

Emulsion Co- and Terpolymerization of Styrene, Methyl Methacrylate, and Methyl Acrylate. I. Experimental Determination and Model Prediction of Composition Drift and Microstructure in Batch Reactions

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SYNOPSIS

In Part I of this series the reactivity ratios of the comonomer pair methyl acrylate–methyl methacrylate were determined with low-conversion bulk polymerizations. It was shown that the binary reactivity ratios of the systems styrene–methyl acrylate, styrene–methyl methacrylate, and methyl acrylate–methyl methacrylate describe composition drift in low-conversion bulk terpolymerizations with these monomers reasonably well. A computer model was developed to simulate the composition drift in emulsion co- and terpolymerizations. The composition drift in two batch emulsion copolymerization systems (styrene–methyl acrylate and methyl acrylate–methyl methacrylate) and one emulsion terpolymerization system (styrene–methyl acrylate–methyl methacrylate) was investigated both experimentally and with the model. Experimental results were compared with model calculations. The copolymer chemical composition distributions (CCD) were determined with gradient polymer elution chromatography (GPEC®). This technique was also used for the first time to obtain information about the extent of composition drift in emulsion terpolymerizations. Cumulative terpolymer compositions were determined with ¹H-NMR as a function of conversion and with this information the three-dimensional CCD was obtained. The composition drift was analyzed with respect to free radical copolymerization kinetics (reactivity ratios) and monomer partitioning. It was shown that in most emulsion copolymerizations the composition drift is mainly determined by the reactivity of the monomers and to a lesser extent by monomer partitioning, except in systems where there is a large difference in water solubility. The model predictions for cumulative terpolymer composition as a function of conversion and the three-dimensional terpolymer CCD showed excellent agreement with the experiments. The GPEC® elution chromatogram of the terpolymer was found to be in accordance with the predicted CCD and the experimentally determined CCD. © 1996 John Wiley & Sons, Inc.

Keywords: emulsion copolymerization • terpolymerization • composition drift • chemical composition distribution • gradient polymer elution chromatography

INTRODUCTION

In the literature not much attention has been paid to emulsion terpolymerizations, and in most cases

no specific model for monomer partitioning was taken into account.^{1–5} For studying a complex matter such as an emulsion terpolymerization, model development is necessary. These models need to take into account at least a proper model for monomer partitioning and an appropriate description of the relation between monomer composition and instantaneous co- or terpolymer composition. Urretabizkaia et al.^{6,7} used an extensive model including both a complete monomer partitioning model and a ki-

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netic model to investigate the emulsion terpolymerization of methyl methacrylate, vinyl acetate, and butyl acrylate. For the purpose of studying the composition drift in emulsion terpolymerization with monomers with low to moderately water-soluble monomers in the present work a computer model was developed: TRISEPS. In this model the terminal model for propagation is applied to describe the correlation between monomer feed composition and instantaneous co- and terpolymer composition. For describing monomer partitioning the simplified equations derived by Maxwell et al.,^{8,9} and by Noël et al.^{10,11} for homo- and copolymerizations and by Schoonbrood et al.¹² for terpolymerizations are used. These are simplified versions of the Morton equation, extended to incorporate more than one monomer by Ugelstad et al.,¹³ for the chemical potential of a monomer in the polymer phase and the Vanzo equation¹⁴ for the chemical potential of a monomer in the aqueous phase. To verify the validity of the model some batch emulsion polymerizations are carried out, the results of which are compared to the model predictions. The monomers used are styrene (S), methyl methacrylate (MMA), and methyl acrylate (MA), because these monomers have a widely differing reactivity in co- and terpolymerization and a different water solubility, which gives rise to a relatively strong composition drift. The emulsion copolymerizations investigated are S-MA and MA-MMA and the emulsion terpolymerization of these monomers. The applicability of the simplified monomer partitioning equations in the systems MA-MMA and S-MMA-MA has been validated by Schoonbrood et al.,¹² in the system S-MMA by Aerdts et al.¹⁵ and in the system S-MA by Van Dorremale et al.¹⁶ In Part II of this series¹⁷ the model is actually used to calculate an optimal addition profile, so that the strong composition drift can be controlled in semi-continuous reactions.

Reactivity Ratios

The reactivity ratios of the systems S-MA¹⁸ and S-MMA¹⁹ are well-known from the literature. The reactivity ratios of the system MA-MMA will be determined with low-conversion bulk polymerizations. The reactivity ratios of the system S-MMA-MA are assumed to be similar to the binary reactivity ratios of the three pertaining comonomer pairs, i.e., the terminal model is assumed to be valid for the terpolymerization as well. Low-conversion bulk terpolymerizations will be performed to check whether the binary reactivity ratios describe the terpolymer composition acceptably.

Co- and Terpolymer Analysis

A description will be given of the analytic technique of Gradient Polymer Elution Chromatography, GPEC® (formerly gradient High-Performance Liquid Chromatography). GPEC® will be used to determine the chemical composition distribution (CCD) of the emulsion copolymers of S and MA and of MA and MMA. The composition drift occurring in the systems S-MA and MA-MMA will also be investigated with the model TRISEPS and will be discussed in the light of the reactivity ratios and the monomer partitioning. The composition drift occurring in the batch emulsion terpolymerization of S, MMA, and MA will be investigated experimentally with ¹H-NMR and GPEC®. With ¹H-NMR the partial conversion of the monomers will be determined and compared with model predictions. From the partial conversions the three-dimensional CCD of the terpolymer will be determined, and compared with the model prediction of TRISEPS and to the GPEC® elution chromatogram. This is the first time that the technique of GPEC® will be applied to true terpolymers: to determine the homogeneity/heterogeneity of batch emulsion terpolymers of S, MMA, and MA in this part, and of semi-continuous emulsion terpolymers of the same monomers in Part II of this series.¹⁷

EXPERIMENTAL

Low-Conversion Bulk Polymerizations

The reactivity ratios (according to the terminal model) of the comonomer pair methyl acrylate-methyl methacrylate (MA-MMA) were determined in bulk at 50°C. The reactivity ratios were obtained by fitting the copolymer composition equation [eq. (1)] to data obtained by analyzing composition (monomer feed composition and corresponding copolymer composition) of copolymers that have been sampled at low conversion:

$$F_i = \frac{r_i f_i^2 + f_i f_j}{r_i f_i^2 + 2f_i f_j + r_j f_j^2} \quad (1)$$

where f_i is the molar fraction of monomer i in the monomer mixture and F_i the molar fraction of monomer i in the copolymer.

