, respectively. Monomer sequence placements were determined by comparing the relative peak areas of the proton or carbon atoms involved. In performing quantitative NMR measurements via compositional or configurational sequence placements, one must take into account differences in nuclear Overhauser effects (NOE) and spin-lattice relaxation times (T_1). No NOE or T_1 values have been determined, but one additional ¹³C NMR experiment was performed on a copolymer with F_M = 0.43 with a much longer delay (15 s) and gating off the decoupler to remove the NOE. The results are identical with those obtained via ¹³C NMR with the standard method. Implicitly we assumed that no differential T_1's are present for different stereoisomeric (mm, mr, and rr) triads or compositional triads (MMM, MMS, SMS, SSS, etc.) in the ¹H or ¹³C NMR spectra. No differential ¹H NOEs were considered to occur. Within these limits relative peak areas are proportional to the numbers of proton and carbon atoms involved. Peak areas were determined via electronic integration methods or planimeter methods (after truncation of overlapping spectral regions).

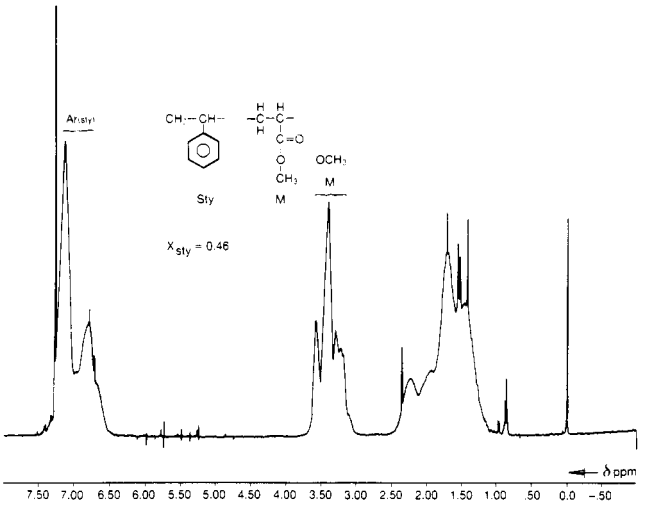

Figure 1. 400-MHz ¹H NMR spectrum of a low-conversion solution styrene (S)-methyl acrylate (M) copolymer in $CDCl_3$ at 25 °C. The mole fraction of styrene (F_S) is indicated on the left.

The COLOC experiments[30] have been used for the observation of long-range couplings between C=O ¹³C NMR carbon atoms and methoxy protons. On concentrated samples (25% w/v in $CDCl_3$) 250 scans were accumulated per t_1 value with a recycle delay of 1 s on the AM 400 spectrometer. The initial data matrix was 2000 Hz (1K) and 800 Hz (128 t_1 values). Before Fourier transformation, double zero filling was used in the F_1 dimension. Moreover, shifted sine-bell window functions $\pi/4$ and $\pi/8$ were applied for the F_1 and F_2 domains, respectively. Delay times (D_1 and D_2) were both set to 25 ms.

Results and Discussion

Low-Conversion Solution Copolymers. ¹H NMR Spectra. Determination of Copolymer Composition and of *r* Values. Figure 1 depicts as a typical example the 400-MHz ¹H NMR spectrum of a low-conversion solution S-M copolymer dissolved in $CDCl_3$ at 25 °C, whereas in Figure 2 expanded 400-MHz spectra are shown for four copolymers and poly(methyl acrylate) (PM). Expansions of the methoxy region are shown since in particular this region displays additional fine splittings due to combined configurational (=tacticity) and compositional sequence effects.[23] The average copolymer composition (mole fraction styrene, $\bar{F}_S$) can be readily obtained by using

$$\bar{F}_S = \frac{3A_1}{3A_1 + 5A_2} \tag{1}$$

where A_1 and A_2 represent the total peak areas of the aromatic and methoxy proton resonances, respectively. The initial feed (q_0 = [S]/[M]), the average copolymer composition, and the conversion are summarized in Table I.

With use of the well-known Kelen-Tüdos low-conversion method and the data, presented in Table I, the *r* values

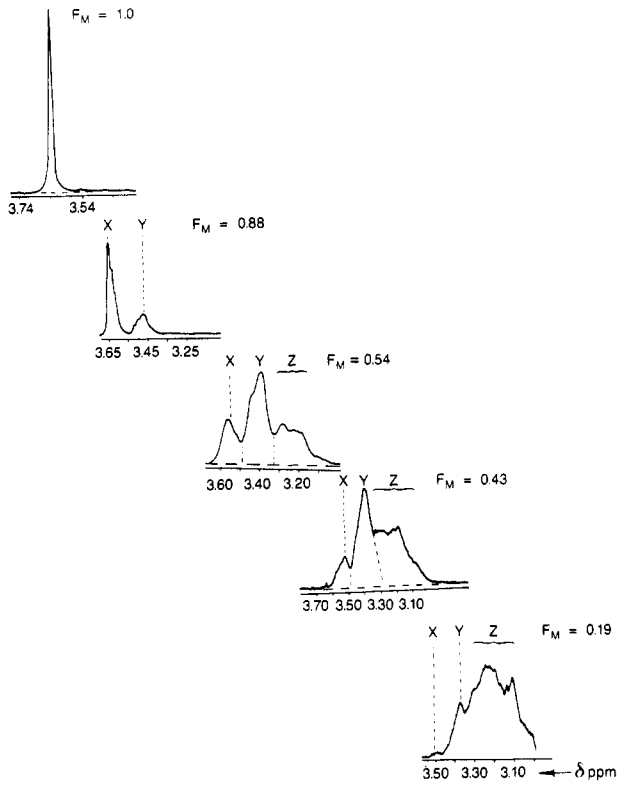

Figure 2. Expanded 400-MHz ^{1}H NMR spectra of low-conversion solution S–M copolymers and homopolymer PM showing the methoxy region only. Spectra were recorded in $CDCl_3$ at 25 °C. Copolymer compositions are indicated for each copolymer. Area measurements have been performed for the regions X, Y, and Z by using the dotted areas.

