

Investigation of the intramolecular structure of styrene–ethyl methacrylate copolymers by ^1H nuclear magnetic resonance:

2. Comparison of the microstructure of solution and emulsion copolymers obtained at high conversion

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The intramolecular structure (triad distribution and tacticity parameter σ_{SE}) of poly(styrene-*co*-ethyl methacrylate) copolymers obtained up to very high conversions by means of solution and emulsion batch processes, using non-ionic as well as anionic surfactants, has been determined by ^1H nuclear magnetic resonance. A model is proposed to predict the total triad distribution in the case of high-conversion solution copolymerization. The instantaneous distribution has been described by classical formulae based on Alfrey–Mayo kinetics. A novel simple analytical expression is derived to describe the conversion distribution, which indicates how much of each instantaneous distribution is present. The agreement found between predicted and observed triad distributions was good for copolymers obtained by high-conversion solution and azeotropic emulsion processes. For copolymers prepared according to non-azeotropic emulsion processes, anomalous effects were observed as compared with the solution copolymers.

(Keywords: poly(styrene-*co*-ethyl methacrylate); high conversion; modelling; emulsion copolymers; ^1H nuclear magnetic resonance; sequence distribution)

INTRODUCTION

Determination of the intramolecular (triad distribution, tacticity) and intermolecular (chemical composition molar mass distribution) structures is increasingly recognized as a prerequisite in copolymer characterization, since revealing the molecular structure may supply information not only about the monomer addition process but also about the preference of monomers to add in a (co)iso- or (co)syndiotactic configuration^{1–4}. In addition, knowledge about the inter- and intramolecular structures is of paramount importance for the understanding of relations between molecular structure and polymer properties^{5–8}.

One of the advanced methods of determining the intramolecular chain structure is nuclear magnetic resonance (n.m.r.). However, the majority of publications concerning the elucidation of chain microstructure deal with copolymers obtained by means of low-conversion (< 15%) bulk or solution processes^{9–17}. Little attention has been paid⁹ to the determination of the chain microstructure of copolymers obtained by high-conversion processes^{18,19}, even though high conversion is of great technological importance.

From recent publications it becomes clear that under certain conditions even the integrated Alfrey–Mayo (AM) model is inadequate to describe high-conversion

copolymerization kinetics^{20–23} and copolymer microstructure^{24,25}. In other cases, however, the course of high-conversion copolymerization processes and the inter- and intramolecular structure could be successfully predicted by kinetic parameters obtained from low-conversion compositional data. For instance O'Driscoll²⁶ reported that the classical AM model is applicable in the high-conversion copolymerization of styrene (Sty) and methyl methacrylate (MMA). Also, the experimentally observed and theoretically predicted intramolecular structures of styrene–methyl methacrylate copolymers obtained from high-conversion bulk copolymerization were in agreement, as confirmed by Ito¹⁸.

Recently, we studied the copolymerization behaviour of styrene (Sty) and ethyl methacrylate (EMA) in dilute solution (1 mol dm⁻³ in toluene). We found that experimental curves of monomer feed ratio *versus* conversion fitted relationship to be expected on the grounds of the integrated AM model¹⁷. Moreover, it appeared that the observed chemical composition distribution (CCD) of these low-conversion copolymers could be predicted by a combination of an extended (according to different molar mass of the monomers as proposed by Tacx) Stockmayer model, the AM model and kinetic parameters obtained at low conversion²⁷.

In addition, we studied the high-conversion copolymerization kinetics in relatively concentrated systems (3 mol dm⁻³ in toluene) as well as the CCD²⁸. From these studies it became apparent that the AM model is still valid in this case of solution copolymerization, despite the relatively high polymer concentration at high conversion. In the case of emulsion

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copolymerization, significantly deviating kinetic behaviour and CCDs were observed²⁸ as compared with solution kinetics and CCDs of solution copolymers.

In order to reveal a more complete and detailed chain structure of the high-conversion products, it is also necessary to determine experimentally the intramolecular structure. For the case of high-conversion solution products, model calculations based on AM kinetics were carried out and compared with the experimental values of the triad fractions. Although for the case of emulsion copolymerizations model calculations exist^{19,29,30}, no attempt was made to verify these models. In order to determine deviations from solution kinetics, the microstructures of some emulsion and solution copolymers with the same average composition were compared.

EXPERIMENTAL

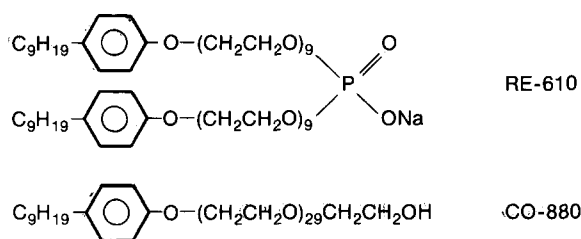
Purification of chemicals

The purification of the chemicals has been described earlier in part 1¹⁷.

Preparation of high-conversion samples

Solution polymerization technique. These reactions were carried out in a stainless-steel SFS reactor, flushed with nitrogen before use. The total monomer concentration was 3 mol dm⁻³, the solvent was toluene and the initial initiator concentration was 5 mmol dm⁻³. The reaction mixtures were thermostated at 335 ± 0.2 K and stirred at 100 rpm. The entire course of the reaction was continually monitored by gas-liquid chromatography (g.l.c.). The g.l.c. conditions have been described in detail elsewhere²⁸.

