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

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Introduction

Determination of the intramolecular (triad distribution and tacticity parameter, $\sigma_{SM}$) of homogenous styrene (S)-methyl acrylate (M) copolymers, obtained by low-conversion solution polymerization, has been studied by $^1$H and $^{13}$C NMR. With the set of reactivity ratios $r_a = 0.73$ 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 $^1$H 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 ($\sigma_{SM} = 0.9$), contrary to the value obtained for alternating copolymers ($\sigma_{SM} = 0.5$). An alternative assignment is possible, which results in $\sigma_{SM} = 0.3$. 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$_2$ resonances. However, the correctness of neither of the two $^1$H 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.

$^1$H 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, $\sigma_{SM}$) of homogenous styrene (S)-methyl acrylate (M) copolymers, obtained by low-conversion solution polymerization, has been studied by $^1$H and $^{13}$C NMR. With the set of reactivity ratios $r_a = 0.73$ 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 $^1$H 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 ($\sigma_{SM} = 0.9$), contrary to the value obtained for alternating copolymers ($\sigma_{SM} = 0.5$). An alternative assignment is possible, which results in $\sigma_{SM} = 0.3$. 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$_2$ resonances. However, the correctness of neither of the two $^1$H 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.

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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$_3$ region 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 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/dm$^3$ in solution-styrene (S)-methyl acrylate (M) copolymer in CDC$_3$ at 25 °C. The mole fraction of styrene ($f_S$) is indicated on the left.

The emulsion copolymers were prepared in a 1-L glass vessel. The monomers (96.3 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 laurel 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 GLC as described elsewhere. Total weight conversion was determined by solid content analysis. These samples were used for recording the NMR spectra.

$^1$H NMR spectra were recorded with a 400-MHz (Bruker AM 400) spectrometer at 298 K, 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. $^{13}$C 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/pont, 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 $^{13}$C 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 $^{13}$C 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 $^1$H or $^{13}$C NMR spectra. No differential $^1$H 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).

The COLOC experiments were used for the observation of long-range couplings between C=O $^{13}$C 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. $^1$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 Keilen–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>$F_S$ conv mol %</th>
</tr>
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<tbody>
<tr>
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<td>0</td>
</tr>
<tr>
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<td>0.12</td>
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<td>0.33</td>
</tr>
<tr>
<td>0.36</td>
<td>0.46</td>
</tr>
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<td>0.55</td>
<td>0.57</td>
</tr>
<tr>
<td>1.98</td>
<td>0.67</td>
</tr>
<tr>
<td>2.97</td>
<td>0.77</td>
</tr>
<tr>
<td>4.78</td>
<td>0.81</td>
</tr>
</tbody>
</table>

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

were determined for an AIBN-initiated system:

\[
\begin{align*}
    r_S &= 0.73 \\
    r_M &= 0.19
\end{align*}
\]

These values are in good agreement with literature data ($r_S = 0.64$ and $r_M = 0.16$ (benzoyl peroxide, 60 °C)\textsuperscript{29} or $r_S = 0.75$ and $r_M = 0.18$ (benzoyl peroxide, 55 °C)\textsuperscript{36}).

**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)\textsuperscript{8} according to Ito and Yamashita\textsuperscript{24} the three different groups of peaks can be assigned to the following combination of M-centered triads:

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

In eq 2, the parameter $\sigma_M$ (= $\sigma_{SM}$ or $\sigma$ 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\textsuperscript{5,23,29}

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

\[
\begin{align*}
    F_{MMM} &= (1 - P(S/M))^2 \\
    F_{MMS} &= 2P(S/M)(1 - P(S/M)) \\
    F_{SMS} &= (P(S/M))^2 \\
    F_{SSS} &= (1 - P(M/S))^2 \\
    F_{SSM} &= 2P(M/S)(1 - P(M/S)) \\
    F_{MSM} &= (P(M/S))^2
\end{align*}
\]

where $P(S/M) = 1/(1 + r_M/q), P(M/S) = 1/(1 + r_S)$ 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–Túdós method. In order to predict the relative intensities of each peak, it is necessary to estimate the values of the coisotactic parameter, $\sigma_M$. Two different types of approaches have been used, the so-called Ito–Yamashita approach\textsuperscript{10,26} and the Harwood–Ritchey (H–R)\textsuperscript{3,24} approach. Both methods rely on the same starting point, i.e., the Ito–Yamashita assignment\textsuperscript{23} as given by eq 2.