Table I
Observed Cumulative Average Copolymer Composition (F_S = Mole Fraction of Styrene) and Final Conversions of Some Low-Conversion Solution S–M Copolymers

q_0[a]	F_S	convn, mol %
0	0	20
0.038	0.12	7
0.11	0.33	5
0.36	0.46	12.6
0.85	0.57	14.3
1.98	0.67	16.1
2.97	0.77	10.2
4.78	0.81	9.7

[a] Initial monomer feed ratio q_0 = [S]/[M].

were determined for an AIBN-initiated system:

$$r_S = 0.73 \quad r_M = 0.19$$

These values are in good agreement with literature data [r_S = 0.64 and r_M = 0.16 (benzoyl peroxide, 60 °C)[29] or r_S = 0.75 and r_M = 0.18 (benzoyl peroxide, 55 °C)[26]].

Sequence Analysis via ^{1}H and ^{13}C NMR. The 10 theoretically possible M-centered triads are not resolved in 10 distinct resonances and up to now the methoxy peak region has been analyzed in terms of the Ito–Yamashita (I–Y) assignment, developed for styrene–methyl methacrylate copolymers (S–MMA).[9] According to Ito and Yamashita,[23] the three different groups of peaks can be assigned to the following combination of M-centered triads:

$$F_X = F_{MMM} + (1-\sigma)F_{MMS} + (1-\sigma)^2F_{SMS}$$
$$F_Y = \sigma F_{MMS} + 2\sigma(1-\sigma)F_{SMS}$$
$$F_Z = \sigma^2 F_{SMS} \qquad (2)$$

In eq 2, the parameter σ_{MS} (=σ_{SM} or σ in shorthand notation) is defined as a measurement of the probability that alternating M and S units adopt a coisotactic configuration. MMM, MMS, and SMS denote the three different kinds of compositionally M-centered triads. More details can be found in earlier work.[3,9,23]

Assuming the Alfrey–Mayo (AM) model (=first-order Markov) to be valid at any moment of the reaction for these low-conversion copolymers, the number fraction (F) of methyl acrylate (M) and styrene-centered (S) triads can be predicted. The relation between intramolecular structure (number fraction of triads) and reaction kinetics is given by the set of equations

$$F_{MMM} = (1-P(S/M))^2$$
$$F_{MMS} = 2P(S/M)(1-P(S/M))$$
$$F_{SMS} = (P(S/M))^2$$
$$F_{SSS} = (1-P(M/S))^2$$
$$F_{SSM} = F_{MSS} = 2P(M/S)(1-P(M/S))$$
$$F_{MSM} = (P(M/S))^2 \qquad (3)$$

where $P(S/M) = 1/(1 + r_M/q)$, $P(M/S) = 1/(1 + r_S q)$ and q = [S]/[M] is the instantaneous feed ratio. F represents the number fraction of triads normalized to unity, and $P(M_1/M_2)$, the probability of a growing chain, having an M_2-type chain end, to add monomer M_1.

All these triad fractions are predicted, by using initial feed ratios (q_0, see Table I) and r values, estimated via the Kelen–Tüdos method. In order to predict the relative intensities of each peak, it is necessary to estimate the values of the coisotactic parameter, σ_{SM}. Two different types of approaches have been used, the so-called Ito–Yamashita approach[9,10,23] and the Harwood–Ritchey (H–R)[3,34] approach. Both methods rely on the same starting point, i.e., the Ito–Yamashita assignment[23] as given by eq 2.

In the I–Y framework various equations can be derived:

$$1 - F_X^{1/2} = \sigma\left(\frac{q}{q + r_M}\right) \text{ or } (1 - F_X^{1/2})^{-1} = \frac{1}{\sigma} + \frac{r_M}{\sigma}\frac{1}{q} \qquad (4a)$$

$$F_Z = \left[\sigma\left(\frac{q}{q + r_M}\right)\right]^2 \text{ or } F_Z^{-1/2} = \frac{1}{\sigma}\left(1 + \frac{r_M}{q}\right) \qquad (4b)$$

$$F_Y^2 = 4F_X F_Y \qquad (4c)$$

$$1 + \frac{2F_X}{F_Y} = \frac{1}{\sigma} + \frac{r_M}{\sigma}\frac{1}{q} \qquad (4d)$$

Equations 2 and 4 can be solved numerically for σ by using the experimental values of a M-centered resonance (vide infra, ^{13}C NMR C=O resonance) for each copolymer. A graphical analysis can also be used (eq 4), assuming the values of σ to be constant over the whole series of copolymers. If both r_M and σ are unknown, the second part of eqs 4a and 4b can be used, plotting the left-hand part (LHP) vs $1/q$. If r_2 is known (underlying case), the first part of eqs 4a and 4b can be used, by plotting $1 - F_X^{1/2}$ vs $q/(q + r_M)$ or F_Z vs $(q/(q + r_M))^2$. From the slopes, the values of σ and σ^2 can be evaluated. The rearrangement of eq 2 put forward by Harwood and Ritchey (H–R approach)[3,34] leads to the following set:

$$\frac{F_X - F_{MMM}}{F_{SMS}} = (1-\sigma)\frac{F_{MMS}}{F_{SMS}} + (1-\sigma)^2 \qquad (5a)$$

$$\frac{F_Y}{F_{SMS}} = \sigma\frac{F_{MMS}}{F_{SMS}} + 2\sigma(1-\sigma) \quad (5b)$$

$$\frac{F_Z}{F_{SMS}} = \sigma^2 \quad (5c)$$

The left-hand part of eqs 5a–c either can be plotted via F_{MMS}/F_{SMS}, assuming for the whole range of polymers σ to be constant, or alternatively can be numerically solved for σ for each polymer, by using experimental values for F_X, F_Y, and F_Z and theoretically calculated or experimentally observed values for F_{MMM}, F_{MMS}, and F_{SMS} (^{13}C NMR).

If the interpretation of the OCH_3 resonances is correct, the graph should be linear and slopes and intercepts should be consistent with a single value of σ.