Emulsion polymerization technique. The copolymer latices were prepared using a 1.5 litre glass vessel. The monomers (300 g in which 1.9 g of n-dodecylmercaptan was dissolved) were added dropwise to the soap solutions (40 g CO-880 or 14 g RE-610 (GAF) dissolved in 1000 g water, distilled twice).



Subsequently, a potassium persulphate (Merck P.A.) solution (2 g dissolved in 25 ml distilled water) was added to the reaction mixture, thermostated at 337 ± 0.5 K.

Total weight conversion was determined by solid content analysis. The feed ratio was calculated from monitoring the monomer concentrations, during the entire course of the reaction. The g.l.c. conditions have been described earlier²⁸.

Working-up procedure of products. All copolymers prepared by means of the solution technique were isolated and purified by pouring into cold hexane. The final

products were dried at 328 K in a vacuum oven for 6 h at 10⁻¹ T and finally for 8 h at 10⁻⁵ T.

The copolymers obtained by emulsion copolymerization were purified from emulsifier, unreacted initiator and residual monomers by pouring into methanol or careful coagulation with aluminium nitrate solution (0.001 M), subsequent decantation and filtration of water and coagulant. The final product was thoroughly washed with boiling water (distilled twice) and dried at 10⁻⁵ T for at least 8 h at 353 K.

Experimental conditions for recording ¹H n.m.r. spectra

¹H n.m.r. spectra were measured with a Bruker CXP-300 spectrometer at 25°C, using CCl₄ as a solvent and (CD₃)₂CO as internal locking agent. Sample concentration was 1% (w/v). Other experimental details have been described earlier¹⁷.

Calculation of theoretical triad fractions

All calculations were carried out on a Burroughs B7900 mainframe computer.

RESULTS AND DISCUSSION

Evaluation of theoretical triad fractions for high-conversion copolymers exhibiting AM kinetics

During the course of most batch copolymerization processes, the monomer feed ratio inevitably shifts as conversion increases³¹. This well known phenomenon gives rise to a shift of triad fractions and composition of the copolymer. The total triad fractions and composition of the copolymers exhibiting AM kinetics can be calculated by taking into account both conversion and instantaneous triad distribution.

For the calculation of conversion triad distribution, a simple analytical expression is presented in which formulae are derived that are compatible with the estimation of *r* values by means of the improved curve-fitting I procedure (ICFIP)³¹⁻³³.

The instantaneous triad fraction may be calculated by means of the classical formulae^{1,2}:

$$F_{EEE} = P(E) \times P(E/E) \times P(E/EE) / P(E) = P^2(E/E) \\ = [1 - P(S/E)]^2$$

$$F_{EES} = 2P(S/E) \times [1 - P(S/E)]$$

$$F_{SES} = P^2(S/E)$$

$$F_{SSS} = [1 - P(E/S)]^2$$

$$F_{SSE} = 2P(E/S) \times [1 - P(E/S)]$$

$$F_{ESE} = P^2(E/S)$$

where $P(S/E) = (1 + r_2/q)^{-1}$, $P(E/S) = (1 + r_1q)^{-1}$, $q = [\text{Sty}]/[\text{EMA}]$ is the instantaneous feed ratio and r_i is the reactivity ratio of monomer *i*. Here *F* is the normalized number fraction of triads, and $P(M_1/M_2)$ is the probability that a growing chain with an *M*₂ chain end will add monomer *M*₁.

The total average triad fraction (\bar{F}) of a copolymer obtained at high conversion can be described by:

