Molar-mass chemical-composition distributions of styrene–methyl acrylate copolymers prepared by solution or emulsion polymerization

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The microstructure of copolymers can be characterized in terms of triad fractions and tacticity parameters (i.e. intramolecular structure), and in terms of a three-dimensional molar-mass chemical-composition distribution (*MMCCD*) (i.e. intermolecular structure). The microstructure obtained is controlled by the copolymerization conditions, for instance by the choice of the reaction system (homogeneous solution or heterogeneous emulsion), the degree of conversion and the choice of reactants. Computer simulations of emulsion copolymerization (SIEMCO), accounting for the main chemical and physical processes occurring, provide *MMCCD* predictions of emulsion copolymers. These *MMCCD*s are calculated by considering the conversion heterogeneity (composition drift) as well as the instantaneous (statistical) composition distribution of the copolymers formed. Cross-fractionation (two-dimensional chromatography) was used to verify the predicted *MMCCD*s of the copolymer products. The copolymers are separated according to molar mass by means of size exclusion chromatography (s.e.c.), and each s.e.c. fraction is subsequently analysed according to chemical composition by means of gradient elution quantitative thin-layer chromatography/flame ionization detection (t.l.c./f.i.d.). The difference in water solubility of the two monomers (styrene (S) and methyl acrylate (MA)) appears to be one of the major factors determining the microstructure of the copolymers. Depending on conversion, monomer ratio and monomer-to-water ratio, the model predicts either single- or double-peaked *MMCCD*s, in full agreement with the experimentally obtained distributions.

(Keywords: molar-mass distribution; chemical-composition distribution; emulsion copolymerization; poly(styrene-*co*-methyl acrylate); cross-fractionation)

INTRODUCTION

Copolymer microstructure is one of the key factors determining final product properties. It is well known that copolymers with the same average chemical composition and molar mass may exhibit different chemical and physical properties depending on the way they have been prepared[1]. This may be attributed to differences in sequence distribution and differences in molar-mass chemical-composition distribution (*MMCCD*). The emulsion copolymer microstructure (*MMCCD*, sequence distribution and tacticity) depends on the choice of reactants and on the process conditions. Important parameters are reactivity ratios and monomer partitioning. The importance of studying emulsion copolymer microstructure is generally recognized. On the one hand, the copolymer microstructure directly reflects the microscopic kinetic events taking place during emulsion copolymerization. On the other hand, the microstructure determines the final product properties. Some progress has been reported on the development of models describing emulsion copolymerization and the molecular microstructure of emulsion copolymers in terms of sequence distribution[2,3] and *MMCCD*[4,5]. From existing theories it appears that, in general, the *MMCCD* of emulsion copolymers deviates significantly from the one that would be expected on the grounds of the classical copolymerization kinetics in (homogeneous) bulk or solution processes, owing to the heterogeneity of the emulsion copolymerization system.

Reliable experimental determination of emulsion copolymer microstructure is a prerequisite in any effort to verify the applicability of newly developed models. Recent progress in orthogonal (two-dimensional) chromatography, i.e. size exclusion chromatography–high performance liquid chromatography (s.e.c.–h.p.l.c.)[6–9] and size exclusion chromatography–thin-layer chromatography/flame ionization detection (s.e.c.–t.l.c./f.i.d.)[10,11], has contributed considerably to the improved analysis of copolymer *MMCCD*s.

Unfortunately, in the open literature hardly any attention has been paid to the experimental *MMCCD* determination of *emulsion* copolymers. Practically all papers describing the experimental analysis of intra- and intermolecular copolymer microstructure deal with solution or bulk copolymers.

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However, besides measurements of, for instance, monomer conversion and particle number during emulsion copolymerization, the determination of copolymer intermolecular microstructure (*MMCCD*) and intramolecular microstructure (sequence distribution) will provide information important to a better understanding of the emulsion copolymerization process. This information is much more detailed and useful than the information merely obtained on the basis of determination of average chemical composition and molar mass.

In the literature there are hardly any investigations of the experimental determination of the *MMCCD*s of styrene (S)–methyl acrylate (MA) (batch) emulsion copolymers. As one of the few, Ramirez[12] investigated the S–MA emulsion copolymerization using differential scanning calorimetry (d.s.c.) in an attempt to determine the copolymer *CCD*. However, d.s.c. is not the most powerful tool in the accurate determination of *CCD*s. The resolution obtained is low and intermolecular interactions may affect the d.s.c. curves.

In this paper an investigation is presented of the intermolecular microstructure of batch solution and emulsion S–MA copolymers. The solution copolymers were used as reference copolymers and to test the cross-fractionation method (viz. s.e.c.–t.l.c./f.i.d.). The experimentally determined copolymer microstructures (viz. *MMCCD*) of the emulsion copolymers were compared with the predictions generated by the simulation model SIEMCO[13], and considered to be a proof of the validity of several model assumptions.