Figure 3 depicts the 100-MHz ^{13}C NMR spectra of poly(methyl acrylate) and four copolymers recorded at room temperature in $CDCl_3$. These spectra only show the carbonyl region and the C_1 ipso region (aromatic C_1 carbon), because sequence splittings are observed and have been assigned tentatively by other workers.[19,26-28] Remarkably the methoxy carbon resonance of all copolymers (contrary to the methoxy proton resonance) is observed as a singlet. Although the pattern of the C_1 ipso resonances is not well understood and the signals are not as resolved as the C=O signal, we tentatively have truncated this spectral region in three areas, which have been assigned to SSS, SSM, and MSM triad sequence placements in a manner analogous to the truncation, executed by Ramirez-Marquez.[19] In Table II the three theoretically calculated triad fractions (using AM statistics) and the experimentally observed values (both M- and S-centered triads) are presented. There is a good agreement between the relative resonance areas and the calculated triad fractions. This reconfirms the findings of Tanabe et al.[26,28] that the carbonyl carbon patterns are only sensitive to sequence effects and that AM statistics hold. Similar arguments (although with considerably less certainty) hold for the S-centered triads.

Considering the ^{1}H NMR methoxy resonances in greater detail for our statistical copolymers (see Figure 2), it is evident, that no tacticity-induced splittings appear for PM, i.e., (mm, mr, rr) MMM all resonate at 3.64 ppm. However, from recent work of Tanabe et al.[25,26,28] on alternating S–M copolymers it is evident that a 3-fold splitting is observed for the OCH_3 resonance. The resonance assignments are 3.54 (rr), 3.39 (mr) and 3.21 (mm) ppm. The calculated coisotacticity parameter for these copolymers amounts to $\sigma_{MS} = 0.5$ (σ_{MS} = [mm/(mm + 2mr + rr) SMS]$^{1/2}$. In Figure 4 are depicted two 400-MHz ^{1}H NMR spectra of an alternating S–M copolymer (synthesized in our laboratory according to a procedure, described by Tanabe[26,28]) and a statistical copolymer, containing the largest amount of SMS triads (in our case $q_0 = 20$, $F_S = 0.92$, $F_{SMS} = 0.98$). From this figure it is evident that similar chemical shifts are observed for the alternating copolymer, as observed by Tanabe et al.,[26] and also that the σ_{SM} parameter is equal to 0.5. Nevertheless, the spectrum of the statistical copolymer is much more complicated than that of the alternating copolymer. However, it is immediately clear that the σ value for this copolymer is much larger than 0.5, because the fractional area intensity of the rr SMS triad (at ~3.50 ppm) is very small. The chemical shift regions belonging to X, Y, and Z are somewhat dependent on the copolymer composition and increase, e.g., for X, from 3.66–3.55 for high F_M copolymers to 3.62–3.48 for low F_M copolymers (see Figure 2). The truncations, used for the determination of the

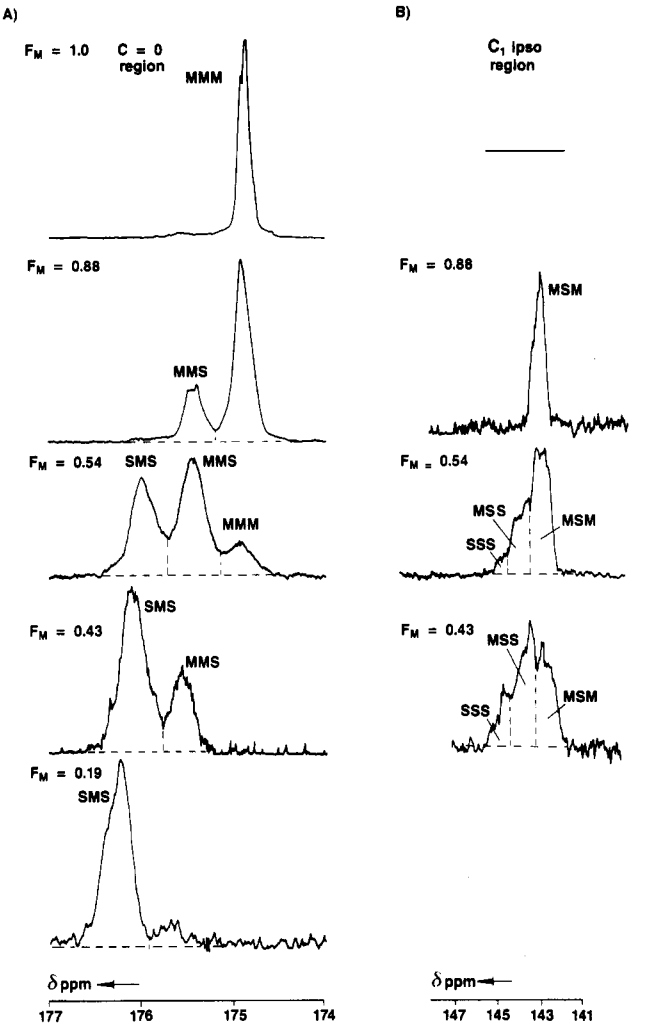

Figure 3. Expanded 100-MHz ^{13}C NMR spectra of four low-conversion solution S–M copolymers and poly(methyl acrylate), showing only the carbonyl region (174–177 ppm) and the quaternary aromatic carbon region C_1 ipso (141–147 ppm). Spectra were recorded in $CDCl_3$ at 25 °C. Copolymer compositions are indicated on the left. Area measurements have been performed on the indicated regions.

experimental F_X, F_Y, and F_Z values, are indicated in Figure 2. In Figure 5 two examples of I–Y plots are shown, by using the experimentally observed values for F_X, etc., collected in Table III and the experimentally observed values for r_2 and q_0, respectively, F_Z versus $(q/(q + r_M))^2$ and $1 - F_X^{1/2}$ versus $(1 + r_M/q)^{-1}$ (cf. eqs 4a and 4b). For the first plot experimentally reliable values for F_Z can be expected mainly at low F_M values; for the second plot reliable values for F_X can be found at high F_M values. In both cases σ_{MS} values, being ~0.9, have been calculated from the slopes. For two copolymers, with F_S being 0.77 and 0.81, two limiting values have been indicated in Figure 4b, somewhat dependent on the fact of whether the tiny area at ~3.50 ppm has to be assigned to F_X or completely neglected ($F_X = 0$, $1 - F_X^{1/2} = 1$) and in fact assigned to F_Y (rr SMS). The LHP of the H–R equations (see eq 5) has been plotted in Figure 6 versus F_{MMS}/F_{SMS}. Calculated triad fractions for F_{MMS} and F_{SMS} (Mayo–Lewis model is valid) and experimentally observed values for F_X, F_Y, and F_Z have been used. From these plots, it is immediately clear that extremely high values of σ are found ($\sigma \geq 0.9$), also in disagreement with the results obtained for alternating copolymers ($\sigma = 0.50$). However, mutual agreement exists between the two different approaches (I–Y) and (H–R). Furthermore, the alternating copolymer