The monomers were weighed into a jacketed glass reactor (200 cm³) and purged with nitrogen. The initiator was 0.5 w% of α, α' -azobisisobutyronitrile. The conversion was monitored by withdrawing samples and adding them to excess nonsolvent (n -

heptane). As soon as some precipitate was observed, the reaction mixtures were short-stopped with hydroquinone. Conversion was always lower than 5%. The polymer was separated from the monomers by subsequent cycles of pouring into excess nonsolvent, decanting, and redissolving in a solvent. After drying under reduced pressure at 50°C, the polymer composition was analyzed with $^1\text{H-NMR}$ with a Bruker AM 400 spectrometer (400 MHz) at 298 K with CDCl_3 as a solvent. The reactivity ratios were determined with two numerical techniques: (1) a simple noniterative nonlinear least-squares fitting procedure (NINLLS),²⁰ and (2) the error-in-variables-model (EVM).²¹ In both methods constant relative errors were assumed. Monomer compositions used to determine the reactivity ratios were varied over a wide range, although it is realized that this may not be the best statistical method for *parameter estimation* according to Tidwell and Mortimer,²² which is by replicating experiments at two well-chosen compositions. The low-conversion copolymers thus obtained were also used as standards for GPEC®.

It was also checked whether the binary reactivity ratios of the monomer pairs S-MA, S-MMA, and MA-MMA can be used to describe the composition of terpolymers of these monomers. For a terpolymerization eq. (2) should be used:²³

$$F_i = \frac{1}{1 + \sum_{\substack{j,k=1 \\ j \neq i, k \neq i}}^3 \frac{f_j(f_i r_{ik} r_{kj} + f_j r_{ki} + f_k r_{ij} r_{ki}) \times (f_i r_{jk} + f_j r_{jk} r_{ji} + f_k r_{ji})}{f_i(f_i r_{jk} r_{kj} + f_j r_{jk} r_{ki} + f_k r_{ji} r_{kj}) \times (f_j r_{ik} + f_i r_{ij} r_{ik} + f_k r_{ij})}} \quad (2)$$

where i, j , and k represent monomers 1, 2, 3. Note that there are now three pairs of reactivity ratios, each pair being the same as used for each comonomer pair ($i-j$, $i-k$, $j-k$).

Gradient Polymer Elution Chromatography (GPEC®)

To analyze the chemical composition distribution (CCD) of the co- and terpolymers GPEC® was applied. This is a distinct form of liquid chromatography that is used to separate copolymers with varying chemical composition by eluting with a solvent-nonsolvent eluent mixture with a time-dependent gradient in solvent strength. A sample of a co- or terpolymer is dissolved in a good solvent (a good

solvent for all polymer chains in the sample). This is injected in the eluent, which has a high content of nonsolvent. This results in separation into a very dilute phase, which is taken up by the eluent, and in a polymer-rich phase, which adheres to the column. The composition of the eluent is gradually changed and the content of the good solvent increased (thus gradient elution). As the eluent contains more solvent, the separation process is reversed and more and more chains are taken up by the eluent and eluted through the column, until finally all chains have been redissolved and eluted. The chains are eluted at varying elution times corresponding to the eluent composition in which they are soluble, which is directly linked to their chemical composition. The polymer chains are thus separated according to chemical composition. The influence of molar mass on the solubility of a chain in a certain eluent composition is normally negligible at the relatively high molar masses obtained in emulsion polymerization.

The procedure for the separation of the polymers in this work has been described elsewhere.²⁴⁻²⁶ The following columns have been used: a silica column (Zorbax Sil precolumn, 4.6 mm \times 15 cm) or a C18 precolumn insert (Nova-Pak® Guard Pak, 3.9 mm \times 1 cm, Waters) without another column. The detector used for the analysis of the S-MA copolymers was a flame ionization detector with a moving wire (MWFID) (Tracor 945 Universal FID Detector). The eluent with polymer dissolved in it is continuously sprayed onto a wire of silica. This wire is applied onto a wheel that is turning, so that the wire plus eluent pass through a heated chamber, where the eluent is evaporated. The wire then passes through the FID detector and the polymer is analyzed. This detector has been described in more detail elsewhere.²⁵ For the other polymers a different detector was used: an evaporative light-scattering detector (ELSD) (model 750/14, Applied Chromatography Systems Ltd). In this detector the eluent is nebulized by a nitrogen flow. This flow is then heated and the eluent evaporates. An aerosol is formed of the nonvolatiles (polymer) and this is detected with light-scattering. It is basically a concentration dependent detector and the possible dependence of the response on chemical composition was not taken into account here. This means that the presented CCDs are only approximations of the real CCDs, although the general shape of the CCDs is reliable. The units of the detector response (mV) are not given in the graphic representations of the CCDs. In Table I details are given for the analysis of the co- and terpolymers here and in Part II.¹⁷

Table I. Column Type, Elution Gradient (Volume Fractions, ϕ) and Detector Used for the Analysis of the Various Co- and Terpolymers^a

Co-/Terpolymer	Column	Elution Gradient, ϕ (%)	Detector
S-MA	SI	80/20 HPT/THF-100 THF	MWFI
MA-MMA	C18GP	100 H ₂ O-100 ACN-100 THF	ELSD
S-MMA-MA	C18GP	100 H ₂ O-100 ACN-100 THF	ELSD

^a SI = silica, C18 = C18 Nova-Pak, C18GP = C18 Nova-Pak Guard Pak, ACN = acetonitrile, HPT = *n*-heptane, THF = tetrahydrofuran. Flow is 1 cm³/min.

Batch Emulsion Copolymerizations

Two batch emulsion copolymerizations (S-MA, MA-MMA) were investigated theoretically by using TRISEPS and experimentally with ¹H-NMR with CDCl₃ as solvent. All monomers (p.a.) were distilled under reduced pressure before use. The monomer to water ratio (M/W) was 0.2 g/g. All reactions were carried out at 50°C with the following recipes (per 100 g of water): sodium dodecyl sulfate (SDS, emulsifier, 99%) 0.11 g (unless stated otherwise); sodium persulfate (SPS, initiator, p.a.) ca. 0.03 g; sodium bicarbonate (SB, buffer, p.a.) ca. 0.01 g; *n*-dodecyl mercaptan (NDM, chain transfer agent, p.a.) 1 w% of monomer (unless stated otherwise).