EXPERIMENTAL

The reference solution copolymers were prepared in toluene at 335 K with azobisisobutyronitrile (AIBN) as initiator. The total monomer concentration was 3 mol l^{-1}. Details have been given in a separate paper[14].

The emulsion copolymerizations were carried out at 50°C. $K_2S_2O_8$ was used as initiator (1.233 mmol l^{-1}), sodium dodecyl sulphate (SDS) was used as emulsifier (0.0116 mol l^{-1}) and $NaHCO_3$ was used as buffer (1.223 mmol l^{-1}). Monomer ratio and monomer-to-water ratio were varied. Normally, n-dodecyl mercaptan was used as chain transfer agent at a concentration of 1 wt% on monomer basis. Prior to *MMCCD* and sequence distribution analyses, the lattices were dialysed in order to remove impurities. N.m.r. experiments, however, were carried out on unpurified samples taken from the reactor during polymerization, which also served for the purpose of dry solid content analyses.

COPOLYMER ANALYSIS

Cross-fractionation method for determining copolymer MMCCD

One of the fundamental issues in the analysis of copolymers is the correlation between *CCD* and *MMD*. To enable evaluation of the two-dimensional distribution (*MMCCD*), cross-fractionation techniques are required. The mutual dependence of chemical-composition and molar-mass analyses is one of the main experimental problems to deal with.

As often erroneously believed, s.e.c. equipped with a dual detector system (e.g. ultraviolet (u.v.) and refractive index (r.i.)) alone is incapable of giving complete information on the chemical heterogeneity. It merely gives information about the average chemical composition at different molar masses. The cross-fractionation method described here is capable of measuring the full molar-mass chemical-composition distribution (*MMCCD*).

The intermolecular microstructure of the S–MA copolymers in terms of the *MMCCD* was determined by means of the cross-fractionation method developed earlier in our laboratory[15] and based on s.e.c.–t.l.c./f.i.d.. First, the copolymer is separated according to molar mass by means of s.e.c. Although the *MMD* of *homopolymers* can be determined accurately by s.e.c., correct information on the *MMD* of *copolymers* cannot always be obtained in a straightforward manner by s.e.c.. The main reason is that separation by s.e.c. is achieved according to the hydrodynamic volume of the molecules in solution. In the case of copolymers, this volume generally depends not only upon the molar mass, but also upon the chemical composition. As was already shown by Teramachi[16], within the range between 45 and 80 mol% styrene of S–MA copolymers, the s.e.c. separation is performed nearly exclusively according to molar mass without a disturbing influence of chemical composition. This accords with a recent study by Davis *et al.*[17]. Subsequently, each s.e.c. fraction of the S–MA copolymer is analysed by means of t.l.c./f.i.d.[11,18–22], exclusively according to chemical composition.

Alternatively, if desired, it is also possible to determine merely the *CCD* of the copolymer without a preceding separation according to molar mass, because the influence of molar mass on the retention factor (R_f) is negligible.

Size exclusion chromatography

Size exclusion chromatography (s.e.c.) was performed on a chromatographic system (Waters Associates) equipped with both a differential refractometer and an ultraviolet (u.v.) detector (254 nm). Using both signals, s.e.c. chromatograms with peaks directly proportional to the relevant amounts of copolymer were calculated using an experimentally determined relation between copolymer composition, on the one hand, and refractometer and u.v. signals, on the other. This calibration of the s.e.c. chromatographic signal was performed without accounting for non-linearity of u.v. response[23] and without accounting for any possible differences in intramolecular structure. However, Garcia[24] showed that the intramolecular microstructure can have some effect on u.v. absorption of copolymers. Because the copolymers under investigation are random copolymers, the relatively small differences in intramolecular structure are expected to have a negligible effect on the ratio of u.v. absorption and refractometer signal. A series of three or four μ-Styragel columns with nominal pore sizes of the packings of (10^1), 10^2, 10^3, 10^4 nm thermostatted at 313 K was used. The s.e.c. columns were calibrated using 18 polystyrene samples, with narrow molar-mass distributions. The tetrahydrofuran (THF) flow rate was set at 0.9 ml min^{-1} in the case of four columns and at 0.6 ml min^{-1} in the case of three columns. The emulsion copolymers were dissolved in THF after purifying the latex. In the case of the conventional s.e.c. analysis for the determination of the *MMD*, a 100 μl (0.1% w/v) sample was injected. However, a 1000 μl (0.15 w/v) sample was injected in the case of the s.e.c. fractionations for subsequent t.l.c./f.i.d.. Typically, the copolymer was fractionated into six, eight or ten fractions. The THF was evaporated from each fraction at 313 K under a nitrogen

flow. Subsequently, the remaining copolymer was redissolved in 10–40 μl toluene. These very small samples contain sufficient copolymer to perform the subsequent t.l.c./f.i.d. analysis.