$$\bar{F} = (1/C_{Mc}) \int_{C_M} F(r_1, r_2, q) dC_M \quad (1)$$

Here *F* is again the normalized triad fraction of the

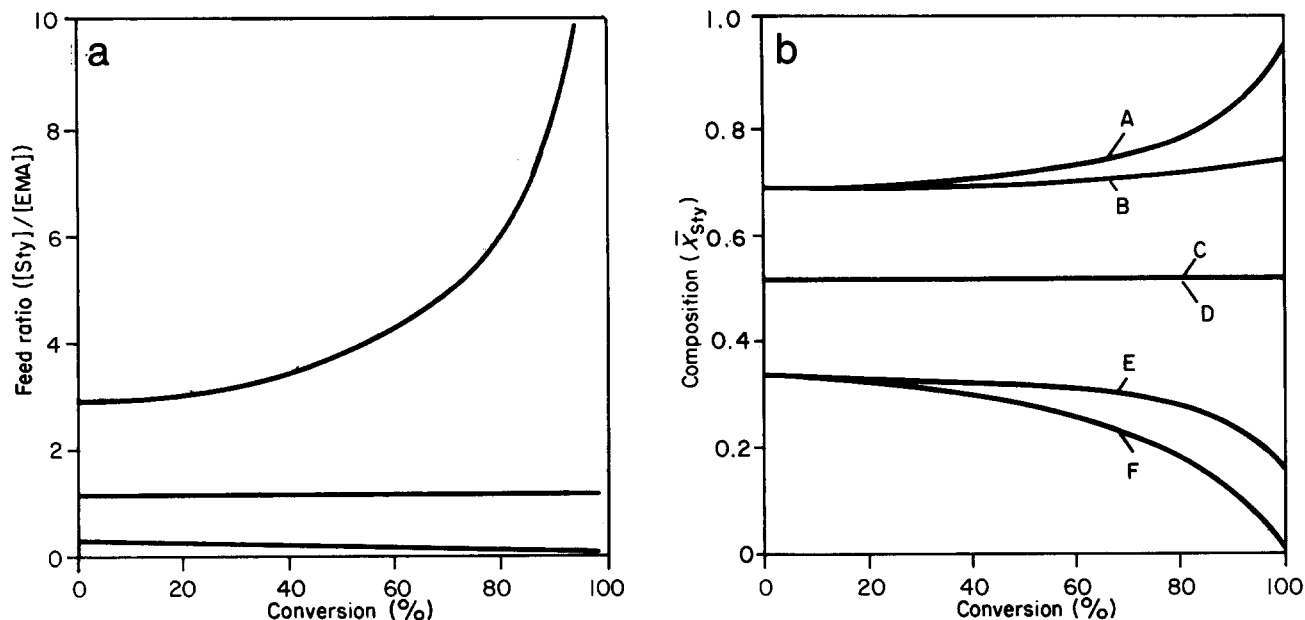


Figure 1 (a) Molar feed ratio versus total molar conversion. Initial feed ratio $q_0 = [\text{Sty}]/[\text{EMA}]$ is 3.0, 1.1 and 0.33. (b) Average composition of instantaneously formed (A, D, F) and cumulative (B, C, E) product at initial feed ratios $q_0 = 3.0$ (A, B), $q_0 = 1.1$ (C, D) and $q_0 = 0.33$ (E, F) versus conversion. Kinetic parameters: $r_1 = 0.49$, $r_2 = 0.40$

instantaneously formed product and \bar{F} the average number fraction of triads of the cumulative copolymer, C_M is the molar fractional conversion and e indicates final conditions. C_{Me} may be regarded as a normalization factor.

By introducing:

$$d(C_M/C_{Me}) = dI_M \quad \text{and} \quad f_c = (dI_M/d\bar{x})$$

equation (1) may be rewritten as:

$$\bar{F} = \int_{\bar{x}} F(r_1, r_2, q) |f_c(\bar{x})| d\bar{x} \quad (2)$$

Here I_M is the integral molar fraction of copolymer and f_c the differential weight distribution function, describing the conversion kinetics. This function may be regarded as a statistical weight function, indicating the relative amount of each instantaneously formed product. The function $f_c(\bar{x})$ can be rewritten as:

$$f_c(\bar{x}) = \left(\frac{dI_M}{d\bar{x}} \right) = \left(\frac{dI_M}{dq} \right) \left(\frac{dq}{d\bar{x}} \right) \quad (3)$$

and (dI_M/dq) and $(dq/d\bar{x})$ can be expressed analytically²⁷, the result being:

$$\frac{dI_M}{dq} = -Z_2 \left(\frac{-1-x_2}{q} + \frac{x_2(1+x_1+x_2)}{qx_2-x_1} + \frac{1}{1+q} \right) \times \left(\frac{1+q}{-Z_{2e}(1+q) + (1+q_0)} \right) \quad (4)$$

$$\frac{dq}{d\bar{x}} = \frac{-[(r_1q+1) + (r_2/q+1)]^2}{(r_1q+1)(-r_2/q^2) - r_1(r_2/q+1)} \quad (5)$$

in which $x_i = (1-r_i)^{-1}$ and Z_2 is expressed as a function of q according to:

$$Z_2 = \left(\frac{q}{q_0} \right)^{-x_2+1} \left(\frac{x_2q-x_1}{x_2q_0-x_1} \right)^{1+x_1+x_2} \quad (6)$$

where 0 indicates initial conditions.

Now, fast numerical integration of equation (2) is

possible since the integrand is analytically expressed as a product of three functions.

In Figure 1a, the feed ratio (q) is given as a function of conversion at three different initial feed ratios, $q_0 = 3.0$, 1.1 and 0.33, using the kinetic parameters of the binary combination of Sty-EMA, i.e. $r_1 = 0.49$, $r_2 = 0.40$. The average composition of the instantaneously formed and cumulative copolymer as a function of conversion is presented in Figure 1b at three different initial feed ratios: $q_0 = 3.0$, 1.1 and 0.33.

In Figures 2a and 2b the triad fractions of the instantaneously formed as well as the cumulative copolymer are shown. One initial feed ratio is omitted, i.e. the azeotropic one ($q_0 = 1.1$). The initial feed ratio ($q_0 = [\text{Sty}]/[\text{EMA}]$) corresponding to azeotropic conditions is approximately 1.1. The non-azeotropic feed ratios chosen deviate significantly from the azeotropic one. Despite this discrepancy, significant shifts from the initial feed ratio do not occur before moderately high conversions are reached. This effect must be attributed to the similarity of the reactivity ratios of both monomers. As a consequence, the change in the instantaneously formed triad fractions only deviates significantly at moderately high conversion. So, the changes of cumulative triad distribution are expected to be relatively small.