Table II
Theoretical and Experimental Cumulative Number Fraction (×100) of both S- and M-Centered Triads of Some Low-Conversion Solution Copolymers

	C=O region						C_1 region					
	theor			exptl			theor			exptl		
q_0[a]	MMM	MMS	SMS	MMM	MMS	SMS	SSS	SSM	MSM	SSS	SSM	MSM
0	100	0	0	100	0	0						
0.038	70	28	2	74	24	2	0	5	95	0	0	100
0.36	12	46	42	13	47	40	4	33	63	5	35	60
0.85	3	30	67	0	28	72	15	47	38	16	47	37
4.78	0	7	93	0	10	90	60	35	5	66	34	0

[a] Initial monomer feed ratio $q_0 = [S]/[M]$.

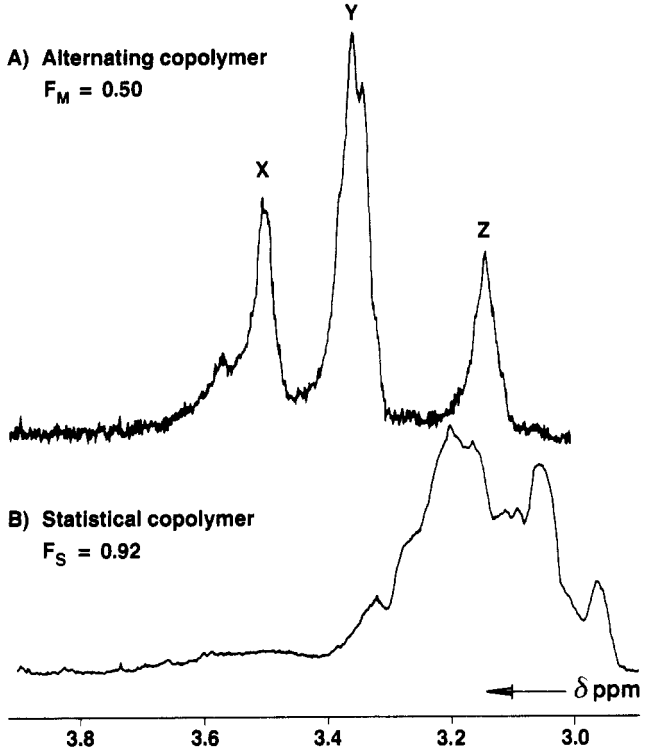

Figure 4. 400-MHz ^{1}H NMR spectra of two low-conversion S–M copolymers showing only the methoxy region: (A) alternating copolymer, (B) statistical copolymer. $q_0 = 20$, $F_S = 0.92$, and $F_{SMS} = 0.98$.

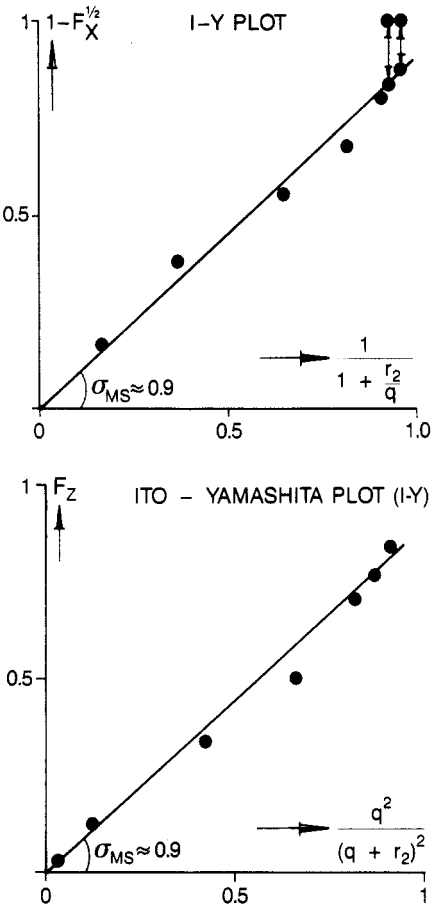

Figure 5. Ito–Yamashita (I–Y) plots for a series of seven S–M low-conversion solution copolymers, according to eqs 4a and 4b (see text).

was prepared in the presence of $ZnCl_2$, which probably forms a ternary molecular complex with methyl acrylate and styrene.[26] Therefore, it is likely that σ has a different value. However, it still remains unexplained as to why the copolymer prepared by means of radical copolymerization is more stereoregular than the alternating copolymer prepared by means of the complex copolymerization process.

From the H–R plot (Figure 6) it is immediately clear that there hardly exists any intensity belonging to the SMM resonance in the low-field area F_X. These considerations, bearing in mind that $(1 - \sigma)^2$ SMS (=rr SMS) resonates at 3.54 ppm (Tanabe et al.[26]), may support the following tentative assignment as reported by Nikman and Harwood,[29] where the resonance assignment order for $(1 - \sigma)^2$ SMS and σ^2 SMS have been interchanged. For alternating copolymers,[26] these values are identical:

$$F_X = F_{MMM}$$

$$F_Y = F_{MMS} + \sigma^2 F_{SMS}$$

$$F_Z = 2\sigma(1 - \sigma)F_{SMS} + (1 - \sigma)^2 F_{SMS} \quad (6)$$

Within the I–Y approach (H–R approach not presented), two equations similar to eqs 4a and 4b can be derived, assuming the set of equations in eq 6 to be valid:

$$1 - F_X^{1/2} = \frac{q}{q + r_M}$$

$$F_Z = (1 - \sigma^2)\left(\frac{q}{q + r_M}\right)^2 \quad (7)$$

From eq 7 and Figure 5b, a value of σ can be estimated, being $\sigma \sim 0.30$. In Table III the best fit values for the Ito assignment and the possibly new assignment have been compared with the experimental values. From an inspection of this table, it becomes evident that, for the triad fractions alone, hardly a discrimination between these two models can be made. Therefore, we have performed 2D COLOC experiments on three samples in an attempt to establish the connectivity over three bonds of the carbonyl C=O resonances and the protons of the OCH_3 resonance. The 2D spectra are shown in Figure 7. From the contour plot of the COLOC experiment on the copolymer with $F_S = 0.12$ (Figure 7a), the alternative