RESULTS AND DISCUSSION

Reactivity Ratios of MA-MMA, S-MA, and S-MMA

The resulting reactivity ratios for the system MA-MMA are displayed in Table II. The reactivity ratios determined with the two analytical methods are in agreement with each other. The values for r_{MMA} are in agreement with the value found by Zubov et al.²⁷ ($r_{\text{MMA}} = 2.23$), but the values for r_{MA} do not correspond to the one found by Zubov et al. ($r_{\text{MA}} = 0.36$). In Figure 1 the 95% confidence region of the MA-MMA reactivity ratios determined with the EVM method is depicted. In Figure 2 the experimental data and the fitted curves with the NINLLS method are depicted, together with the copolymer compo-

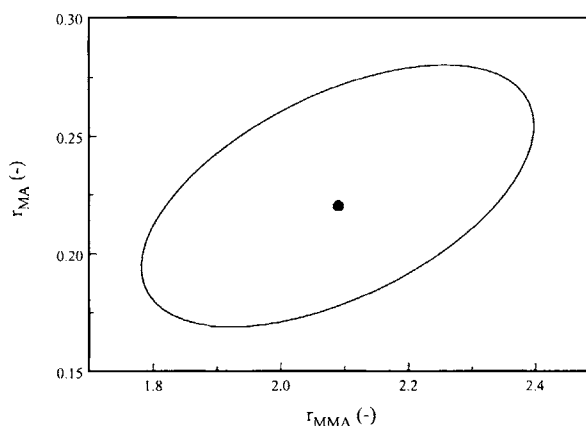
sition curves for the pair S-MA, calculated with the reactivity ratios determined by Van Doremale et al.¹⁸ $r_{\text{S}} = 0.73 \pm 0.05$, $r_{\text{MA}} = 0.19 \pm 0.05$, and for the pair S-MMA, calculated with $r_{\text{S}} = 0.48 \pm 0.03$, $r_{\text{MMA}} = 0.42 \pm 0.09$, determined by Maxwell et al.¹⁹ Although there seems to be a discrepancy between the reactivity ratios determined with both methods for MA-MMA, the curves are almost identical [see Fig. (2)]. There are binary azeotropes for S-MA at $f_{\text{MA}} = 0.25$ and for S-MMA at $f_{\text{MMA}} = 0.47$.

Application of Binary Reactivity Ratios to the Terpolymerization System S-MMA-MA

It has been shown in literature that the terpolymer composition in many termonomer systems can be adequately described with the terminal model [eq. (2)], e.g., for the systems methacrylonitrile-styrene- α -methyl styrene²⁸ and styrene-methyl methacrylate-benzyl acrylate.²⁹ Kobayashi³⁰ used the terminal model to describe the diad concentrations of methyl methacrylate in the terpolymerization with styrene and butyl acrylate. Six reactivity ratios are needed for describing a terpolymerization with the terminal

Table II. Reactivity Ratios of the Bulk Copolymerization of MA and MMA at 50°C Determined with Two Different Analytical Methods

	NINLLS	EVM
r_{MA}	0.26 ± 0.06	0.22 ± 0.05
r_{MMA}	2.49 ± 0.7	2.09 ± 0.3

**Figure 1.** 95% confidence region of the reactivity ratios, analyzed with the EVM method, of the bulk copolymerization of MA and MMA at 50°C.

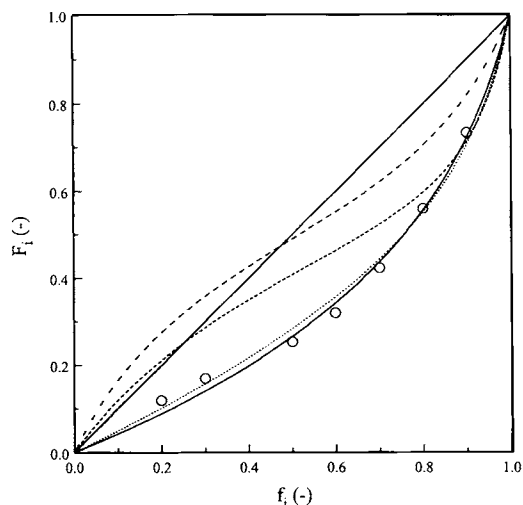


Figure 2. Molar fraction of monomer i in the copolymer (F_i) versus molar fraction in the feed (f_i) for MA-MMA (F_{MA}, f_{MA} ○). Calculated lines: MA-MMA (F_{MA}, f_{MA} —with $r_{MA}/r_{MMA} = 0.26/2.49$ and F_{MA}, f_{MA} ··· with $r_{MA}/r_{MMA} = 0.22/2.09$), S-MA (F_{MA}, f_{MA} --- with $r_{MA}/r_S = 0.19/0.73$) and S-MMA (F_{MMA}, f_{MMA} - - - with $r_{MMA}/r_S = 0.42/0.48$).

model [see eq. (2)]. If the terminal model is really valid, these reactivity ratios are exactly equal to the six reactivity ratios that are needed to describe the copolymerizations of each of the three pairs. To test this for the system S-MA-MMA, low-conversion bulk experiments were performed to obtain composition data without the interference of composition drift. The procedure was as described above for the copolymerizations. The results are shown in Ta-

ble III. The composition data were recalculated with eq. (2) with the reactivity ratios for MA-MMA as obtained with the NINLLS method and for S-MA and S-MMA as given in the literature (see above).

As can be seen, there is reasonable agreement between experimental and predicted values, except for very low f_{MA} /high f_S and for high f_{MA} /low f_S . There is no ternary azeotrope. Terpolymer composition values calculated with the reactivity ratios of the pair MA-MMA as determined with the EVM method, are not significantly different from those calculated with the reactivity ratios obtained with the nonlinear least-squares method. These binary reactivity ratios will be further applied to describe the emulsion terpolymerization of these monomers.

