1H and 13C NMR investigation of the intramolecular structure of solution and emulsion styrene-methyl acrylate copolymers

Citation for published version (APA):

DOI:
10.1021/ma00221a005

Document status and date:
Published: 01/01/1990

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.

Download date: 17. Sep. 2023
\textbf{1H and 13C NMR Investigation of the Intramolecular Structure of Solution and Emulsion Styrene–Methyl Acrylate Copolymers}

G. H. J. van Doremela and A. L. German\textsuperscript{*}

\textit{Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5500 MB Eindhoven, The Netherlands}

N. K. de Vries and G. P. M. van der Velden\textsuperscript{*}

\textit{DSM-Research BV, P.O. Box 18, 6160 MD Geleen, The Netherlands}

Received March 17, 1989; Revised Manuscript Received February 27, 1990

\textbf{ABSTRACT} The intramolecular structure (triad distribution and tacticity parameter, $\sigma_{\text{IS}}$) of homogenous styrene (S)–methyl acrylate (M) copolymers, obtained by low-conversion solution polymerization, has been studied by \textit{1H} and \textit{13C} 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 \textit{1H} NMR spectra it is difficult to make a correct peak assignment. Two different assignments can fit the observed data on trial level. The well-known Ito–Yamasita (I–Y) assignment leads for the random copolymers to a high degree of coisotacticity ($\sigma_{\text{IS}} = 0.9$), contrary to the value obtained for alternating copolymers ($\sigma_{\text{IS}} = 0.5$). An alternative assignment is possible, which results in $\sigma_{\text{IS}} = 0.3$. 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\textsubscript{3} resonances. However, the correctness of neither of the two \textit{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.

\textbf{Introduction}

Determination of the intramolecular (triad distribution and 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.\textsuperscript{1–3} Moreover, knowledge about the intramolecular structure is of paramount importance for the understanding of relations between molecular structure and polymer properties.\textsuperscript{4–6} Furthermore, the microstructure depends upon the polymerization process and provides information on the reaction mechanisms occurring during polymerization.\textsuperscript{7,8} NMR methods provide information on the average copolymer composition as well as on the intramolecular structure.\textsuperscript{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.\textsuperscript{9–13} Far less attention has been paid to the determination of the microstructure of copolymers obtained by high-conversion solution processes\textsuperscript{14,15} or high-conversion emulsion processes,\textsuperscript{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.\textsuperscript{14,20–23} Similar results were obtained by our group on the styrene (S)–ethyl methacrylate (EMA) system.\textsuperscript{13,15} However, due to the overlap of OCH\textsubscript{3} or OCH\textsubscript{2} resonances (in the S-MMA and S-EMA systems, respectively) and the methine main-chain backbone resonances in the \textit{1H} NMR spectra of the above-mentioned systems,\textsuperscript{11,12} as already put forward by Kale et al. on the S-MMA system.\textsuperscript{22} Therefore, we have studied the styrene–(S) methyl acrylate (M) system, because (i) no overlap occurs between the OCH\textsubscript{3} resonances and the other main-chain resonances,\textsuperscript{23} (ii) mixed configurational and compositional sequence effects are reported to occur for the OCH\textsubscript{3} \textit{1H} NMR resonances,\textsuperscript{23–25} and (iii) the polymer statistics can be rigorously tested via an analysis of the \textit{13C} carbonyl carbons.\textsuperscript{26–28} Contrary to S-MMA or S-EMA systems,\textsuperscript{13} the \textit{13C} chemical shifts of these carbons in the S–M system are only influenced by compositional sequence effects.\textsuperscript{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 \textit{13C} NMR data). Moreover, we have tried to distinguish between on the one hand Ito’s earlier peak assignment\textsuperscript{25} (tentatively based on the same assignment order for S–MMA copolymers), which results in an extremely high coisotacticity ($\sigma_{\text{IS}} = 0.8–0.9$), and on the other hand an alternative assignment\textsuperscript{29} apparently resulting in a much lower $\sigma_{\text{IS}}$. In an attempt

\textsuperscript{*}Present address: DSM Kunststoffen BV, P.O. Box 604, 6160 AP Geleen, The Netherlands.
to achieve this goal, 2D NMR COLOC experiments were performed on three well-defined homogeneous low-conversion copolymers, thus trying to correlate the $^1$H NMR OCH$_3$ and the $^{13}$C NMR carbonyl region. Related 2D NMR techniques have been performed very recently on the alternating S–MMA system. 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. 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. With the aid 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/dm$^3$ 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/dm$^3$. 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 325 K in a vacuum stove for at least 6 h at 10$^{-3}$ Torr and finally for 2 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 K, and 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/dm$^3$ 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/dm$^3$. 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 325 K in a vacuum stove for at least 6 h at 10$^{-3}$ Torr and finally for 2 h at 10$^{-5}$ Torr.