Table III
Observed and Normalized Area Intensities (×100) of Peaks *X*, *Y*, and *Z* Representing the Oxymethylene Region and the Calculated Values of *X*, *Y*, and *Z* Using Ito's Assignment (Equation 2) (See Text) and an Alternative Assignment (Equation 6) (See Text) of Some Low-Conversion Solution Copolymers

	exptl			Ito's assignt (σ = 0.92)			alt assignt (σ = 0.32)		
q_0[a]	*X*	*Y*	*Z*	*X*	*Y*	*Z*	*X*	*Y*	*Z*
0	100	0	0	100	0	0	100	0	0
0.038	70	27	3	73	25	2	69	28	3
0.11	38	49	13	45	44	10	40	48	12
0.36	19	47	34	16	48	35	12	50	38
0.85	10	40	50	7	39	54	3	37	60
1.98	4	25	71	3	29	68	1	24	75
2.97	2	21	77	2	26	72	0	20	79
4.78	1	15	84	2	23	77	0	17	83

[a] Initial monomer feed ratio q_0 = [S]/[M].

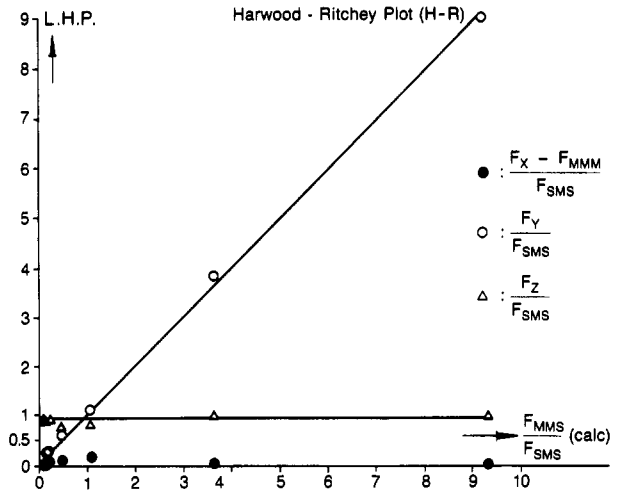

Figure 6. Harwood–Ritchey (H–R) plot of the left-hand part (LHP) of eqs 5a–c vs F_{MMS}/F_{SMS} for a series of seven low-conversion solution copolymers.

assignment has to be rejected in favor of the earlier I–Y assignment, because of the presence of the peak that correlates the X peak in the ^{1}H NMR spectrum with the MMS peak in the ^{13}C NMR spectrum. Moreover, as depicted in the COLOC contour plots of the copolymers with F_S = 0.46 and F_S = 0.57, the X peak correlates with part of the SMS peak and the MMS peak in the ^{13}C NMR spectrum. This also favors Ito's assignment and would reject the alternative assignment. However, in case of F_S = 0.46 the MMM peak correlates clearly with the Y peak instead of correlating with the X peak, which would be expected on the grounds of the ^{1}H NMR spectrum of methyl acrylate homopolymer. The influence of pentads could probably explain the unexpected difference. The MMMMM pentad resonates at 3.64 ppm, and the SMMMM and SMMMS pentads possibly resonate at higher field. Although the COLOC experiments do not fully discriminate between the two assignments and therefore the correct assignment of the methoxy proton region is still unknown, it is still possible to use ^{1}H NMR to determine the M-centered triads of S–M copolymers using either of the assignments. Although the problems involved in a proper assignment deserve further attention in further investigations, the present situation remains undecided. Therefore, on behalf of the present interpretations, the I–Y assignment will be used in the following, in order to remain compatible with earlier literature.

High-Conversion Solution Copolymers. In Table IV a comparison is made between on the one side the experimentally observed values of the copolymer composition, triad fractions, and the fractional intensities of peaks *X*, *Y*, and *Z* representing the methoxy proton region and on the other side the predicted values using the integrated form of the Alfrey–Mayo (AM) model,[15] σ = 0.9, and *r* values obtained from the low-conversion compositional data (r_S = 0.73, r_M = 0.19).[15]

Both calculated and experimentally determined values are therefore average (cumulative) number fractions of the high-conversion copolymers. Taking into account the poor peak resolution of the C_1 ipso region, it can be concluded from the data in Table IV that the solution copolymer microstructure can be described according to the integrated AM model until high conversion.

Emulsion Copolymers. Emulsion copolymerization is a heterogeneous process. Therefore, a model describing emulsion copolymerization and emulsion copolymer microstructure is necessarily more complex and contains more parameters as compared with a model that describes a homogeneous process like solution copolymerization.

The average copolymer composition and the sequence distribution of the emulsion copolymers were calculated by using a computer simulation program based on a comprehensive model description of the emulsion copolymerization and copolymer structure. In this article, only the basic concepts of this model, required to understand how the predicted emulsion copolymer microstructures were obtained, will be presented. A more detailed discussion on the model and its predictive properties will be published separately.[35]

The model used takes into account the monomer partitioning between the three phases in the system, i.e., monomer droplets, water phase, and latex particles.[17,32,36–38] With use of the local monomer feed ratio inside the latex particles in combination with the *r* values, determined for solution copolymerization, the instantaneous copolymer composition as well as the instantaneous triad fractions can be calculated assuming first-order Markov (i.e., Mayo–Lewis) kinetics to be valid. Numerical integration provides the cumulative average copolymer composition and cumulative triad fractions. We have assumed in our model that all copolymer is formed inside latex particles, i.e., any possible solution polymerization in the water phase is being neglected. This condition may not be completely met, especially at the very beginning of the reaction,[7,37,38] since methyl acrylate is moderately water soluble.