¹H nuclear magnetic resonance

Determination of copolymer composition. In Figure 3, 300 MHz spectra of three Sty-EMA copolymers, obtained in high-conversion azeotropic solution and emulsion processes, are presented. Furthermore, Figure 4 depicts nine expanded spectra of copolymers obtained from solution and emulsion processes. These spectra only display the oxymethylene region, since this region in particular displays additional fine splittings, due to combined configurational and compositional sequence effects^{3,17}.

The copolymer composition can be readily obtained,

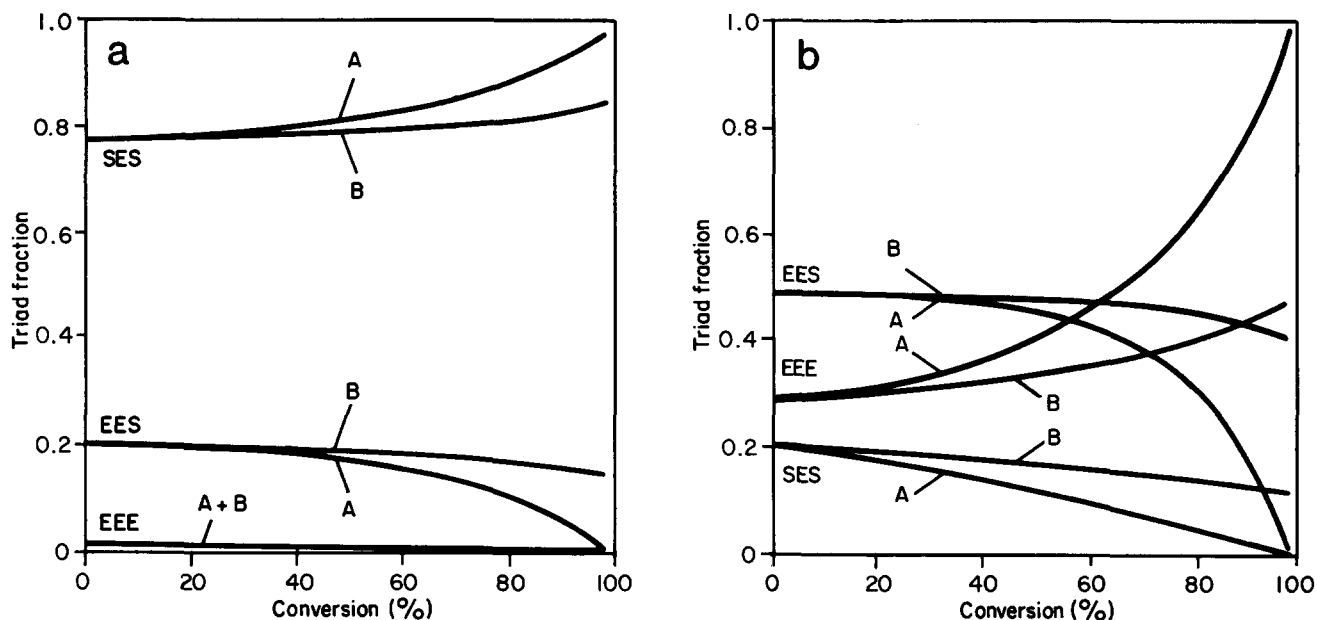


Figure 2 (a) Triad fractions of instantaneously formed (A) and cumulative (B) copolymers versus conversion at initial feed ratio $q_0=3.0$. (b) Triad distribution of instantaneously formed (A) and cumulative (B) copolymers versus conversion at initial feed ratio $q_0=0.33$

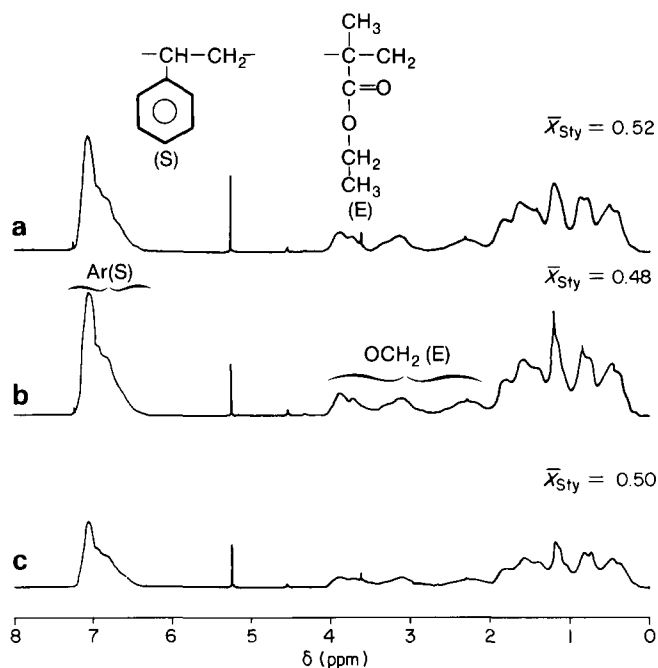


Figure 3 300 MHz ^1H n.m.r. spectra of three copolymers obtained by (a) solution and by emulsion using (b) non-ionic surfactant and (c) anionic surfactant. Initial feed ratio $q_0=1.1$

using:

$$X_{\text{Sty}} = \frac{10A_1}{7A_1 + 5A_2} \quad (7)$$

where A_1 and A_2 represent the aromatic and aliphatic proton resonances respectively.

In Table 1 the initial feed ratio (q_0), final conversion, and expected and observed copolymer compositions are indicated. From the table it appears that expected and observed compositions are in very good agreement.