Gradient thin-layer chromatography/flame ionization detection

The chromarods (Iatron Lab., type S) were activated in a vacuum oven at 393 K and subsequently scanned twice. In order to obtain accurate copolymer *CCD*s by means of t.l.c./f.i.d. it is extremely important that the sample (0.2 μl 1% w/v) is spotted on the rod very meticulously with a syringe, resulting in little spot broadening. Also, spotting should be carried out in a solvent-saturated atmosphere. Furthermore, and in contrast to common practice in t.l.c. when low-molar-mass samples are analysed, the rods were not dried after spotting and prior to elution. This procedure prevents precipitation of the copolymer on the rods and as a consequence the copolymer will stay in dynamic equilibrium with solvent and adsorbent. Without these precautions, precipitation of the copolymer occurs prior to elution and this leads to slow redissolution during elution, giving tailing and thus resulting in an apparent *CCD*. A few (2–4) rods of each set of 10 rods, held by a metal frame, were not spotted with samples from s.e.c.. Instead, these rods were spotted with a mixture of well defined reference copolymers, i.e. homogeneous copolymers prepared by low-conversion solution copolymerization. The R_f values of the reference copolymers were used to calibrate the chromatograms of the unknown samples. A correction was made to account for small differences in the elution front distances observed among the 10 different rods. However, these differences were minimized (<3%) by selecting rods that show similar elution rate behaviour. For MA-rich copolymer samples, reference copolymers were taken with copolymer compositions, in terms of S molar fractions, of 0, 0.12, 0.33, 0.46, 0.57 and 0.76. In the case of S-rich samples, the chemical composition of the reference copolymers were 0.46, 0.57, 0.76, 0.81 and 1. All reference copolymers had molar masses of approximately $M_n = 40\,000$ (g mol^{-1}).

A gradient elution technique was applied by adding polar liquids to a rather apolar starting eluent during elution. In order to prevent precipitation of the copolymer during elution, leading to a molar-mass dependence of the retardation factor (R_f), and thus in an apparent *CCD*, the copolymer was eluted permanently under saturated solvent conditions. This appeared to be a prerequisite for a molar-mass-independent retardation factor. The absence of a possible and unwanted molar-mass dependence was checked by comparing the R_f values of several copolymers of the same chemical composition but with different molar masses. In *Figure 1* it is shown that the molar-mass dependence on R_f is negligible in a wide range of molar mass. In order to minimize peak broadening and to obtain an optimal separation, the elution procedure was adapted to the average copolymer composition involved. For MA-rich S–MA copolymers, 25 ml toluene was introduced into the special development tank as described by Tacx[11]. After an equilibration time of 15 min, elution was started by adding 75 ml toluene. After 1, 2, 3 and 4 cm elution front position, 5 ml acetone was added to the eluent. At 5 and 6 cm, 10 ml acetone was added, and finally at 7 and 8 cm, 5 ml methanol was added. Elution was allowed to continue until the elution front position had reached a level of 9 cm above the spotting point. This procedure resulted in an excellent separation in the MA-rich area. Pure PMA also migrated under these conditions ($R_f = 0.05$–0.1). In *Figure 2* a typical chromatogram demonstrates the resolving power of this technique.

For S-rich S–MA copolymers, a different elution procedure was used, starting with 85 ml CCl_4 (by adding 60 ml to the 25 ml CCl_4 used for 15 min equilibration) and adding 10 ml toluene at 1 and 2 cm elution front positions, followed by adding each time 5 ml acetone at 4, 5, 6 and 7 cm. After 8 cm the elution was stopped.

After elution the rods were dried in a vacuum oven at 393 K for ca. 30 min. The t.l.c./f.i.d. scanning apparatus Iatroscan TH-10 was used to detect the separation pattern of the (co)polymers. The electronic f.i.d. amplifier of the Iatroscan was replaced by a Carlo Erba amplifier type EL-480 for improved linearity. The optimal conditions for complete detection and minimal rod damage were 1 atm H_2 pressure, an air flow rate of 1800 cm^3 min^{-1}

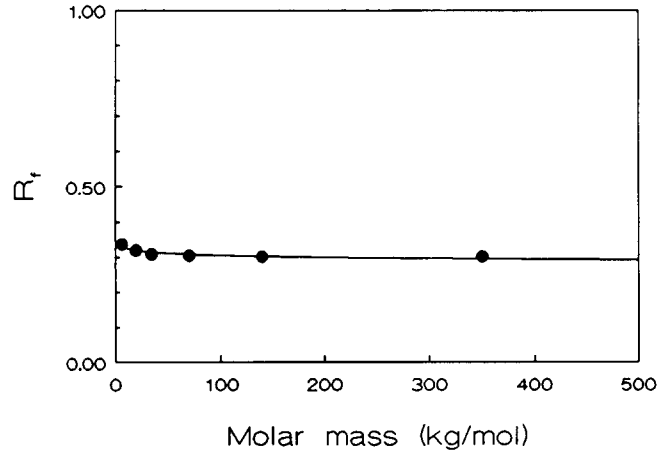

Figure 1 R_f values as a function of molar mass at constant copolymer composition (33 mol% S)