The Emulsion Co- and Terpolymerization Simulation Model TRISEPS

For the purpose of calculating composition drift in emulsion co- and terpolymerizations and comparing these calculations with experimental data, a computer model was developed called TRISEPS (TRI-monomeric Seeded Emulsion Polymerization Simulation). It is partly based on the computer model SIEMCO developed by Van Doremale.³¹ The model can predict the course of composition drift in seeded batch and semi-continuous emulsion co- and terpolymerizations of low to moderately water-soluble monomers. It can calculate the resulting two-dimensional CCDs of copolymers and three-dimensional CCDs of terpolymers by applying the Stock-

Table III. Molar Fraction in the Feed (f_i) and Experimental/Calculated Molar Fraction in the Terpolymer ($F_{i,exp}/F_{i,calc}$) for Low-Conversion Bulk Terpolymers of S-MA-MMA

f_S	f_{MMA}	f_{MA}	$F_{S,exp}$	$F_{S,calc}$	$F_{MMA,exp}$	$F_{MMA,calc}$	$F_{MA,exp}$	$F_{MA,calc}$
0.10	0.10	0.80	0.27	0.26	0.28	0.19	0.45	0.55
0.10	0.20	0.70	0.24	0.24	0.38	0.33	0.38	0.44
0.10	0.30	0.60	0.21	0.23	0.45	0.43	0.33	0.34
0.20	0.10	0.70	0.44	0.37	0.18	0.16	0.39	0.47
0.20	0.20	0.60	0.37	0.35	0.39	0.28	0.24	0.37
0.20	0.30	0.50	0.33	0.34	0.39	0.38	0.28	0.28
0.20	0.50	0.30	0.29	0.32	0.60	0.53	0.11	0.15
0.30	0.20	0.50	0.42	0.43	0.27	0.26	0.31	0.31
0.30	0.30	0.40	0.40	0.42	0.39	0.35	0.20	0.23
0.30	0.40	0.30	0.41	0.40	0.44	0.43	0.15	0.16
0.30	0.50	0.20	0.39	0.39	0.54	0.50	0.07	0.10
0.40	0.30	0.30	0.48	0.48	0.34	0.34	0.18	0.18
0.40	0.40	0.20	0.50	0.47	0.36	0.42	0.14	0.11
0.50	0.20	0.30	0.56	0.55	0.24	0.25	0.21	0.21
0.50	0.40	0.10	0.50	0.52	0.49	0.42	0.01	0.06
0.50	0.30	0.20	0.52	0.53	0.43	0.34	0.06	0.13

mayer equation³² for the statistical broadening of the composition distribution. It can also calculate optimal addition profiles for semi-continuous reactions (see Part II¹⁷). It cannot predict particle nucleation, the overall rate of polymerization or molecular weight distributions.

The basic assumptions are that:

1. The composition of the co- and terpolymers can be described with the terminal model.
2. The monomer partitioning of the low to moderately water-soluble monomers can be described with the simplified equations published recently⁸⁻¹² (see above).
3. For the statistical broadening of the chemical composition distribution a uniform kinetic chain length can be assumed (e.g., 1000), because normally in emulsion polymerizations the molecular weights are very high. A pseudo-copolymer approach was used for the statistical broadening of the terpolymers by taking the analytical solution for copolymers, because an analytic solution of the Stockmayer distribution for terpolymers is still lacking. This is done as follows. The total range of compositions is divided into 10,000 discrete compositions. For each of these compositions the chemical broadening is calculated by keeping the fraction of one monomer constant and by applying the Stockmayer expression to calculate the broadening varying the other two monomer fractions. For each discrete composition this procedure is repeated twice keeping either of the two other monomer fractions constant. It should be noted that statistical broadening only gives a small contribution to the width of the peaks of the CCD compared with the broadening due to composition drift and—in CCDs measured with GPEC® or other chromatographic methods—the chromatographic broadening.

The developments of the individual monomer concentrations, co- and terpolymer composition and the CCD as a function of conversion are obtained by dividing the whole conversion range in small conversion steps, during which it is assumed that composition drift is negligible. The calculations for each conversion step are based on a combination of the monomer partitioning equations and the mass balances of each monomer in the two or three phases, which are changed according to the individual, relative monomer consumption rates. The solution of the set of equations thus obtained is found with the

Simplex-method. The input parameters include the binary reactivity ratios according to the terminal model, the solubilities in the aqueous phase, the swellabilities of the polymer particles by each monomer, the densities of the monomers and the polymer and the total amount of seed latex polymer.

For the calculations used here and in Part II,¹⁷ the most important input parameters are (at 50°C):

1. The reactivity ratios: $r_S = 0.73$ and $r_{MA} = 0.19$; $r_S = 0.48$ and $r_{MMA} = 0.42$; $r_{MA} = 0.26$ and $r_{MMA} = 2.49$; $r_S = 0.95$ and $r_{BA} = 0.18$;³³ $r_{MA} = 1$ and $r_{BA} = 1$ (BA = butyl acrylate).³¹
2. The solubilities in the aqueous phase: $C_{Saq,s,h} = 0.0043$ mol/dm³;³⁴ $C_{MMAaq,s,h} = 0.15$ mol/dm³;³⁴ $C_{MAaq,s,h} = 0.6$ mol/dm³;^{31,6} $C_{BAaq,s,h} = 0.01$ mol/dm³.³⁵
3. The swellability of the polymer particles by each monomer: $C_{Sp,s,h} = 5.8$ mol/dm³;³ $C_{MMAp,s,h} = 6.3$ mol/dm³;³ $C_{MAp,s,h} = 6.6$ mol/dm³;³ $C_{BAP,s,h} = 5.8$ mol/dm³.³ These values are good estimates for the latices used, and are based on average values. From a sensitivity analysis with TRISEPS (not shown) it was concluded that the values of the polymer swellabilities could be changed within a reasonable range without having a noticeable effect on composition drift.

BATCH EMULSION COPOLYMERIZATIONS

Two batch emulsion copolymerizations have been investigated experimentally and with the model TRISEPS: S-MA and MA-MMA. The emulsion copolymerization of the third pair, S-MMA, has been studied extensively in literature, e.g., by Forcada and Asua³⁶ who observed limited composition drift, mainly at high or low overall fractions of either monomer. The limited composition drift is the result of the fact that the reactivity ratios of both monomers are equal and relatively close to unity, and of the fact that their water solubilities are quite low in comparison to that of MA for instance.

Styrene-Methyl Acrylate

In this system the more reactive monomer (S) is also the less water-soluble monomer, which results in considerable composition drift, as will be shown. Three batch reactions were performed with M/W = 0.2 g/g, but with varying average compositions: F_{MA} (average fraction of S in copolymer) = 0.20, 0.50, and 0.75. The amount of SDS was 0.33 g per

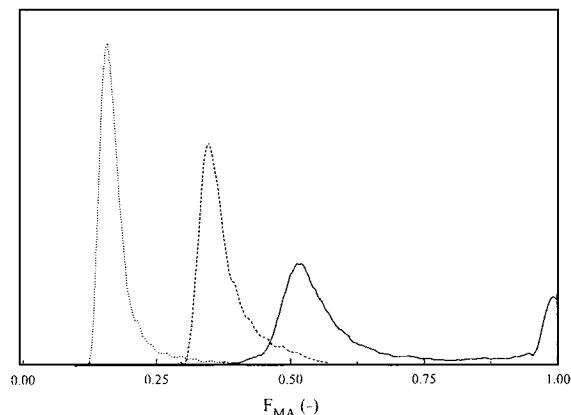


Figure 3. Chemical composition distributions of S-MA batch emulsion copolymers with $M/W = 0.2$ and $F_{MA} = (\cdots) 0.20$, $(---) 0.50$, and $(—) 0.75$, determined with GPEC®/MWFID. (The y-axis label is not shown, see text.)