It should be realized that r values are important parameters in the prediction of the instantaneous as well as the cumulative triad distributions. Hence, accurate

estimation of the kinetic parameters is a necessity. One of the methods that has been found to lead to a reliable estimation of reactivity ratios is g.l.c. analysis of the reaction mixture in conjunction with the improved curve-fitting I procedure (ICFIP)³¹⁻³³. This procedure accounts for measurement errors in both variables. Therefore, this procedure was also applied in the present investigation. The results are given in Table 2 and are used to predict cumulative triad distributions.

Experimental triad evaluation of the ^1H n.m.r. spectra of high-conversion solution polymers. In Figures 4a-c the expanded spectra of the copolymers obtained by high-conversion batch solution polymerization are presented. From a comparison of these spectra with spectra of Sty-EMA copolymers obtained at low conversion¹⁷, it appears that these spectra display a similar resonance pattern and fine structure in the oxymethylene region.

Owing to an improved resolution of the n.m.r. spectrometers, it appeared that the original assignments in spectra of Sty-MMA copolymers were not correct. As a result, San-Roman¹⁶ and Uebel^{14,15} reassigned part of the resonances in the oxymethylene region. Unfortunately, the improvements of Uebel, valid for Sty-MMA copolymers, appeared to be inapplicable to Sty-EMA copolymers. In order to explain this anomaly, Tacx *et al.* proposed a new assignment¹⁷. A summary of the assignments of Ito, Uebel and Tacx is given in Table 3. The slight reassessment proposed by Kale *et al.* for Sty-MMA copolymers put forward very recently³⁴ has also been included. In this table, the parameter σ_{SE} is defined as a measure of the probability that alternating Sty- and EMA-centred units adopt a coisotactic configuration. EEE, EES and SES denote the three different kinds of compositionally EMA-centred triads.

In Table 4 the predicted number fraction of EMA-centred triads is shown, using the calculation method, r values and conversions as mentioned in Tables 1 and 2. In order to compare the experimentally observed and theoretically predicted peak areas, each having the