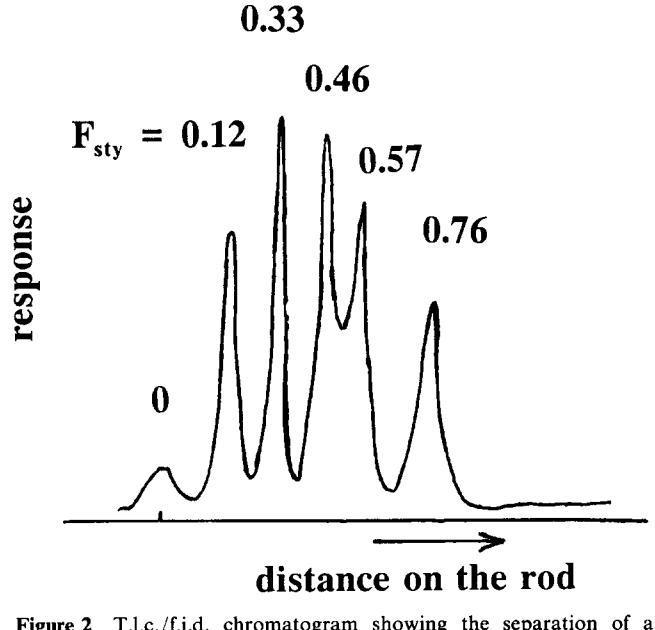

Figure 2 T.l.c./f.i.d. chromatogram showing the separation of a mixture of five reference copolymers each having a narrow distribution according to chemical composition, but having a different average chemical composition

and a scanning speed of 0.42 cm s^{-1}. The effect of copolymer composition on the f.i.d. response was investigated and appeared to be very small. Therefore, it was neglected in the calculation of all *CCD*s of the S–MA copolymers.

The small peak corresponding to copolymer material that remained on the spotting place was always less than 5% of the total peak areas. This little peak was neglected in the *CCD* calculations. The average copolymer compositions, as determined from the measured *CCD*s, were verified by means of ^{1}H n.m.r.

Tacx[11] has shown that the t.l.c./f.i.d. method failed for emulsion copolymers prepared in the presence of certain emulsifiers (Antarox CO-880 and RE-610), presumably due to chemical bonding of emulsifier to the polymer chains during polymerization. However, emulsion copolymers prepared in the presence of sodium dodecyl sulphate (SDS) could be analysed very well, provided they were well purified from SDS by dialysis. Generally, the difference between the average S–MA copolymer composition determined by means of t.l.c. and that determined by ^{1}H n.m.r. was less than 3 mol% styrene.

Cross-fractionation data treatment

S.e.c. and t.l.c./f.i.d. chromatograms were digitized and the distributions were calculated on a personal computer using both calibration curves. In the *CCD* plots, the relative weight (R_w) is given *versus* the mole fraction of one of the monomer units. In those cases where pure PMA or pure PS is present in the sample, direct use of the calculated t.l.c. calibration curves would result in physically impossible negative styrene fractions (for PMA) or physically impossible styrene fractions larger than 1 (for PS) owing to chromatographic peak broadening. To deal with this problem in *CCD*s, the homopolymer peaks were corrected using the convention that, in the distribution plot, the pure components have a peak broadening of 1%. Because the distribution is normalized to unity and the composition is given in mole per cent styrene, pure homopolymer (PS or PMA) will have a height of 100 in *CCD* plots. Alternatively, in some plots the area under the distribution curve was normalized to the molar conversion.

RESULTS AND DISCUSSION

Accuracy and reliability of gradient t.l.c./f.i.d.

In *Figure 3* the experimentally determined *CCD* of a low-conversion solution S–MA copolymer ($(S/MA)_0$ = 0.11 (mol/mol); conversion = 3 (mol%); M_w = 62 700 (g mol^{-1})) is compared with the model *CCD*, calculated using the modified Stockmayer equation proposed by Tacx[25]. *Figure 3* demonstrates that a low-conversion solution copolymer indeed has a narrow chemical distribution. The molar mass of the copolymer is given, since the instantaneous (=statistical) chemical heterogeneity depends strongly on the copolymer molar mass[26].