100 g of water. Figure 3 shows the CCDs of these polymers as determined with GPEC®/MWFID.

It can be clearly seen that the broadness of the CCD depends strongly on the overall composition. The higher F_{MA} the broader the CCD, which means that composition drift is strongest in the case of the highest F_{MA} . The composition drift is so strong that S is depleted long before MA, so in the last stage of the reaction MA homopolymerizes, which leads to a bimodal distribution. This can be explained qualitatively with the monomer partitioning data and reactivity ratios. The monomer partitioning behavior of this system in interval 2, as determined by Van Doremale et al.,¹⁶ is such that the composition drift due to the difference between the monomer ratio in the particles and the overall monomer ratio is not strongly dependent on the overall fraction of MA. This can be shown with mass balance calculations in combination with monomer partitioning data,¹⁶ which experimentally verified the equations given in Reference 9. The relatively strong composition drift with high fractions of MA must result primarily from the copolymerization kinetics as described by the reactivity ratios ($r_S = 0.73$ and $r_{MA} = 0.19$). As can be seen in Figure 2, the higher f_{MA} /lower f_S , the higher the difference between F_{MA} and f_{MA} and the stronger the composition drift. Figure 4 shows the results of some calculations with TRISEPS of composition drift in batch S-MA emulsion copolymerizations with $F_{MA} = 0.75/F_S = 0.25$.

In Figure 4(a) the monomer to water ratio was varied. An M/W of 100 can be compared to conditions in a bulk copolymerization. Some homopolymer of MA is formed when S is depleted at a

conversion of 0.84. Decreasing the M/W leads to a stronger composition drift, as more MA is retained in the aqueous phase. The point at which S is depleted is reached at a lower conversion: in all cases a bimodal CCD is the result.³¹ It can be seen that there is only a large effect of monomer partitioning on composition drift if the M/W is varied widely. In Figure 4(b) the saturation concentration of MA in the aqueous phase ($C_{MAaq,s,h}$) was varied and given fictitious values, while M/W was kept constant. It can be seen that decreasing $C_{MAaq,s,h}$ by a factor of 10 at $M/W = 0.2$ does not have a large influence on the extent of composition drift (the effect is dependent on M/W and large at very low values of M/W). Both figures indicate that composition drift is mainly determined by the reactivity ratios, and that monomer partitioning in this system with the mod-

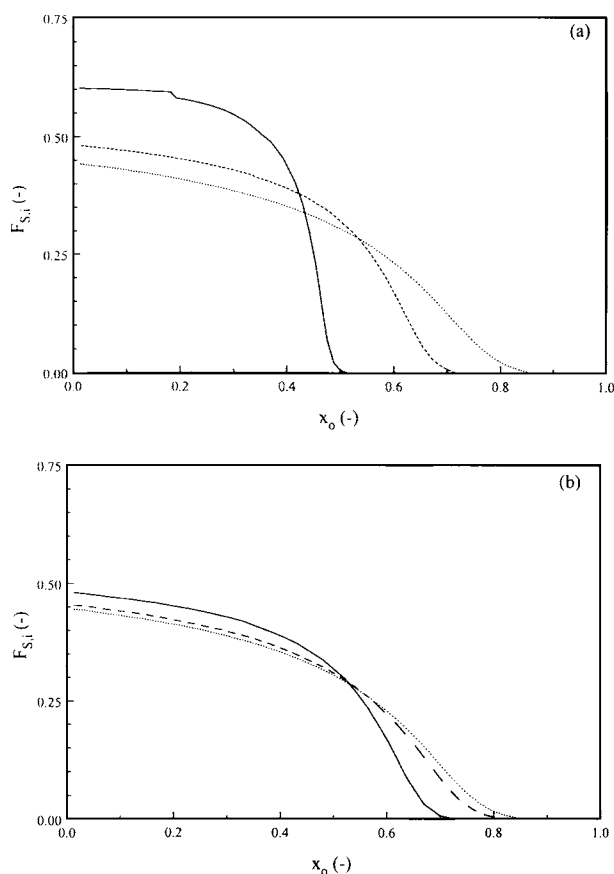


Figure 4. Instantaneous fraction of S ($F_{i,S}$) in S-MA batch emulsion copolymerizations ($F_S = 0.25$) versus overall conversion (x_0) as calculated with TRISEPS: (a) varying M/W : $(—) 0.05$, $(---) 0.2$, $(\cdots) 100$, and (b) varying $C_{MAaq,s,h}$: $(—) 0.6 \text{ mol/dm}^3$, $(---) 0.2$, and $(\cdots) 0.06$ ($M/W = 0.2$).

erately water-soluble MA has a significant effect only at a M/W that is far below values commonly used in practical applications of emulsion polymerization.

Methyl Acrylate–Methyl Methacrylate

The composition drift in the emulsion copolymerization of MMA and MA was studied and compared with that in the system S–MA. The simplified partitioning equations have been shown to hold also for this monomer system.¹² In Figure 2 the copolymer composition curves of both systems S–MA and MA–MMA are depicted. It can be seen that at high fractions of MA the extent of composition drift is the same for both systems, but at high fractions of MMA or S, composition drift in the MA–MMA system is stronger; there is no azeotrope as there is in the S–MA system. This seems to contradict the fact that in the copolymerization S–MMA, S is slightly more reactive. MMA being less water-soluble than MA increases the extent of composition drift in MMA–MA even more, although the difference in water solubility is not as large as in the system S–MA.

In Figure 5 the CCDs of three MA–MMA emulsion copolymerizations with M/W = 0.2 and $F_{MA} = 0.25, 0.50$, and 0.75 are shown. The composition drift is stronger than in the S–MA system and in two cases bimodal distributions can be seen. This means that the effect of a smaller difference between the water solubilities of MA and MMA than between MA and S is more than counteracted by the effect of the reactivity ratios.