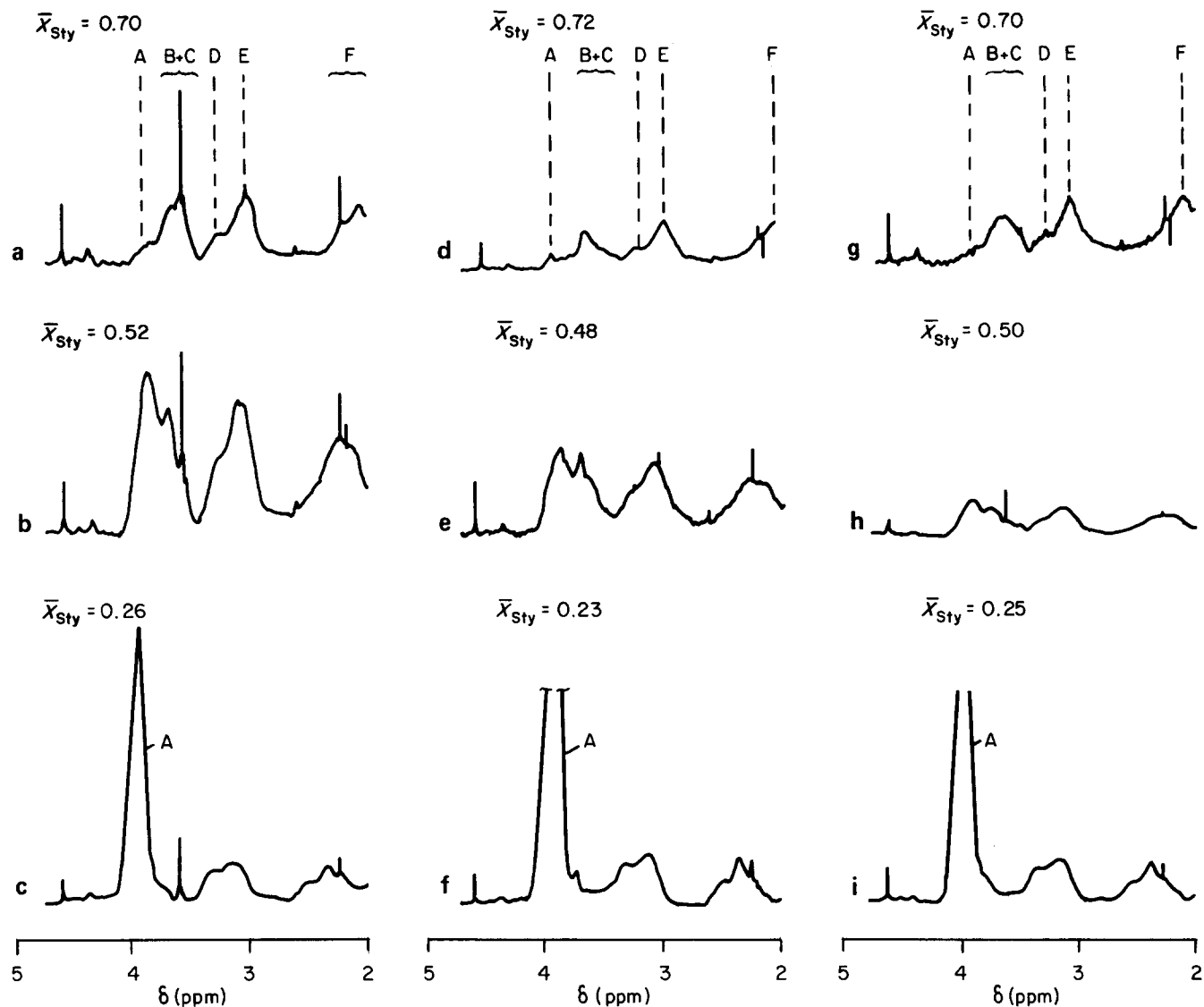


Figure 4 Expanded spectra of copolymers obtained by (a–c) high-conversion solution, and by high-conversion emulsion using (d–f) non-ionic surfactant CO-880 and (g–i) anionic surfactant RE-610. Additional details about reaction conditions can be found in *Table 1*

Table 1 Initial feed ratio $q_0 = [\text{Sty}]/[\text{EMA}]$, observed and predicted cumulative copolymer composition (\bar{X}_{Sty} mole fraction styrene) and final conversions of nine high-conversion Sty–EMA copolymers: (a)–(c) obtained by solution; (d)–(f) obtained by emulsion (non-ionic emulsifier CO-880); and (g)–(i) obtained by emulsion (anionic emulsifier RE-610) processes

Process	Initial feed ratio, q_0	Composition observed (mol% Sty)	Cumulative composition predicted (mol% Sty)	Final conversion (total mol%)
Solution	(a) 3.00	70	70	69
	(b) 1.12	52	51	98
	(c) 0.33	26	25	99
Emulsion CO-880 non-ionic emulsifier	(d) 3.00	72	74	99
	(e) 1.11	48	50	99
	(f) 0.33	23	25	99
Emulsion RE-610 anionic emulsifier	(g) 3.01	70	73	98
	(h) 1.12	50	50	99
	(i) 0.33	25	25	99

appropriate assignment, it is necessary to estimate the coisotacticity parameter σ_{SE} . This calculation is outlined below. Since the value of the coisotacticity parameter σ_{SE} may be dependent on the type of assignment used, it is worth while to investigate the reliability of the three current assignments of Ito, Uebel and Kale, and Tacx.

From *Table 5*, it appears that according to the model of Ito the predicted area of A (i.e. assumed to be caused only by EEE triad) is severely underestimated, irrespective of the value of σ_{SE} . Similar discrepancies were also observed in the assignments of triads to peaks in spectra of Sty–MMA¹⁵ and Sty–EMA¹⁷ copolymers obtained at low

conversion. So, it might again be inferred that the original assignments of Ito^{10,12} have to be reconsidered. According to Uebel's and Kale's and our reassignments, peak A is assumed to be caused by a twin resonance of EEE and $(1-\sigma)$ EES triads. Consequently, the calculation of the value of σ_{SE} is independent of the type of model used.

The number fraction of triads of the resonances (i.e. EEE and EES) can be predicted using our model, valid for high-conversion batch solution AM copolymerization. The area of A is obtained from experimental data. The coisotacticity parameter σ_{SE} is now easily estimated according to:

$$\text{Area of A} = \bar{F}_{EEE} + (1-\sigma)\bar{F}_{EES} \quad (8)$$

\bar{F} being the cumulative number fraction of a certain kind of triad. This calculation procedure may also be applied to other triad resonances. This extension is feasible, but less reliable, since the other peaks are either not as highly resolved as peak A (e.g. B+C, D) or do not cover such a wide range of area intensities (e.g. E and F). Moreover, the results of the calculation of σ_{SE} may then become dependent on the type of assignment. So, it might be concluded that calculation of σ_{SE} according to equation (8) leads to the most reliable estimation of σ_{SE} , provided the AM model is valid to high conversion and peak A is correctly assigned. The results are also summarized in Table 4. From this table it appears that the value of σ_{SE} for copolymers of Sty-EMA obtained at very high conversion and low pressure (0.1 MPa, 1 bar) does not deviate significantly from the value of σ_{SE} for copolymers obtained at low conversion and high pressure (120 MPa)¹⁷. As an important result, it might be

concluded that σ_{SE} is nearly independent of pressure within the range 0.1 MPa-120 MPa.

Considering observed relative intensities of peaks B+C, D and E and the predicted ones according to the assignment of Uebel, significant discrepancies show up. This can be verified from the results of Table 5. These discrepancies resemble the ones observed in spectra of Sty-EMA copolymers obtained at low conversion¹⁷. The observed and predicted relative intensities of peaks A and F are in reasonable agreement.

The recently suggested improved reassignment, apparently valid for Sty-MMA copolymers³⁴, leads to an even greater imbalance of the theoretically calculated areas of peaks D and E (the only difference between Uebel's model and Kale's model) in comparison with the experimentally observed parameters, giving rise to smaller values for E and larger values for D.

In order to cope with the discrepancies between predicted and observed relative intensities, a reassignment was proposed for Sty-EMA copolymers¹⁷. This new reassignment, in which the $2\sigma(1-\sigma)$ SES, $(1-\sigma)^2$ SES and σ EES triads have been changed as compared to the assignment of Uebel, also leads in the case of high-conversion Sty-EMA copolymers to the best fit that can be achieved between integral resonance pattern and copolymer structural features. This can be verified from the results of Table 5.