However, the obtained experimental data (Figures 8 and 9) of the experiment described are in very good agreement with model calculations and give no evidence of any significant water-phase polymerization. The monomer partitioning between latex particles, water phase, and monomer droplets in stages I and II of the emulsion polymerization is calculated by using the set of equilibrium equations (eq 8), the molar mass balance equations (eq 9),

and eq 12 (the iteration process).

$$[M_a]_p = K_a x_a$$
$$[M_b]_p = K_b x_b$$
$$[M_a]_w = k_a x_a$$
$$[M_b]_w = k_b x_b \quad (8)$$

In eq 8 $[M_a]_p$ and $[M_a]_w$ are the molar concentrations of monomer a in, respectively, the swollen latex particles and the water phase (mol/L); K_a, K_b, k_a, and k_b are equilibrium constants (mol/L) and x_a (=1 − x_b) is the molar fraction of monomer a inside the monomer droplets

$$[M_a]_p \upsilon_p N_T + V_w[M_a]_w + M_{ad} = (1 - X_a)M_{a0}$$
$$[M_b]_p \upsilon_p N_T + V_w[M_b]_w + M_{bd} = (1 - X_b)M_{b0} \quad (9)$$

where M_{ad} = content of monomer a in monomer droplets per liter of emulsion (mol/L), V_w = volume ratio of water phase per liter of emulsion, υ_p = volume of a single swollen latex particle (L), X_a = molar conversion of monomer a, M_{a0} = amount of initial monomer a per liter of emulsion (mol/L), and N_T = total number of latex particles per liter of emulsion (1/L). During stage III of the emulsion copolymerization, when no monomer droplets are present, eq 10–12 are used:

$$[M_a]_p \upsilon_p N_T + V_w[M_a]_w = (1 - X_a)M_{a0}$$
$$[M_b]_p \upsilon_p N_T + V_w[M_b]_w = (1 - X_b)M_{b0} \quad (10)$$
$$[M_a]_p = K_a/k_a[M_a]_w$$
$$[M_b]_p = K_b/k_b[M_b]_w \quad (11)$$

Styrene and methyl acrylate both swell their (co)polymers very well but differ strongly in water solubility. It is assumed that the monomer ratio inside the latex particles equals the monomer ratio inside the monomer droplets; i.e., $K_a = K_b$.[19,32,37]

The swollen latex particle volume, υ_p, is calculated by using eq 12 assuming volume additivity of each component

$$\upsilon_p = \frac{\upsilon_p[M_a]_p M_a}{\rho_a} + \frac{\upsilon_p[M_b]_p M_b}{\rho_b} + \frac{M_{t0} X_t M_p}{\bar{\rho}_p N_T} \quad (12)$$

where ρ_a = density of monomer a (g/L), $M_{t0} = M_{a0} + M_{b0}$ = total monomer content at the beginning of the reaction per liter of emulsion (mol/L), X_t = total conversion (mol fraction), $\bar{\rho}_p$ = average copolymer density (g/L), M_a = molar mass of monomer a (g/mol), $M_p = F_a M_a + F_b M_b$ = average molar mass of the monomer units of the cumulative copolymer (g/mol), and N_T = number of particles per liter of emulsion (1/L). The number of latex particles may vary during reaction but has little or no influence on the instantaneous and cumulative average copolymer composition and sequence distribution.

Under the conditions that $K_a = K_b$ and that K_a and K_b are independent of the latex particle volume, only the total organic phase/water volume ratio determines the local monomer feed ratio inside the latex particles. Therefore, at a certain conversion the value of N_T only influences the particle volume and does not affect the organic phase/water volume ratio or the local monomer feed ratio inside the latex particles. The simulation has to be initiated at very low conversion (e.g., X_{t0} = 0.001 mol fraction) with a certain copolymer composition, representative of the emulsion system (e.g., F_S = 0.5).

Table IV
Experimentally Observed Cumulative Triad Fractions, Molar Fraction S (F_S), and Functional Area Intensities (X, Y, Z) for Two High-Conversion Solution Copolymers[a]

	q_0 = 0.85 convn = 92 mol %		q_0 = 5.7 convn = 99 mol %	
	exptl	model	exptl	model
		^{13}C NMR		
MMM	10.1	9.5	0	0
MMS	38.6	40.5	7	7
SMS	51.3	50.0	93	93
SSS	13.0	12.0	78	68
SSM	41.8	38.0	22	28
MSM	45.2	50.0	0	4
		^{1}H NMR		
F_S	0.53	0.5	0.88	0.85
X (σ = 0.9)	14.4	14.5	0	2
Y	44.5	44.0	14	23
Z	41.1	41.5	86	75

[a] Theoretically calculated values for all experimentally observed values are also depicted.

Table V
Numerical Values of Constants Used in Figures 8 and 9 Showing Model Calculations Describing the Course of the Cumulative Triad Fractions and Copolymer Composition as a Function of Conversion

K_a = 5 mol/L
K_b = 5 mol/L
k_a = 0.6 mol/L
k_b = 0.003 mol/L
$\rho_a = 0.9 \times 10^3$ g/L
$\rho_b = 0.95 \times 10^3$ g/L
$\rho_p = 1.1 \times 10^3$ g/L
$N_T = 3 \times 10^{17} + 1.2 \times 10^{17} X_t$ 1/L
X_{t0} = 0.001
F_{S0} = 0.5
dX_t = 0.001

a = styrene
b = methyl acrylate

At any conversion increment (e.g., dX_T = 0.001 mol fraction) the monomer concentrations inside the latex particles, water phase, and monomer droplets then can be calculated. The instantaneous and cumulative copolymer composition and sequence distribution are calculated assuming no change in monomer feed concentrations inside the latex particles during each small conversion increment. In Figure 8 the predicted and experimentally observed cumulative copolymer compositions have been plotted. In Figure 9 the theoretically predicted triad fractions are shown together with the measured triad fractions using the well-known peak assignment of the carbonyl and the C_1 ipso region of the ^{13}C NMR spectra (respectively, representative for M- and S-centered triads) and the methoxy region in the ^{1}H NMR spectra described above. The model predictions have been calculated by using the set of parameters shown in Table V.