In *Figure 4* an experimental *CCD* of a high-conversion solution S–MA copolymer ($(S/MA)_0$ = 0.85 (mol/mol); conversion = 97 (mol%); M_w = 48 800 (g mol^{-1})) is compared with the model *CCD*. The model *CCD*s have been calculated accounting for both the composition drift and the instantaneous heterogeneity due to the statistical character of the monomer addition process. The model also takes into account the difference in molar mass

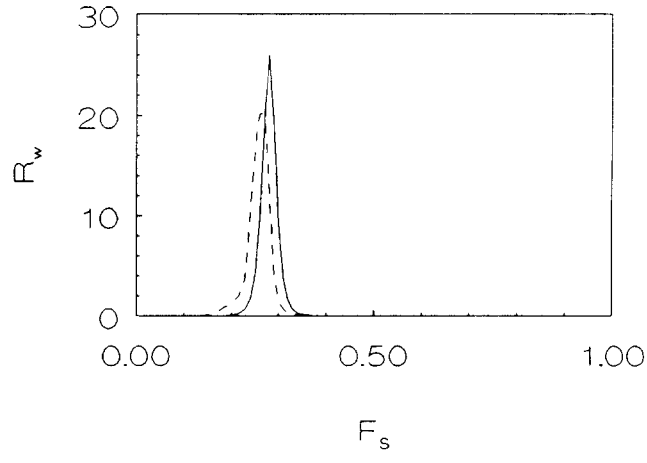

Figure 3 Experimental (– – –) and model (——) *CCD* of a low-conversion solution S–MA copolymer. $(S/MA)_0$ = 0.11 (mol/mol), conversion = 3 (mol%), M_w = 62 700 (g mol^{-1})

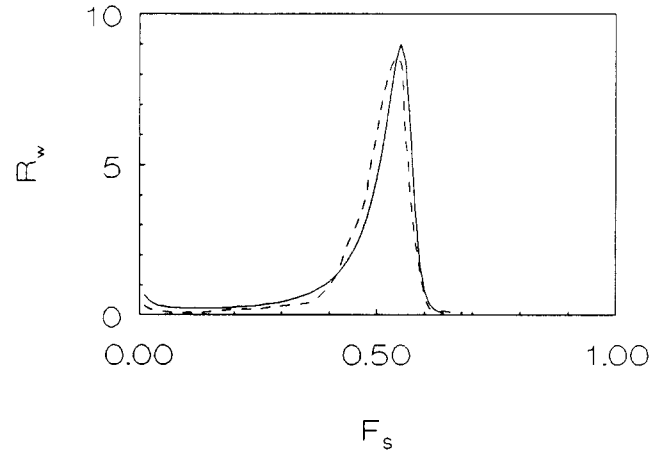

Figure 4 Experimental (– – –) and model (——) *CCD* of a high-conversion solution S–MA copolymer. $(S/MA)_0$ = 0.85 (mol/mol), conversion = 97 (mol%), M_w = 48 800 (g mol^{-1})

between the two monomers. The excellent agreement between theory and t.l.c. results gives confidence in both the reliability of the t.l.c. method of determining the *CCD* and the validity of the model calculations.

Figure 5a shows the cross-fractionation result of a low-conversion (3 mol%) solution S–MA copolymer having an average composition of styrene of 33 (mol%) and a M_w = 62 600 (g mol^{-1}). All s.e.c. fractions exhibit symmetrically shaped *CCD*s. It is clearly shown that the calibration by means of the low-conversion solution reference copolymers with $M_w \approx 40\,000$ (g mol^{-1}) is quite satisfactory for all s.e.c. fractions, indicating once again the independence of R_f in t.l.c. of copolymer molar mass. Finally, in *Figure 5b* an experimentally determined *MMCCD* of a high-conversion copolymer prepared with q_0 = 5.7 (mol/mol) at 99 (mol%) and with M_w = 46 700 (g mol^{-1}) is given, demonstrating the occurrence of a composition drift towards the styrene-rich side for all s.e.c. fractions: all s.e.c. fractions exhibit asymmetrically shaped *CCD*s.

From these results it can be concluded that the t.l.c./f.i.d. technique is useful for the *CCD* determination of S–MA copolymers provided extreme care is taken during sample spotting and during development of the rods.