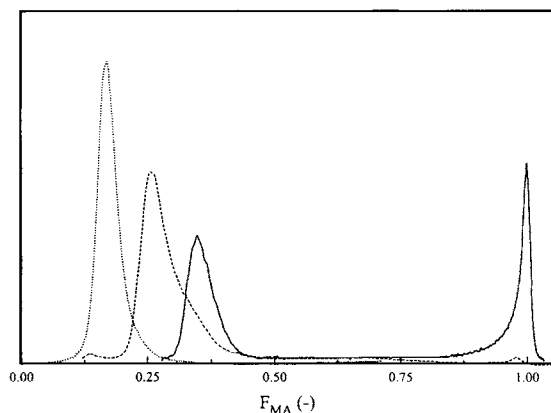


Figure 5. The chemical composition distributions of three MA–MMA batch emulsion copolymers with M/W = 0.2 and with $F_{MA} = (\cdots) 0.25$, $(---) 0.50$, and $(—) 0.75$, experimentally determined with GPEC®/ELSD. (The y-axis label is not shown, see text.)

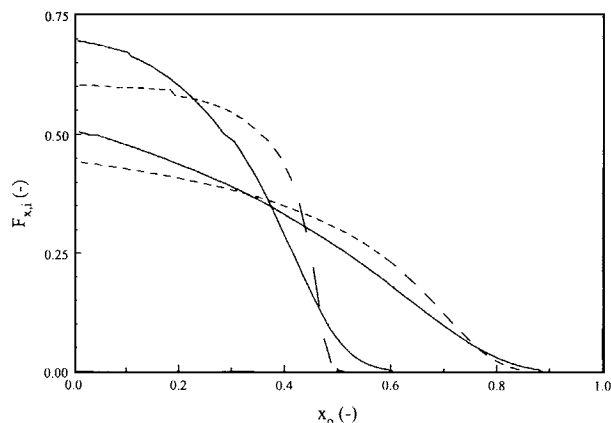


Figure 6. The calculated instantaneous fractions ($F_{i,x}$) of (—) MMA and (---) S in their emulsion copolymerizations with MA, with F_{MMA} and $F_S = 0.25$, and with varying M/W: 0.05 (two lines with highest intercepts) and 100 (two lines with lowest intercepts). Calculations with TRISEPS.

In Figure 6 the instantaneous fractions of MMA and S (calculated with TRISEPS) in their emulsion copolymerizations with MA with various values of M/W, are given. It can be seen that in the first part MMA is indeed more reactive in its emulsion copolymerization with MA for both values of M/W. As MMA is being consumed relatively quicker than S, $F_{i,MMA}$ ($F_{i,x}$ being the instantaneous fraction of monomer x in the polymer) drops quicker than $F_{i,S}$. At higher conversions, $F_{i,S}$ drops below $F_{i,MMA}$ again. This is due to the fact that in interval 3 the aqueous phase is closer to saturation than the polymer phase, i.e., relatively more monomer resides in the aqueous phase. Because MMA is more water-soluble than S, this effect is more significant for MMA, and the concentration of MMA in the particles is relatively lower than that of S, so that its consumption rate becomes lower than that of S.

Batch Emulsion Terpolymerizations of S–MMA–MA

In this part of the series the composition drift occurring in the batch emulsion terpolymerization of S, MMA and MA will be extensively studied with the experimental techniques ¹H-NMR and GPEC®/ELSD. Three overall monomer compositions are used: $F_S, F_{MMA}, F_{MA} = (0.2, 0.5, 0.3)$, $(0.33, 0.33, 0.33)$, and $(0.2, 0.3, 0.5)$. These have increasing fractions of MA. Emulsion copolymerizations of S and MA and of MMA and MA, as discussed above, show a strong composition drift that becomes stron-

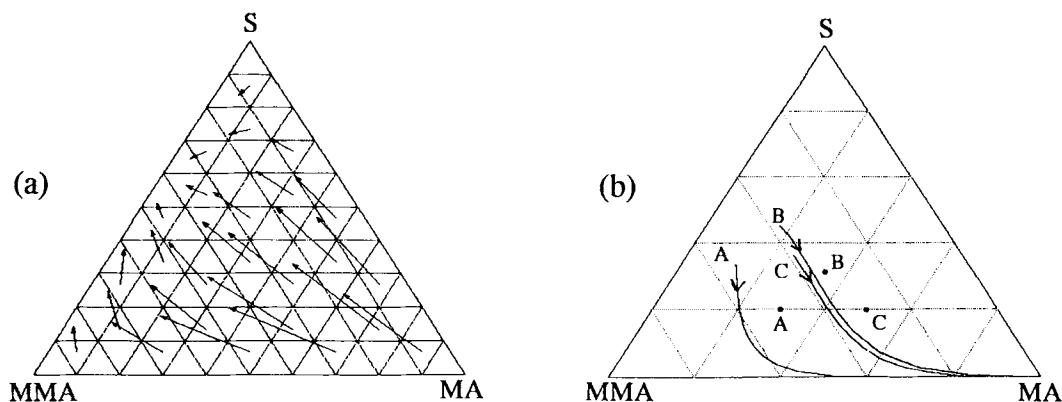


Figure 7. (a) Triangular composition diagrams representing the initial composition drift occurring in S-MMA-MA batch emulsion terpolymerizations with $M/W = 0.2$, and (b) the course of the composition drift in three batch emulsion terpolymerizations with varying overall compositions: $[0.2, 0.5, 0.3]$ (A), $[0.33, 0.33, 0.33]$ (B), and $[0.2, 0.3, 0.5]$ (C). The lines represent the instantaneous compositions of the terpolymers successively formed in the course of the reactions.

ger when the overall fraction of MA is increased. This is expected to be the case also for the present terpolymers.

In Figure 7 two triangular terpolymer composition diagrams, calculated with TRISEPS, are shown. In Figure 7(a) the initial composition drift in the batch emulsion terpolymerization of S, MMA, and MA with $M/W = 0.2$ is shown. The arrows represent the overall monomer composition (start of arrow) and the corresponding initial terpolymer composition (end of arrow). It can be seen that there is strong composition drift. In the second diagram the course of the composition drift in three batch emulsion terpolymerizations is shown. The lines represent the

instantaneous compositions of the terpolymers as they are successively formed in the course of the reactions. As can be seen, they all end at pure MA [poly(MA)]. In Figure 7(b) it can be seen that S is the most reactive monomer and that eventually a copolymer MA-MMA is formed.