The excellent agreement between experimental and model predictions in both cases strongly supports the validity of the assumptions made in the emulsion polymerization model.

For comparison and in order to prove the necessity of a heterogeneous model, the average cumulative chemical composition together with the triad fractions has been calculated by using a homogeneous model (Figures 10 and 11). According to Ramirez-Marquez et al.,[37] who calculated apparent r values for the S–M emulsion copolymerization as a function of the monomer water ratio using a similar model, the apparent r values are r'_S = 0.88 and r'_M = 0.13 at a monomer water ratio of 0.5 (g/g). Figures 10 and 11 show that the average chemical composition and the S-centered triad fractions as a function of conversion are predicted very well when apparent r values are used.

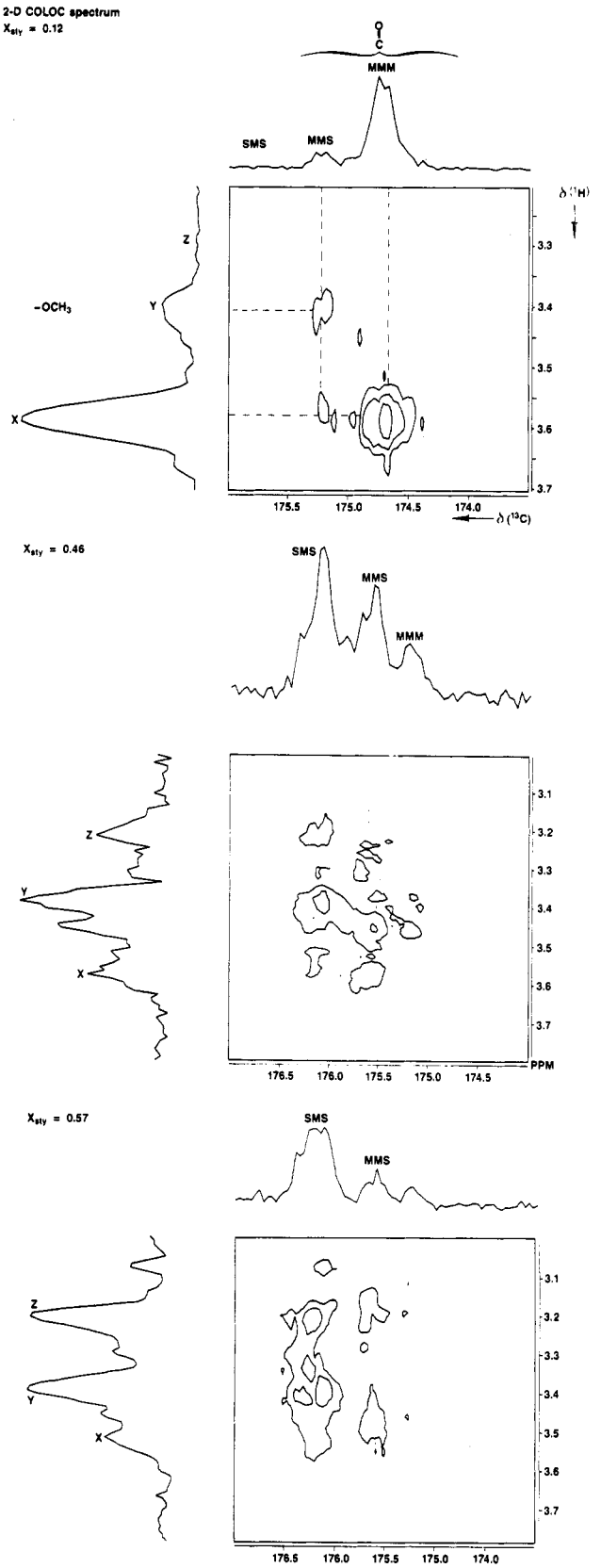

Figure 7. Contour plot from three 2D NMR COLOC experiments, of low-conversion solution copolymers (F_S = 0.12, 0.46, and 0.57), showing long-range correlation between carbonyl ^{13}C atoms and protons of the methoxy group.

However, the M-centered triads are not well predicted by the homogeneous model. This proves the necessity of using the heterogeneous model based on local monomer concentrations and "real" r values, in emulsion copolymerization.

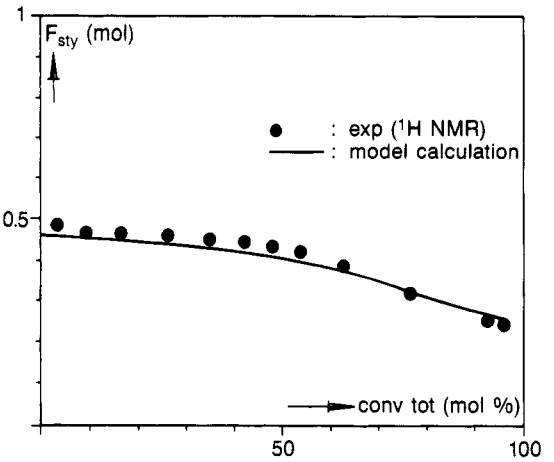

Figure 8. Cumulative emulsion copolymer composition versus conversion. Initial monomer feed ratio S/M 0.33 (mol/mol). Initial monomer/water ratio M/W = 0.5 (g/g).