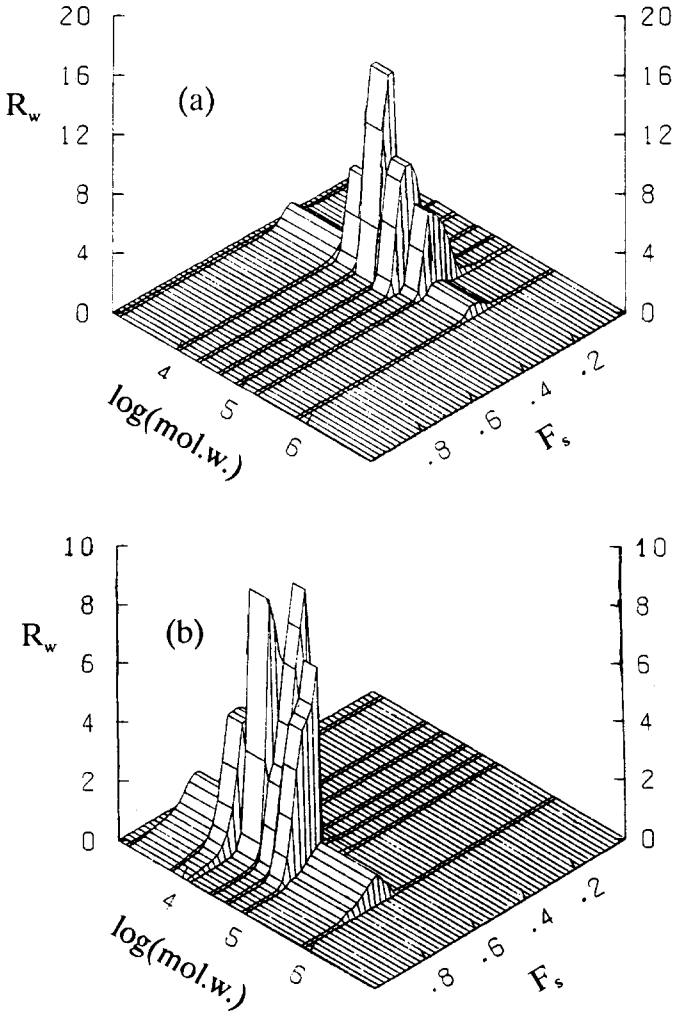

Figure 5 Typical experimental *MMCCDs* of solution copolymers: (a) $(S/MA)_0 = 0.11$ (mol/mol), conversion = 3 (mol%), $M_w = 62\,000$ (g mol^{-1}); (b) $(S/MA)_0 = 5.7$ (mol/mol), conversion = 99 (mol%), $M_w = 46\,700$ (g mol^{-1})

Model calculations: monomer reactivity ratios and monomer partitioning

All model predictions were calculated using the simulation program SIEMCO[13]. Comparison of experimental data and model calculations on the chemical composition distributions of the copolymers formed provides a necessary test of SIEMCO. The composition drift is exclusively determined by the reactants, reactivity ratios and monomer partitioning. All these parameters were independently determined and none were adjustable (i.e. determined by some kind of iterative model fitting procedure). The reactivity ratios[27] and the experimentally determined parameters[13] (K_p and K_w) for the relations describing monomer partitioning are given in *Table 1*.

The concentration of monomer i in the latex particles $[M_i]_p$ (mol l^{-1}) and its concentration in the aqueous phase $[M_i]_w$ (mol l^{-1}) are given as experimentally determined functions of the mol fraction (f_i) of monomer i in the monomer droplets:

$$[M_i]_p = K_{p1,i} f_i + K_{p2,i} f_i^2 \quad (1)$$

$$[M_i]_w = K_{wi} f_i \quad (2)$$

In the absence of monomer droplets, the monomer partitioning behaviour is calculated by equation (3) obtained by combining equations (1) and (2):

$$[M_i]_p = (K_{p1,i}/K_{wi})[M_i]_w + \{K_{p2,i}/(K_{wi})^2\}[M_i]_w^2 \quad (3)$$

The experimentally determined values valid for the monomer partitioning in copolymer lattices of composition 50/50 (mol/mol) are given in *Table 1*. The values of these equilibrium parameters fulfil the condition of equal monomer ratios in both organic phases. For other copolymer compositions the values of the equilibrium parameters are different, because (co)polymer composition affects the equilibrium total monomer concentration in the particles.

For bulk copolymerizations it has been demonstrated by Davis *et al.* that, in contrast to the composition drift behaviour, the kinetic behaviour of the S–MA system obeys the more complex penultimate model[17].

Molar-mass chemical-composition distribution of S–MA emulsion copolymers

As a result of the difference between the water solubilities of MA and S, in the case of emulsion copolymerization, the occurrence and composition of the azeotropic monomer feed depends on the overall monomer-to-water ratio. But using an overall initial monomer feed ratio of $(S/MA)_0 = 3$ (mol/mol) (this is the azeotropic composition in S–MA solution copolymerization), at an initial monomer-to-water ratio of $(M/W)_0 = 0.2$ (g/g), little composition drift is observed during emulsion copolymerization. Hence it might be expected that the copolymer formed is homogeneous. In *Figure 6* the experimental *MMCCD* (determined by means of t.l.c./f.i.d.) and the model *CCD* of this particular emulsion S–MA copolymer are depicted. From this figure it can be concluded that under these conditions, at least up to 90 mol% conversion, the copolymer formed is homogeneous with respect to the chemical composition. As expected in this case, the average chemical compositions of all s.e.c. fractions are almost identical. The narrow composition distribution indicates that the polymer particles are the main site of polymerization. However, under different conditions (e.g. higher temperature and higher initiator concentrations) we have found that non-negligible polymerization in the aqueous phase and polymerization inside the very small, precursor particles during the early stages of emulsion polymerization (interval I) may lead to anomalous *CCDs*, because the monomer ratio then will be different at the various sites of (co)polymerization[28].