To obtain more details (as a function of conversion) these reactions have also been studied experimentally. In Figure 8 the partial conversions of the monomers are plotted versus overall conversion for the overall composition $(0.33, 0.33, 0.33)$ and the monomer to water ratios $M/W = 0.2$ and 0.05 . The data were obtained with gravimetry and $^1\text{H-NMR}$, the lines are calculated with TRISEPS. It can be

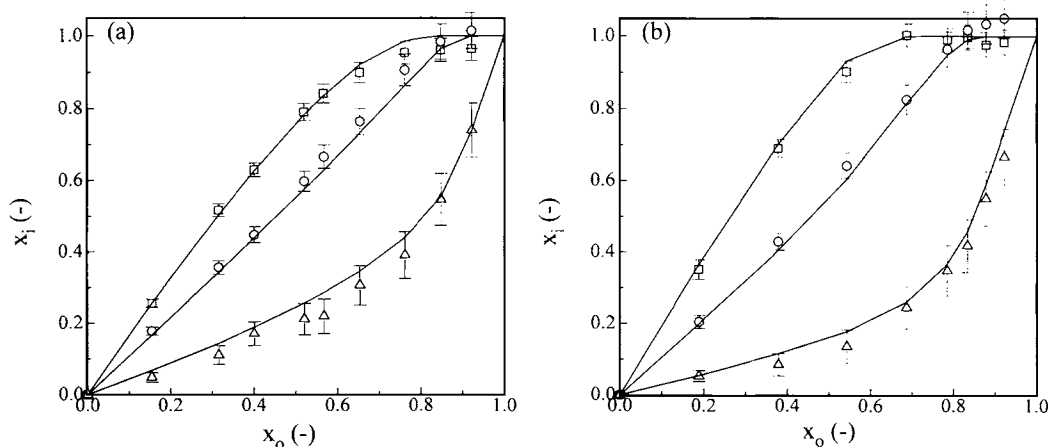


Figure 8. The partial conversions (x_i) of (\square) S, (\circ) MMA, and (\triangle) MA of the batch emulsion terpolymerization of S-MMA-MA versus overall conversion (x_o) with $F_S, F_{\text{MMA}}, F_{\text{MA}} = (0.33, 0.33, 0.33)$ and $M/W =$ (a) 0.2 and (b) 0.05 . The lines are calculated with TRISEPS.

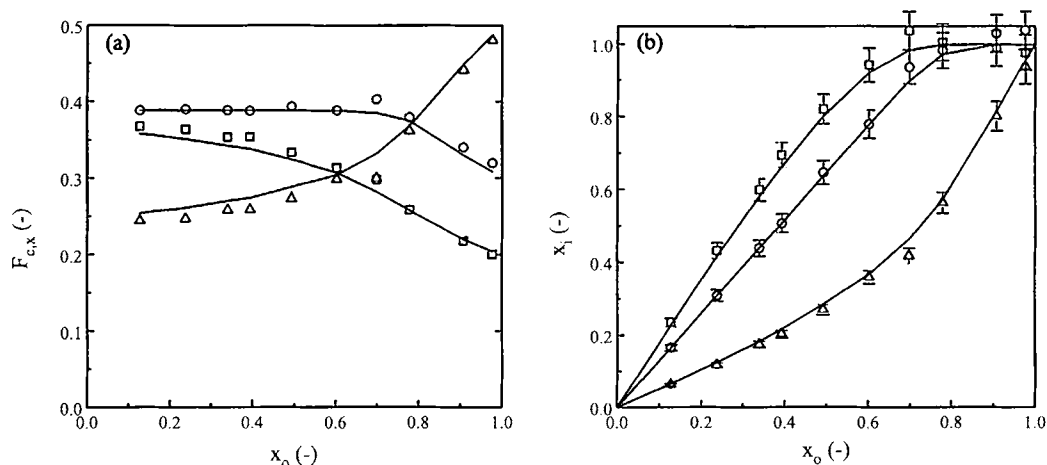


Figure 9. (a) Cumulative fractions ($F_{c,x}$), determined with $^1\text{H-NMR}$, and (b) partial conversions (x_i) of (\square) S, (\circ) MMA, and (\triangle) MA of batch terpolymer (0.2, 0.3, 0.5) with $M/W = 0.2$, versus overall conversion. The lines are calculations with TRISEPS.

seen that indeed MA is the least reactive monomer, and, in these cases, S the most reactive. This monomer is depleted first, and a copolymer of MA and MMA is formed until all MMA is depleted as well, after which the remaining MA polymerizes. It is also evident that the lower M/W the stronger the composition drift, and the lower the conversion of MA and the lower the overall conversion at which S is depleted. The same behavior was observed in the

case of the overall composition (0.2, 0.5, 0.3). (not shown)

In Figure 9 the cumulative fractions and the partial conversions of each monomer in the terpolymer (0.2, 0.3, 0.5) with $M/W = 0.2$ are plotted versus the overall conversion. The composition drift behavior is the same again. That composition drift is considerable, can also be seen clearly in Figure 10. In this plot are displayed the chemical composition distri-

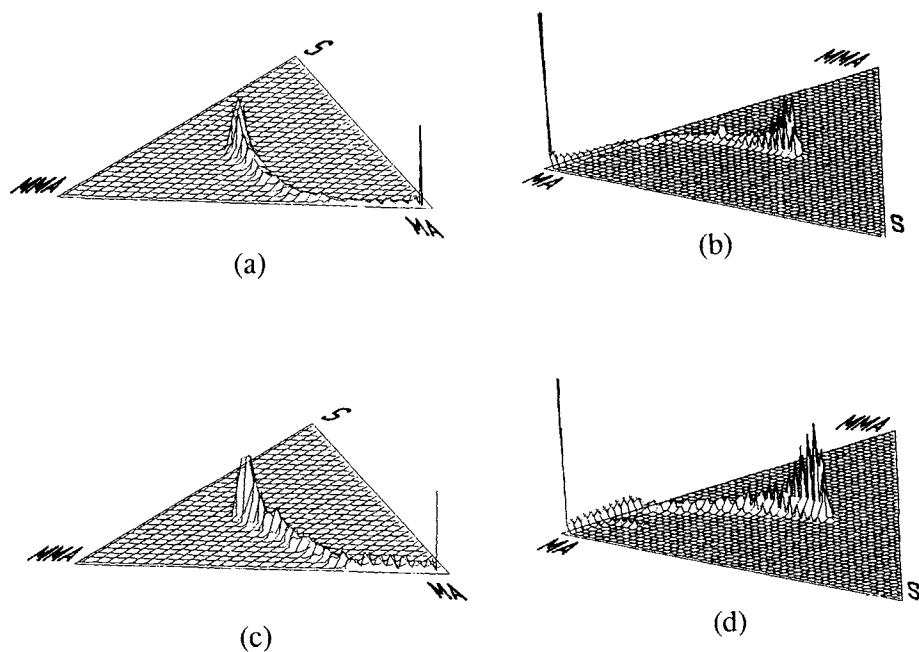


Figure 10. (a) and (b) The chemical composition distribution of the batch terpolymer (0.2, 0.3, 0.5) as calculated with TRISEPS, (c) and (d) as calculated from the experimental data in Figure 9(b).

bution (CCD) of this terpolymer as calculated with TRISEPS [Figs. 10(a) and (b), from two different perspectives] and the CCDs calculated from the experimental data in Figure 9(b) [Figs. 10(c) and (d), from the same two perspectives].