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

\[
\begin{align*}
    1 - F_X^{1/2} &= \sigma \left( \frac{q}{q + r_M} \right) \\
    1 - F_Y^{1/2} &= \sigma \left( \frac{q}{q + r_M} \right) \\
    1 + \frac{2F_X}{F_Y} &= \frac{1 + \frac{r_M}{r_S}}{1 + \frac{r_S}{r_M}}
\end{align*}
\]

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 $F_Z^{1/2}$ vs $(q/(q + r_M))^{1/2}$ From the slopes, the values of $r_M$ and $\sigma^2$ can be evaluated. The rearrangement of eq 2 put forward by Harwood and Ritchey (H–R approach)\textsuperscript{3,24} leads to the following set:

\[
\begin{align*}
    \frac{F_X - F_{MMM}}{F_{SMS}} &= (1 - \sigma) \frac{F_{MMS}}{F_{SMS}} + (1 - \sigma)^2
\end{align*}
\]
The left-hand part of eqs 5a-c either can be plotted via $F_{\text{MMMS}}/F_{\text{FSMS}}$, assuming for the whole range of polymers $\sigma$ to be constant, or alternatively can be numerically solved for $\sigma$ for each polymer, by using experimental values for $F_X$, $F_Y$, and $F_Z$ and theoretically calculated or experimentally observed values for $F_{\text{MMMS}}$, $F_{\text{MMMS}}$, and $F_{\text{FSMS}}$ (13C 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 $\sigma$.

Figure 3 depicts the 100-MHz 13C 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. 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, QSM, and QMS. The truncations, used for the determination of the copolymer composition are indicated on the left. Area measurements have been performed on the indicated regions.

Considering the 1H 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.,$^{26,28}$ 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 $\sigma_{\text{MS}} = 0.5$ (1-[mm/(mm + 2mr + rr) SMS])$^{1/2}$. In Figure 4 are depicted two 400-MHz 1H 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 $q_0 = 20, F_S = 0.92, F_{\text{SMS}} = 0.98$). 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 $\sigma_{\text{MS}}$ 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 ~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 3. 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 $(q/(q + r_2))$ and $1 - F_Z^{1/2} + (1 - r_2/(q + r_2))$ (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 $\sigma_{\text{MS}}$ 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 $(F_X = 0, 1 - F_Z^{1/2} = 1)$ 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 $F_{\text{SMS}}/F_{\text{FSMS}}$. Calculated triad fractions for $F_{\text{MMMS}}$ and $F_{\text{FSMS}}$ (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 (×100) of both S- and M-Centered Triads of Some Low-Conversion Solution Copolymers

<table>
<thead>
<tr>
<th>q₀</th>
<th>theor</th>
<th>C=O region</th>
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<td>0</td>
<td>0</td>
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</tr>
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</tr>
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<td>7</td>
<td>93</td>
<td>0</td>
<td>10</td>
<td>90</td>
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</table>

* Initial monomer feed ratio q₀ = [S]/[M].

was prepared in the presence of ZnCl₂, which probably forms a ternary molecular complex with methyl acrylate and styrene. Therefore, it is likely that s 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 Fₓ. These considerations, bearing in mind that (1 – σ)² SMS (=rr SMS) resonates at 3.54 ppm (Tanabe et al.,) may support the following tentative assignment as reported by Nikman and Harwood, where the resonance assignment order for (1 – σ)² SMS and σ² SMS have been interchanged. For alternating copolymers, these values are identical:

\[ F_X = F_{MMM} \]
\[ F_Y = F_{MMS} + σ²F_{SMS} \]
\[ F_Z = 2σ(1 – σ)F_{SMS} + (1 – σ)²F_{SMS} \] (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:

\[ 1 - F_X^{1/2} = \frac{q}{q + r_M} \]
\[ F_Z = (1 - σ²)\left(\frac{q}{q + r_M}\right)² \] (7)

From eq 7 and Figure 5b, a value of σ can be estimated, being σ ~ 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 OCH₃ resonance. The 2D spectra are shown in Figure 7. From the contour plot of the COLOC experiment on the copolymer with Fₛ = 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 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 SM MMMM 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,\textsuperscript{15} $\sigma = 0.9$, and $r$ values obtained from the low-conversion compositional data ($r_S = 0.73, r_M = 0.19$).\textsuperscript{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.\textsuperscript{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.\textsuperscript{17,22,24,36-38} 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,\textsuperscript{7,57,38} 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),

Table III

<table>
<thead>
<tr>
<th>$q^0$</th>
<th>$X$ (exptl)</th>
<th>$Y$ (exptl)</th>
<th>$Z$ (exptl)</th>
<th>$X$ (Ito's assign)</th>
<th>$Y$ (Ito's assign)</th>
<th>$Z$ (Ito's assign)</th>
<th>$X$ (alt assign)</th>
<th>$Y$ (alt assign)</th>
<th>$Z$ (alt assign)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.038</td>
<td>70</td>
<td>27</td>
<td>3</td>
<td>73</td>
<td>25</td>
<td>2</td>
<td>69</td>
<td>28</td>
<td>3</td>
</tr>
<tr>
<td>0.11</td>
<td>38</td>
<td>49</td>
<td>13</td>
<td>45</td>
<td>44</td>
<td>10</td>
<td>40</td>
<td>48</td>
<td>12</td>
</tr>
<tr>
<td>0.36</td>
<td>15</td>
<td>47</td>
<td>34</td>
<td>15</td>
<td>48</td>
<td>35</td>
<td>12</td>
<td>50</td>
<td>38</td>
</tr>
<tr>
<td>0.85</td>
<td>10</td>
<td>40</td>
<td>50</td>
<td>7</td>
<td>39</td>
<td>54</td>
<td>3</td>
<td>37</td>
<td>60</td>
</tr>
<tr>
<td>1.98</td>
<td>4</td>
<td>25</td>
<td>71</td>
<td>3</td>
<td>29</td>
<td>68</td>
<td>1</td>
<td>24</td>
<td>75</td>
</tr>
<tr>
<td>2.97</td>
<td>2</td>
<td>21</td>
<td>77</td>
<td>2</td>
<td>26</td>
<td>72</td>
<td>0</td>
<td>20</td>
<td>79</td>
</tr>
<tr>
<td>4.78</td>
<td>1</td>
<td>15</td>
<td>84</td>
<td>2</td>
<td>23</td>
<td>77</td>
<td>0</td>
<td>17</td>
<td>83</td>
</tr>
</tbody>
</table>