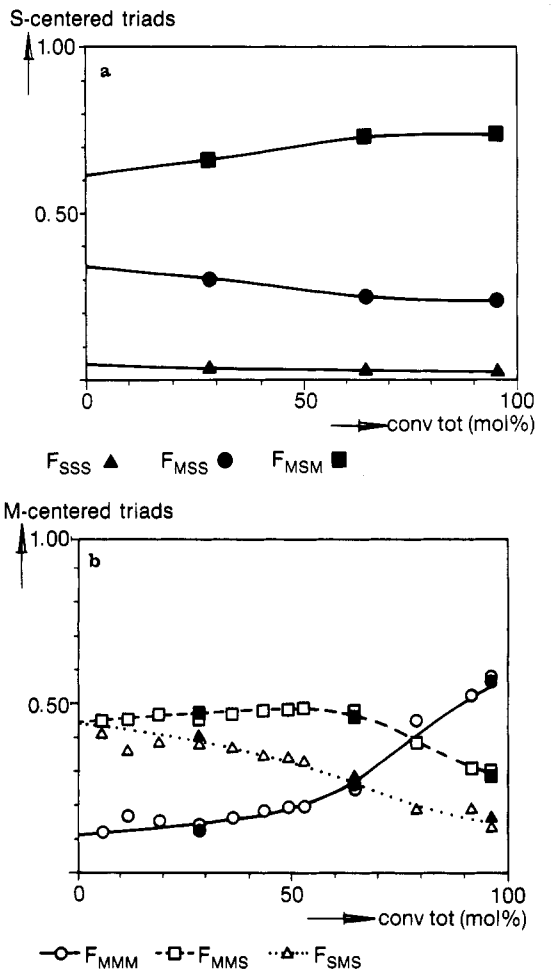

Figure 9. Cumulative emulsion copolymer triad fractions as a function of conversion. Initial monomer feed ratio S/M 0.33 (mol/mol). Initial monomer/water ratio M/W = 0.5 (g/g). (a) S-centered triads. (b) M-centered triads.

The combination of the moderate water solubility of M and the very low water solubility of S has a strong influence on the composition drift during the batch emulsion copolymerization.

In this particular experiment, at ca. 60 mol % conversion all styrene already has polymerized, and hereafter almost pure poly(methyl acrylate) (PM) is being formed, resulting in a strong increase of the cumulative MMM and a strong decrease of the cumulative MMS and SMS triad fractions. Because almost no styrene is present after 60 mol %

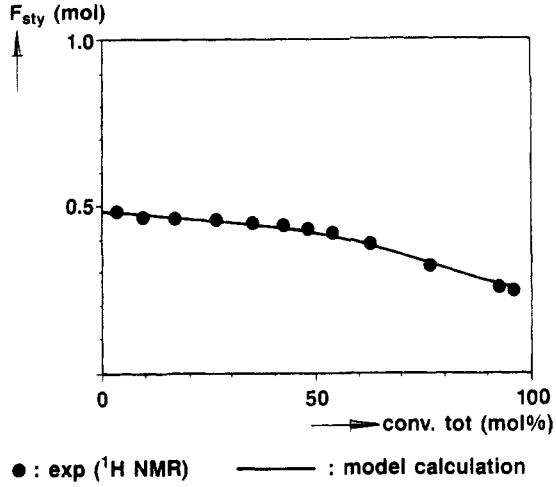

Figure 10. Experimental cumulative emulsion copolymer composition versus conversion compared with the homogeneous model calculation using apparent r values and overall concentrations.

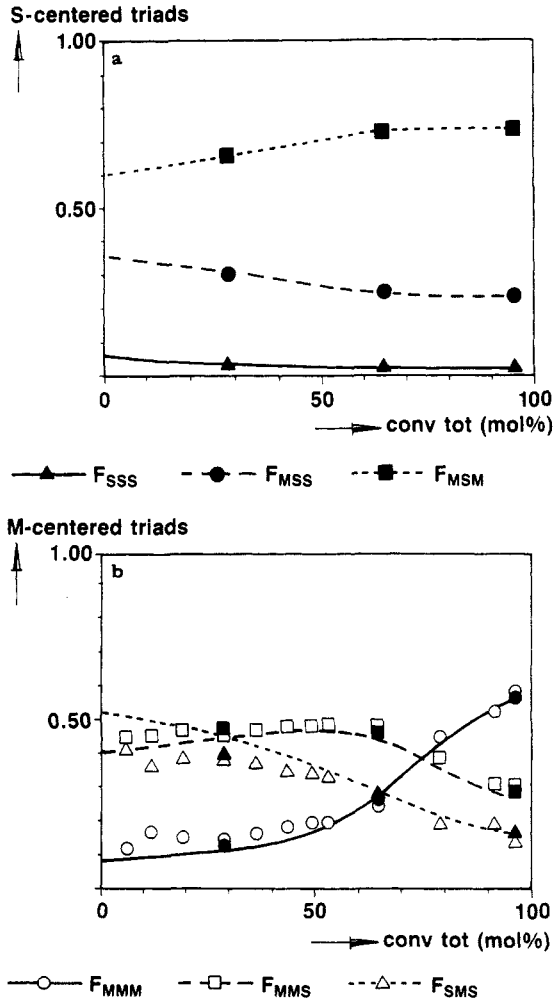

Figure 11. Experimental cumulative emulsion copolymer triad fractions as a function of conversion compared with the homogeneous model using apparent r values and overall concentrations. Initial monomer feed ratio S/M 0.33 (mol/mol). Initial monomer/water ratio M/W = 0.5 (g/g). (a) S-centered triads. (b) M-centered triads.

conversion, the cumulative styrene triad fractions remain constant. Moreover, it is shown in Figure 9 that ^{1}H NMR is also useful in determining the values of the M-centered triads of emulsion copolymers.

When Ito's[23] earlier peak assignment of the methoxy proton region is used, the ^{1}H NMR spectra of the emulsion copolymers provide sequence distribution information only in terms of the M-centered triad fractions.

The M-centered triad fractions calculated from the σ values determined for solution copolymers showed an excellent agreement with the theoretical M-centered triad fractions.

Conclusions

It can be concluded that composition and sequence distribution of solution S–M copolymers can be described according to the integrated Alfrey–Mayo model.

The experimental sequence distribution, in terms of triad fractions of emulsion S–M copolymers determined by means of ^{13}C NMR, confirms the validity of the model calculations used.

Moreover, a comparison between the ^{1}H NMR spectra of the emulsion copolymers and the model calculations of the triad fractions, demonstrates that, under the described experimental conditions, the coisotacticity parameter of S–M copolymers is independent of the polymerization process used (i.e., solution or emulsion polymerization); i.e., $\sigma_{MS} = 0.9$, provided the I–Y assignment is correct or $\sigma_{MS} = 0.3$ provided the alternative assignment is correct.

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