The emulsion copolymers were 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 K, and the final products were dried at 325 K in a vacuum stove for at least 6 h at 10$^{-3}$ Torr and finally for 2 h at 10$^{-5}$ Torr.

Results and Discussion

Low-Conversion Solution Copolymers. $^1$H NMR Spectra. Determination of Copolymer Composition and of r Values. Figure 1 depicts as a typical example the 400-MHz $^1$H 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. The average copolymer composition (mole fraction styrene, $F_S$) can be readily obtained by using

$$F_S = \frac{3A_1}{3A_1 + 5A_2}$$

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–Tudos 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

<table>
<thead>
<tr>
<th>$q_0$</th>
<th>$F_S$</th>
<th>Convn, mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>0.038</td>
<td>0.12</td>
<td>7</td>
</tr>
<tr>
<td>0.11</td>
<td>0.33</td>
<td>5</td>
</tr>
<tr>
<td>0.36</td>
<td>0.46</td>
<td>12.6</td>
</tr>
<tr>
<td>0.85</td>
<td>0.57</td>
<td>14.3</td>
</tr>
<tr>
<td>1.98</td>
<td>0.67</td>
<td>16.1</td>
</tr>
<tr>
<td>2.97</td>
<td>0.77</td>
<td>10.2</td>
</tr>
<tr>
<td>4.78</td>
<td>0.81</td>
<td>9.7</td>
</tr>
</tbody>
</table>

$^a$ 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).$^8$ According to Ito and Yamashita,$^23$ the three different groups of peaks can be assigned to the following combination of M-centered triads:

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

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

$$F_Z = \sigma^2 F_{SMS}$$

In eq 2, the parameter $\sigma_{MS} (=\sigma_{SM} \text{ or } \sigma \text{ in shorthand notation})$ 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.$^8,23$

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

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

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

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

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

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

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

where $P(S/M) = 1/(1 + r_M/q)$ and $P(M/S) = 1/(1 + r_S)$, 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–Tudos method. In order to predict the relative intensities of each peak, it is necessary to estimate the values of the coisotactic parameter, $\sigma_{MS}$. Two different types of approaches have been used, the so-called Ito–Yamashita approach,$^{10,26}$ and the Harwood–Ritchey (H–R)$^{3,24}$ 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:

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

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

$$F_Y^2 = 4F_XF_Y$$

$$1 + \frac{2F_X}{F_Y^2} = \frac{1 + r_M}{\sigma q}$$

Equations 2 and 4 can be solved numerically for $\sigma$ 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 $\sigma$ to be constant over the whole series of copolymers. If both $r_M$ and $\sigma$ 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 $q/(q + r_M)^3$. From the slopes, the values of $\sigma$ and $\sigma^2$ can be evaluated. The rearrangement of eq 2 put forward by Harwood and Ritchey (H–R approach)$^{3,24}$ leads to the following set:

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

(H–R approach)$^{3,24}$
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 $\sigma$.

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 single peak. 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 $\sigma_{MM} = 0.5$ ($\sigma_{MS} = [mm/mm + 2mr + rr]$ 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$^{25,26}$) and a statistical copolymer, containing the largest amount of SMS triads (in our case $q_0 = 20$, $F_X = 0.92$, $F_{SMM} = 0.98$). 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 $\sigma_{MS}$ 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 $\sigma$ value for this copolymer is much larger than 0.5, because the fractional area intensity of the rr SMS triad (at $\sim 3.50$ 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 FM copolymers to 3.62–3.48 for low FM copolymers (see Figure 2). The truncations, used for the determination of the 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 $(q_0/q + r_M)^2$ and $1 - F_Y^{1/2}$ 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 $\sigma_{MS}$ values, being $\sim 0.9$, have been calculated from the slopes. For two copolymers, with $F_X$ 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 $\sim 3.50$ 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 $F_{SMM}/F_{SMS}$. Calculated triad fractions for $F_{SMM}$ 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 $\sigma$ 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 \((\times 100)\) of both S- and M-Centered Triads of Some Low-Conversion Solution Copolymers

<table>
<thead>
<tr>
<th>(q_0^a)</th>
<th>theor C=O region</th>
<th>exptl</th>
<th>theor C_1 region</th>
<th>exptl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMM</td>
<td>MMS</td>
<td>SMS</td>
<td>MMM</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>0.038</td>
<td>70</td>
<td>28</td>
<td>2</td>
<td>74</td>
</tr>
<tr>
<td>0.36</td>
<td>12</td>
<td>46</td>
<td>42</td>
<td>13</td>
</tr>
<tr>
<td>0.85</td>
<td>3</td>
<td>30</td>
<td>67</td>
<td>0</td>
</tr>
<tr>
<td>4.78</td>
<td>0</td>
<td>7</td>
<td>93</td>
<td>0</td>
</tr>
</tbody>
</table>

---

\(q_0^a\) 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. \(q_0 = 20, F_S = 0.92, \text{and } F_{SMS} = 0.98\).