The calculations for Figures 10(c) and (d) are based on the derivatives of the cumulative fractions of the monomers versus the overall conversion. The derivative is a measure for the instantaneous terpolymer composition. The following should be noted with respect to this way of determining the CCD:

1. This method can only be used reliably if no other polymerization mechanism is taking place concurrently. In that case a change in cumulative composition can be attributed completely to a change in conversion and/or instantaneous composition due to the one polymerization taking place. If two polymerization mechanisms are taking place concurrently (for instance, within the polymer particles and in the aqueous phase) a change in cumulative composition is governed by both mechanisms. Without further information it is then impossible to calculate the instantaneous composition pertaining to either mechanism. In such cases a chromatographic method is needed, which can *separate* the co- or terpolymers formed according to either mechanism.
2. The statistical broadening cannot be determined in this way, but under normal conditions this is not a major disadvantage.
3. The disadvantage of chromatographic methods, namely chromatographic broadening, does naturally not apply.

In the present case it means that the CCDs of Figure 10(c) and (d) are only meaningful if it can be assumed that aqueous phase polymerization can be neglected. The only possibility for aqueous phase polymerization would be the propagation of persulfate-derived oligomers in the aqueous phase. However, one can safely say that the maximum degree of polymerization of these oligomers is so low that this can hardly contribute to the formation of polymer.^{37,38}

For the calculations of these CCDs a simplification of the Stockmayer expression was applied with a uniform kinetic chain length of 1000, as described above (the Stockmayer distribution was also applied to the experimentally determined CCD). As can be seen, there is quite good agreement between the calculated CCD and the measured CCD.

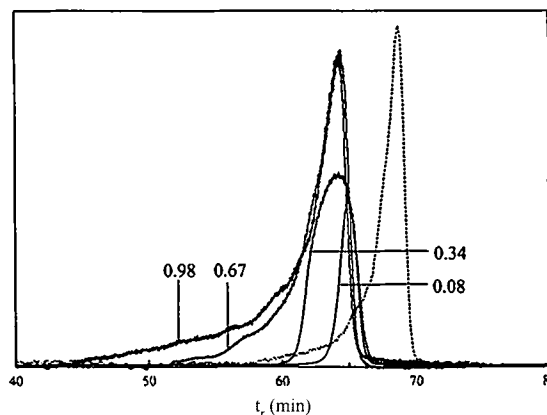


Figure 11. Elution chromatogram, determined with GPEC®, of the S-MMA-MA batch emulsion terpolymer (—, 0.2, 0.3, 0.5), at various stages of conversions (indicated in the figure) and of batch terpolymer (---, 0.33, 0.33, 0.33) at high conversion, determined with GPEC®/ELSD. (The y-axis label is not shown, see text.)

To validate further the calculated CCDs and those obtained from calculations with ¹H-NMR data, GPEC®/ELSD was applied to the terpolymers. In Figure 11 the elution chromatograms are displayed of samples of the batch terpolymer (0.2, 0.3, 0.5), taken at various stages of conversion and of batch terpolymer (0.33, 0.33, 0.33) at high conversion. Note that an elution chromatogram is not a chemical composition distribution. It is not possible (yet) to link retention time to terpolymer composition, because one elution run does not provide enough information. Terpolymers with different compositions can in principle elute at the same time. A second elution run under different conditions (different solvents, etc.), or even better, an elution after which cross-fractionation can be performed, is needed to determine the CCD of a terpolymer.

However, a fortunate aspect of the monomer system used here is that as the composition drift proceeds, the instantaneous composition changes from S-rich, to MMA-rich and then to MA-rich and thus that the polarity of the instantaneously produced terpolymer increases monotonically. The solvent strength needed for dissolution in the solvent combination used in GPEC® (in this case H₂O-acetonitrile-tetrahydrofuran) increases monotonically in the order MA, MMA, S. In other words, the retention time of a certain polymer chain decreases monotonically with the extent of conversion at which this terpolymer chain was grown. So, in this case there will be no terpolymer chains with different compositions, having the same retention time. The different terpolymers can be separated and the elu-

tion chromatogram approaches the CCD quite closely, as if the elution chromatogram is a two-dimensional representation of the three-dimensional CCD, except for the fact that the retention time has not been transformed into some measure for the chemical composition. Bearing the above in mind, one can compare this elution chromatogram with the three-dimensional CCD in Figures 10(b) and (d). If those CCDs, with the S-MA axis in the foreground, are examined, the similarities can be seen.

Figure 11 also shows the development of the elution chromatogram as a function of conversion of the batch terpolymer (0.2, 0.3, 0.5). It can be seen that the higher the conversion, the more MA-rich polymers are formed, as expected. It can also be seen that no MA-rich polymer material is observed at low conversion, which should be the case if aqueous phase polymerization were to play a non-negligible role. This means that the NMR-method for determining the terpolymer CCD [Figs. 10(c) and (d)] was reliable. The highest conversion measured was 98%, which is why no poly(MA) peak was seen with GPEC®.

CONCLUSIONS

In this article the composition drift occurring in batch emulsion copolymerizations of low to moderately water-soluble monomer pairs S and MA and MA and MMA are outlined extensively. The composition drift could be understood on the basis of the reactivity ratios and monomer partitioning, the latter having a smaller effect than the first. ¹H-NMR was used to show that in this system true copolymers are formed. GPEC® was used successfully for determining the CCDs of the copolymers. It was shown that the composition drift in the corresponding terpolymer is similar to that occurring in the systems S-MA and MMA-MA: in all cases S and MMA can be depleted before the end of the reaction leading to homopolymerization of MA and bimodal CCDs. For the terpolymers two ways of determining the CCDs experimentally were investigated, one using ¹H-NMR data and one using GPEC®. As a result of the nature of the S-MMA-MA system, the resulting elution chromatograms in GPEC® are almost equivalent to a two-dimensional representation of the three-dimensional CCDs. The CCDs determined with ¹H-NMR and GPEC® are in good agreement. The model TRISEPS, developed to predict composition drift in emulsion co- and terpolymerizations, gave results that were in very good agreement

with experimental data, including the CCDs experimentally determined with ¹H-NMR.

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