Under the same reaction conditions, but by applying a different recipe (non-azeotropic conditions), asymmetrically shaped and even bimodal *MMCCDs* can be obtained.

Table 1 Reactivity ratios and monomer partitioning parameters of the S–MA emulsion copolymerizations

Monomer	r	s	K_{p1}[a]	K_{p2}[a]	K_w
S	0.73	0.94	8.94	−2.83	0.003
MA	0.19	0.11	6.89	1.18	0.61

[a]Values valid for copolymer lattices with a composition of 50/50 (mol/mol)

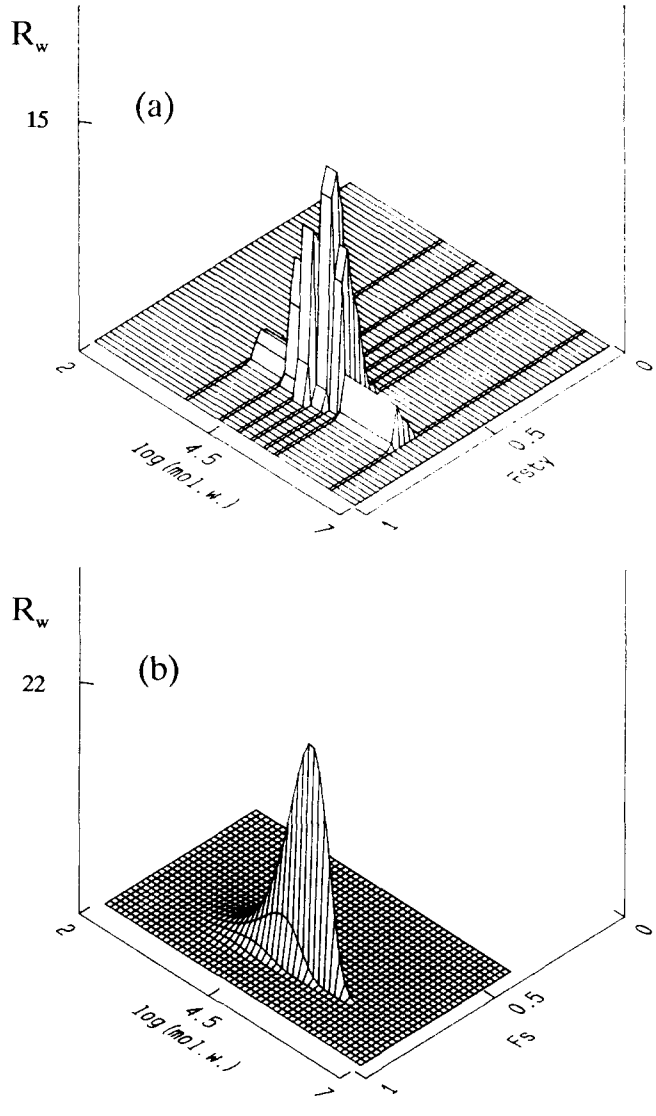

Figure 6 *MMCCD* of a styrene–methyl acrylate emulsion copolymer prepared under almost azeotropic conditions: $(S/MA)_0 = 3$ (mol/mol), $(M/W)_0 = 0.2$ (g/g), conversion = 90 mol%, $M_w = 160000$ (g mol^{-1}). (a) Experimentally determined by means of s.e.c.–t.l.c./f.i.d.; (b) model prediction

Neglecting aqueous-phase polymerization, which generally comprises less than 1% of the total polymer formed[29–31], the monomer ratio inside the latex particles, together with the reactivity ratios, governs the instantaneous copolymer composition. The local monomer ratio inside the latex particles is equal to the monomer ratio in the droplets but differs from the overall monomer feed ratio in the latex. In the present case, the latex particles will contain more styrene as compared with the overall monomer ratio. Therefore, also the copolymer initially formed will be richer in styrene as compared with expectations based on homogeneous systems. In the case of MA-rich recipes this results in a strong composition drift during polymerization towards compositions richer in the less reactive and more water-soluble monomer, i.e. MA, eventually leading to a considerable amount of pure PMA formation at high conversion (*Figure 7*).

This bimodality in copolymer *MMCCD* is reflected in the occurrence of two glass transition temperatures due to phase separation: one at ~15°C characteristic of the PMA-rich domains, and one at a temperature between 15 and 100°C depending on the chemical composition of the (mixed) copolymer peak domain.

The predicted and observed *MMCCD*s are in favourable agreement. The model calculations also predict homopolymerization at high conversion (*Figure 7b*).