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 \(\sigma\) 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.\(^{29}\)), may support the following tentative assignment as reported by Nikman and Harwood,\(^{29}\) where the resonance assignment order for \((1 - \sigma)^2\) SMS and \(\sigma^2\) SMS have been interchanged. For alternating copolymers,\(^{26}\) these values are identical:

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

(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:

\[
1 - F_X^{1/2} = \frac{q}{q + r_M} \\
F_Z = (1 - \sigma^2)\left(\frac{q}{q + r_M}\right)^2
\]

(7)

From eq 7 and Figure 5b, a value of \(\sigma\) 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
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, $\sigma = 0.9$, and $r$ values obtained from the low-conversion compositional data ($r_S = 0.73, r_M = 0.19$).

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 $^1$H 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.

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. 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, 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).

\[
[M_a]_p = K_a x_a
\]

\[
[M_b]_b = K_b x_b
\]

\[
[M_a]_w = k_a x_a
\]

\[
[M_b]_w = k_b x_b
\]

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 \(x_a\) is the molar fraction of monomer a inside the monomer droplets.

\[
[M_a]_p v_p N_T + V_w [M_a]_w + M_{ad} = (1 - x_a) M_{a0}
\]

\[
[M_b]_p v_p N_T + V_w [M_b]_w + M_{bd} = (1 - x_b) M_{b0}
\]

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

\[
[M_a]_p v_p N_T + V_w [M_a]_w = (1 - X_a) M_{a0}
\]

\[
[M_b]_p v_p N_T + V_w [M_b]_w = (1 - X_b) M_{b0}
\]

\[
[M_a]_p = K_a k_a [M_a]_w
\]

\[
[M_b]_p = K_b k_b [M_b]_w
\]

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 is independent of the latex particle volume, only the particle volume and does not affect the organic phase/water volume 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

<table>
<thead>
<tr>
<th>Exponentially Observed Cumulative Triad Fractions, Molar Fraction S ((F_S)), and Functional Area Intensities (X, Y, Z) for Two High-Conversion Solution Copolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q_0 = 0.85)</td>
</tr>
<tr>
<td>(convn = 92) mol %</td>
</tr>
<tr>
<td>(exptl)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(1^3C) NMR</th>
<th>(1^3C) NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMM</td>
<td>10.1</td>
</tr>
<tr>
<td>MMS</td>
<td>38.6</td>
</tr>
<tr>
<td>SMS</td>
<td>51.3</td>
</tr>
<tr>
<td>SSS</td>
<td>13.0</td>
</tr>
<tr>
<td>MSM</td>
<td>41.8</td>
</tr>
<tr>
<td>SMM</td>
<td>45.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(^1H) NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_S)</td>
</tr>
<tr>
<td>(X) (c = 0.9)</td>
</tr>
<tr>
<td>(Y)</td>
</tr>
<tr>
<td>(Z)</td>
</tr>
</tbody>
</table>

*Theoretically calculated values for all experimentally observed values are also depicted.

### Table V

<table>
<thead>
<tr>
<th>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</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_a = 5) mol/L</td>
</tr>
<tr>
<td>(K_b = 5) mol/L</td>
</tr>
<tr>
<td>(k_a = 0.6) mol/L</td>
</tr>
<tr>
<td>(k_b = 0.003) mol/L</td>
</tr>
<tr>
<td>(\rho_a = 0.9 \times 10^6 ) g/L</td>
</tr>
<tr>
<td>(\rho_b = 0.95 \times 10^6 ) g/L</td>
</tr>
<tr>
<td>(\rho_b = 1.1 \times 10^6 ) g/L</td>
</tr>
<tr>
<td>(N_T = 3 \times 10^{17} + 1.2 \times 10^7 X_1 ) 1/L</td>
</tr>
<tr>
<td>(a =) styrene</td>
</tr>
<tr>
<td>(b =) methyl acrylate</td>
</tr>
</tbody>
</table>

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 \(^1H\) 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., 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/L). 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.
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.

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%
composition versus conversion compared with the homogeneous constant. Moreover, it is shown in Figure 9 that \textsuperscript{1}H NMR concentrations. Figure 10.

4214

model calculation using apparent proton region is used, the \textsuperscript{1}H NMR spectra of the emulsion is also useful in determining the values of the M-centered triads. (b) M-centered triads.

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 \textsuperscript{13}C NMR, confirms the validity of the model calculations used.

Moreover, a comparison between the \textsuperscript{1}H NMR spectra of the emulsion copolymers and the model calculations of the triad fractions, demonstrates that, under the described experimental conditions, the coisotactity 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.

Acknowledgement. We express our gratitude to Prof. H. R. Harwood and Prof. R. Chújo for valuable discussions and suggestions. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

References and Notes

(17) Llauro, M. F.; Pichot, C.; Guillot, J.; Rios, L.; Cruz, M. A.; Guzman, C. Polymer 1986, 27, 869.

Registry No. (MAHS) (copolymer), 25036-19-5.