Other suggestions failed to lead to a significantly better fit or were unlikely to occur for the same reasons as discussed in detail in earlier work¹⁷. Hence, we believe that the proposed reassignment, valid for spectra of low-conversion Sty-EMA copolymers, is also the best one to assign the spectra of high-conversion batch solution copolymers. The calculation of σ_{SE} is also in this case independent of the type of assignment used (Uebel's and Kale's or ours), although it should be realized that the AM model has to be valid even at high conversion²⁸.

Table 2 Reactivity ratio of the binary monomer combination Sty (1) and EMA (2) at 62°C and at different pressures as determined by the improved curve-fitting I procedure³¹. The r values obtained at 0.1 MPa and 1 mol dm⁻³ monomer concentration fitted experimental curves of feed ratio (q) and conversion according to the integrated AM model. So, it might be concluded that r values are not strongly affected by the concentration within the range 1-3 mol dm⁻³

Pressure (MPa)	Monomer concentration (mol dm ⁻³)	r_1	r_2
0.1	1	0.49 ± 0.02	0.40 ± 0.03
0.1	3	0.49	0.40
118	1	0.59 ± 0.03	0.50 ± 0.02

Table 4 Predicted cumulative number fraction of EMA-centred triads, using initial feed ratio (q_0) as indicated and kinetic parameters as given in Table 2, i.e. $r_1=0.49$ and $r_2=0.40$. Moreover, observed intensity of peak A and calculated σ_{SE} are indicated

Initial feed ratio, q_0	F_{EEE}	F_{EES}	F_{SES}	Area of A	σ_{SE}
3.00	0.01	0.18	0.81	0.07	0.67
1.10	0.07	0.39	0.54	0.20	0.67
0.33	0.46	0.41	0.13	0.60	0.66

Table 3 Literature and new assignments of triads for Sty-EMA copolymers

Peak	A	B+C	D	E	F
Chemical shift region (ppm)	4.2-3.85	3.85-3.5	3.5-3.3	3.3-3.0	2.7-2.1
Ito-Bovey ¹⁰⁻¹³	EEE	$(1-\sigma)$ EES $(1-\sigma)^2$ SES	σ EES	$2\sigma(1-\sigma)$ SES	σ^2 SES
Uebel and Dinan ^{14,15}	EEE $(1-\sigma)$ EES	$(1-\sigma)^2$ SES	σ EES	$2\sigma(1-\sigma)(\text{ESESE} + \text{ESESS} + \text{SSESS})$ $= 2\sigma(1-\sigma)$ SES	σ^2 SES
Kale <i>et al.</i> ³⁴	EEE $(1-\sigma)$ EES	$(1-\sigma)^2$ SES	σ EES + $2\sigma(1-\sigma)$ ESESE	$2\sigma(1-\sigma)$ SES - $2\sigma(1-\sigma)$ ESESE	σ^2 SES
This work	EEE $(1-\sigma)$ EES	$2\sigma(1-\sigma)$ SES	$(1-\sigma)^2$ SES	σ EES	σ^2 SES

Table 5 Normalized peak areas of the oxymethylene resonances of three Sty-EMA copolymers obtained by *high-conversion batch solution* processes. Predicted intensities calculated using the model valid for high conversion and $r_1=0.49$, $r_2=0.40$, $\sigma_{SE}=0.67$ and various initial feed ratios $q_0=[\text{Sty}]/[\text{EMA}]$

Feed ratio, q_0	Copolymer composition (mole fraction Sty)	Relative intensities					Assignment
		A	B+C	D	E	F	
3.00	0.70	0.06	0.27	0.10	0.23	0.34	Observed
		0.01	0.15	0.12	0.36	0.36	Ito
		0.07	0.09	0.12	0.36	0.36	Uebel
		0.07	0.36	0.09	0.18	0.36	Tacx
1.1	0.52	0.20	0.17	0.09	0.23	0.31	Observed
		0.07	0.19	0.26	0.24	0.24	Ito
		0.20	0.06	0.26	0.24	0.25	Uebel
		0.20	0.24	0.06	0.26	0.25	Tacx
0.33	0.26	0.60	0.03	0.08	0.14	0.16	Observed
		0.46	0.15	0.25	0.06	0.09	Ito
		0.60	0.02	0.25	0.06	0.09	Uebel
		0.60	0.06	0.02	0.25	0.09	Tacx

Moreover, the r values have to be determined very accurately, since the model in conjunction with the kinetic parameters is applied to predict the twin resonance of EEE and EES triads.

Experimental triad evaluation of the ^1H n.m.r. spectra of high-conversion emulsion copolymers. In previous work for low-conversion solution copolymers, in which we used the initial feed ratio (q_0) as a tool to obtain relations between kinetics and structure, we proposed a reassignment of ^1H n.m.r. spectra of Sty-EMA. In the previous section we have used the conversion as a tool to correlate high-conversion solution kinetics and structure of the resulting copolymers; this new assignment was again confirmed. This reassignment can be now used to investigate experimentally the intramolecular structure of polymers obtained by processes exhibiting, possibly, anomalous AM kinetics.