* Initial monomer feed ratio $q^0 = [S]/[M]$. 

Figure 6. Harwood-Ritchey (H-R) plot of the left-hand part (LHP) of eqs 5a vs $F_{F_{MMMS}}/F_{F_{FSMS}}$ for a series of seven low-conversion solution copolymers.
and eq 12 (the iteration process).

\[ [M_a]_p = K_a x_a \]
\[ [M_b]_p = K_b x_b \]
\[ [M_a]_w = k_a x_a \]
\[ [M_b]_w = k_b x_b \]

(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.

\[ [M_a]_p v_p N_T + V_w [M_a]_w + M_{ad} = (1 - x_b) M_{a0} \]
\[ [M_b]_p v_p N_T + V_w [M_b]_w + M_{bd} = (1 - x_b) M_{b0} \]

(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, \(v_p = \) 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:

\[ [M_a]_p v_p N_T + V_w [M_a]_w = (1 - x_b) M_{a0} \]
\[ [M_b]_p v_p N_T + V_w [M_b]_w = (1 - x_b) M_{b0} \]

(10)

\[ [M_a]_p = K_a / k_a \]
\[ [M_b]_p = K_b / k_b \]

(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., \(K_a = K_b = 93.92 \).

The swollen latex particle volume, \(v_p\), is calculated by using eq 12 assuming volume additivity of each component

\[ v_p = v_p [M_a]_p M_a + v_p [M_b]_p M_b + M_{ad} X_a M_a + M_{bd} X_b M_b \]

(12)

where \(v_p = \) density of monomer a (g/L), \(M_{a0} = M_{a0} + M_{b0} = \) total monomer content at the beginning of the reaction per liter of emulsion (mol/L), \(X_a = \) total conversion (mol fraction), \(v_p = \) average copolymer density (g/L), \(M_a = \) molar mass of monomer a (g/mol), \(M_b = \) 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., \(X_{a0} = 0.001\) mol fraction) with a certain copolymer composition, representative of the emulsion system (e.g., \(F_3 = 0.5\)).

### Table IV

<table>
<thead>
<tr>
<th>Experimentally Observed Cumulative Triad Fractions, Molar Fraction S ((F_S)), and Functional Area Intensities ((X, Y, Z)) for Two High-Conversion Solution Copolymers*</th>
<th>(q_0 = 0.85)</th>
<th>(q_0 = 5.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>convn = 92 mol %</td>
<td>convn = 99 mol %</td>
</tr>
<tr>
<td>exptl</td>
<td>model</td>
<td>exptl</td>
</tr>
<tr>
<td><strong>1H NMR</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(F_S)</td>
<td>0.53</td>
<td>0.5</td>
</tr>
<tr>
<td>(X (\sigma = 0.9))</td>
<td>14.4</td>
<td>14.8</td>
</tr>
<tr>
<td>(Y)</td>
<td>44.5</td>
<td>44.0</td>
</tr>
<tr>
<td>(Z)</td>
<td>41.1</td>
<td>41.5</td>
</tr>
</tbody>
</table>

*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 |
| | \(\mu_a = 0.9 \times 10^{-5}\) g/L | \(\mu_b = 0.95 \times 10^{13}\) g/L |
| | \(\rho_a = 1.1 \times 10^{13}\) g/L | \(N_T = 3 \times 10^{17} + 1.2 \times 10^{17} X_l /L\) |
| | \(a = \) 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 \(1^H\) 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-Marez 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/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.

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Figure 7. Contour plot from three 2D NMR COLOC experiments of low-conversion solution copolymers (FS = 0.12, 0.46, and 0.57), showing long-range correlation between carbonyl 13C 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 %
conversion, the cumulative styrene triad fractions remain constant. Moreover, it is shown in Figure 9 that $^1$H NMR 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.

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.

The M-centered triad fractions calculated from the $\sigma$ 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 $^1$H 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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References and Notes

\[ ^1\text{H} \text{ and } ^{13}\text{C NMR Investigation of S–M Copolymers} \quad 4215 \]


Registry No. (MA)S (copolymers), 25036-19-5.