Several emulsion copolymers were prepared using $(S/MA)_0 = 0.33$ (mol/mol) and $(M/W)_0 = 0.2$ (g/g) (non-azeotropic conditions), but applying different n-dodecyl mercaptan (NDM) contents varying from 1 to 8 wt% on the monomer. As was expected, the use of higher NDM concentrations results in a lower molar mass of the copolymer formed. In *Table 2* the s.e.c. results of the emulsion S–MA copolymers are given in order to

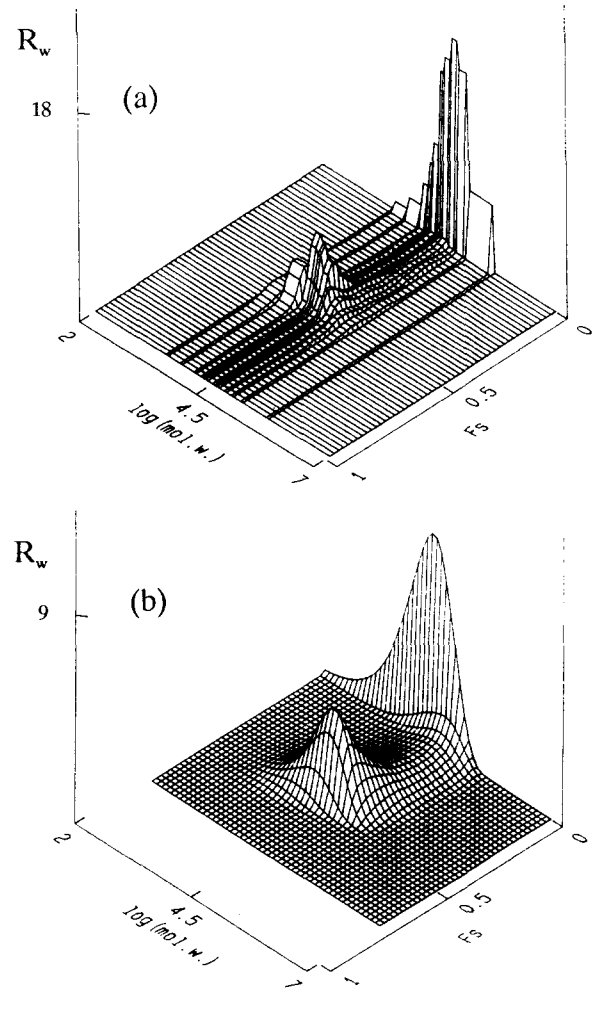

Figure 7 Experimental (a) and model (b) *MMCCD* of a high-conversion (95 mol%) S–MA emulsion copolymer: $(S/MA)_0 = 0.33$ (mol/mol), $(M/W)_0 = 0.5$ (g/g), 1 wt% NDM, 50°C, and $M_w = 110000$ (g mol^{-1})

Table 2 Results of u.v. and r.i. detection in s.e.c. measurements on several emulsion S–MA copolymers, all prepared with $(S/MA)_0 = 0.33$ (mol/mol) and $(M/W)_0 = 0.2$ (g/g), but with various NDM concentrations

NMD (%)	M_n (g mol^{-1})		M_w (g mol^{-1})	
	U.v.	R.i.	U.v.	R.i.
1	27000	32400	70384	79800
4	9500	10200	18600	23200
8	7500	7900	12200	14500

show the results obtained with u.v. and r.i. detection. The u.v. (254 nm) detector is only sensitive to styrene units and not to methyl acrylate units, whereas the r.i. detector is sensitive to both monomeric units. Therefore, the ratio of both s.e.c. detector signals is a measure of the average chemical composition at each molar mass. Compared with u.v. detection, r.i. detection results in higher calculated molar masses of the emulsion copolymers given in *Table 2*. This indicates an increase of average MA content on increasing molar mass of the copolymer molecules. Without any further knowledge this could be attributed to a gradual drift in copolymer composition with molar mass. However, it is clear from *Figure 7a* that the microstructure is more complex. The emulsion copolymer has a bimodal *MMCCD*, where PMA has a significantly higher molar mass than the copolymer. This could be attributed to an earlier depletion of NDM. The model-calculated *MMCCD* shows PMA with a lower molar mass, contrary to the observation. However, the uncertainty of several parameters describing the chain transfer to chain transfer agent (and monomer) results in a limited predictive value of the SIEMCO model with respect to the copolymer molecular weight. This is in contrast to the composition drift, which is described without any adjustable parameters, using independently determined parameters only.

CONCLUSIONS

Copolymer analysis by means of s.e.c.–t.l.c./f.i.d. is a powerful tool in the experimental determination of the *MMCCD* of copolymers in which the two monomer units differ moderately in polarity. This method was successfully applied to styrene–methyl acrylate batch emulsion copolymers. The effects on copolymer microstructure of different water solubilities of the monomers in combination with varying monomer-to-water ratios were correctly predicted by the SIEMCO model.

When modelling the emulsion copolymerization process of water-soluble monomers it must be taken into account that the aqueous phase is a monomer reservoir strongly affecting copolymer microstructure.

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