One of these processes is emulsion copolymerization, in which a non-polar monomer (Sty) reacts with a polar monomer (EMA). In a batch emulsion copolymerization, there exists a partition of monomers over at least three phases, i.e. the monomer droplets, water phase and growing latex particles. The relevant partition coefficients may significantly differ. Hence, the triad distribution of the resulting emulsion copolymers might deviate from the triad distribution expected on grounds of the high-conversion AM solution kinetics.

In *Figure 4*, expanded ^1H n.m.r. spectra representing the oxymethylene region are shown of Sty-EMA copolymers obtained by high-conversion emulsion processes, using the non-ionic emulsifier CO-880 (*Figures 4d-f*) and the anionic emulsifier RE-610 (*Figures 4g-i*) respectively. The chemical structures of both surfactants (see 'Experimental' section) show a certain resemblance at one chain end but the other chain end differs considerably. By means of this experimental set-up, the effect of the nature of the surfactant on the kinetics and resulting copolymers may be investigated.

In *Table 6* the experimentally observed relative intensities of peaks A to F in the copolymers obtained by solution and both emulsion batch processes are presented. Taking into account the accuracy of the area measurements, it appears that discrepancies between the intensities of peaks A to F of products obtained by

Table 6 Type of process, initial feed ratio $q_0=[\text{Sty}]/[\text{EMA}]$ and observed normalized intensities of peaks A to F representing the oxymethylene region. 'Emulsion 1 and 2' indicates emulsion processes using non-ionic and anionic surfactants, respectively. Also σ_{SE} values calculated by equation (9) are indicated

Process	Feed ratio, q_0	Observed relative intensities					σ_{SE}
		A	B+C	D	E	F	
Solution	3.00	0.06	0.25	0.10	0.25	0.34	0.73
Emulsion 1	3.00	0.07	0.12	0.10	0.26	0.44	0.88
Emulsion 2	3.00	0.09	0.13	0.10	0.24	0.44	0.87
Solution	1.00	0.20	0.17	0.09	0.23	0.31	0.78
Emulsion 1	1.00	0.21	0.12	0.10	0.22	0.35	0.85
Emulsion 2	1.00	0.23	0.12	0.08	0.23	0.35	0.85
Solution	0.33	0.60	0.03	0.08	0.14	0.16	0.84
Emulsion 1	0.33	0.48	0.03	0.10	0.18	0.22	0.94
Emulsion 2	0.33	0.57	0.04	0.08	0.13	0.18	0.90

various processes only show up in the case of non-azeotropic conditions.

Regardless of the previous spectral assignments it appears that in the case of emulsion products obtained at an initial feed ratio $q_0=3$, the peak B+C decreases whereas F increases as compared with the solution products. In the case of a feed ratio of $q_0=0.33$, the intensity of peak A decreases slightly and that of peak F increases hardly at all as compared with the solution products. These small differences in experimentally determined triad distributions may be caused by a combined effect of on the one hand a deviating tacticity parameter σ_{SE} and on the other a deviating local feed ratio resulting in apparent r values. In order to discriminate between these two effects the σ_{SE} parameter must be estimated.

Unfortunately, the parameter σ_{SE} , which was successfully calculated using predictions of the high- and low-conversion AM kinetics and the experimentally observed intensities of the twin resonance of peak A, cannot be estimated in this way in the case of emulsion copolymers because of the lack of *a priori* knowledge regarding the kinetic model. As a consequence, the tacticity parameter σ_{SE} has to be estimated independent of the type of model. This can be achieved by solving two independent equations and substituting experimental

data according to:

$$\sigma = \frac{1}{1 + (B + C)/2F} \quad (9)$$

This equation is only valid for the Tacx model¹⁷ for Sty-EMA copolymers. It should be realized that this method is less reliable owing to the relatively large errors of measurements. The results are also summarized in Table 6. Comparing the average value of σ_{SE} calculated in this way with the method using the intensity of peak A for copolymers obtained by high-conversion solution processes, it becomes clear that this σ_{SE} (=0.67) is shifted towards a higher value (0.76). This shift may be attributed to increased inaccuracy. Since the area of B + C in the case of $q_0 = 0.33$ cannot be measured accurately, the value of σ_{SE} at this initial feed ratio has not been taken into account in the average σ_{SE} . Comparing the high-conversion solution value ($\sigma_{SE} = 0.76$) with the parameters of products obtained by emulsion processes using non-ionic surfactant ($\sigma_{SE} = 0.87$) and anionic surfactant ($\sigma_{SE} = 0.86$), it is immediately clear that these values are slightly higher. This slight increase of the σ_{SE} value cannot account for the differences observed in the triad fractions. So, the triad distributions (EEE, EES and SES) have to be different in the case of emulsion products. This might be caused by different partition coefficients of the monomers in the phases of the heterogeneous emulsion system.

CONCLUSIONS

The results of the present investigation indicate that the calculation model proposed leads to a reliable prediction of triad distribution in the case of high-conversion solution and even azeotropic emulsion processes. The tacticity parameter ($\sigma_{SE} = 0.67$) of copolymers obtained by high-conversion solution processes did not deviate significantly from that obtained at low conversion. However, the σ_{SE} of emulsion products appeared to be slightly higher. A comparison of the experimentally observed total triad distributions indicates that the distribution is dependent on the polymerization conditions, e.g. solution or emulsion polymerization.

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