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**Citation for published version (APA):**

van Doremaele, G. H. J., Schoonbrood, H. A. S., Kurja, J., & German, A. L. (1992). Copolymer composition control by means of semicontinuous emulsion copolymerization. *Journal of Applied Polymer Science*, 45(6), 957-966. <https://doi.org/10.1002/app.1992.070450603>

**DOI:**

[10.1002/app.1992.070450603](https://doi.org/10.1002/app.1992.070450603)

**Document status and date:**

Published: 01/01/1992

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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# Copolymer Composition Control by Means of Semicontinuous Emulsion Copolymerization

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## SYNOPSIS

The effect of two different monomer addition strategies on the chemical composition distribution of the copolymer formed by the (seeded) semicontinuous emulsion copolymerization of styrene and methyl acrylate has been investigated. 1. The addition of a mixture of the monomers at a constant feed rate results in a homogeneous copolymer, provided that extremely long process times are used (starved conditions). When not starting from a seed latex, aqueous phase polymerization was observed at low feeding rates. When using a seed latex, aqueous phase polymerization appeared to be negligible. 2. In order to achieve an optimal monomer addition pattern, a pragmatic approach is presented. An optimal monomer addition profile was calculated from accurate monomer partitioning data using a short iteration procedure. Gradient high performance liquid chromatography (HPLC) was successfully applied as a rigorous test of the homogeneity of the copolymer formed. The information obtained contains much more detail than in the case of using differential scanning calorimetry of  $^1\text{H}$  NMR. In contrast to  $^1\text{H}$  NMR that provides only average cumulative chemical compositions, the complete chemical composition distribution can be obtained by means of HPLC.

## INTRODUCTION

The semicontinuous (sometimes called semibatch) emulsion copolymerization process is widely used in industry. The main advantages of this process as compared with conventional emulsion batch processes include a convenient control of emulsion polymerization rate in relation to heat removal, and control of the particle morphology and chemical composition of the copolymer. The latter is important in the preparation of specialty or high performance polymer latices. Semicontinuous emulsion copolymerization processes can be performed by applying various monomer addition strategies. The most widely investigated and described procedure is the addition of a given mixture of the monomers at a constant rate (sometimes pre-emulsified monomers are added).<sup>1-9</sup> For instance, this procedure has

been described in many papers dealing with the semicontinuous emulsion copolymerization of vinyl acetate and *n*-butyl acrylate.<sup>10-15</sup> With respect to the monomer addition rate two main situations can be distinguished: (1) flooded conditions, where the addition rate is higher than the polymerization rate, and (2) starved conditions, where the monomers are added at a rate lower than the maximum attainable polymerization rate (if more monomer had been present). The latter process (starved conditions) is often applied for the preparation of homogeneous copolymers. Sometimes semicontinuous processes with a variable feed rate (power feed) are used to prepare latex particles with a core-shell morphology.<sup>16</sup>

One of the main problems of the semicontinuous process performed under starved conditions is the extremely long reaction time required for the preparation of homogeneous copolymers. A more advanced method is the semicontinuous process performed in a controlled composition reactor.<sup>14,17,18,19,20</sup> The overall monomer concentrations then have to be monitored, e.g. by means of on-line GLC. The

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monomer concentrations are kept at the constant level required to obtain a desired copolymer composition by controlled feeding of the separate monomers into the reactor. Due to scatter of the GLC data it is usually difficult to maintain constant levels of the monomer concentrations in the reactor. Furthermore, the required optimal overall monomer concentrations may change, because the volume ratio of organic to aqueous phase continuously changes and consequently the monomer partitioning changes.

A method described in literature by Arzamendi and Asua<sup>21,22</sup> is the so-called optimal monomer addition strategy. By using this method Asua demonstrated that within a relatively short period of time homogeneous vinyl acetate (VAc)-methyl acrylate (MA) emulsion copolymers can be prepared in spite of the large difference between the pertaining reactivity ratios. The reactor was initially charged with all of the less reactive monomer (viz., VAc) plus the amount of the more reactive monomer (viz., MA) needed to initially form a copolymer of the desired composition. Subsequently, the more reactive monomer (MA) was added at a (time variable) flow rate in such a way as to ensure the formation of a homogeneous copolymer. However, it should be realized that, despite all efforts, genuinely predictive modelling of emulsion copolymerization is not yet possible. However, modelling with the use of a comparatively small number of strategic measurements is currently possible.

The time-dependent average number of radicals per particle [ $\bar{n}(t)$ ] and thus polymerization rate and optimal monomer addition profiles still cannot be predicted in advance. Generally,  $\bar{n}(t)$  is determined by the entry rate and exit rate and the bimolecular termination rate of free radicals. These rate values cannot be predicted without several strategic experiments. Arzamendi<sup>21,22</sup> surmounted this difficulty [unknown values of  $\bar{n}(t)$ ] by applying a semiempirical method that comprises a series of semicontinuous emulsion copolymerizations, which were used to correlate  $\bar{n}$  with the volume fraction of polymer in the latex particles ( $\phi_p$ ) and thus to find the time-dependence of  $\bar{n}(t)$ . In this paper a more pragmatic approach is presented. This method can be applied without actually calculating  $\bar{n}(t)$  or  $\bar{n}(\phi_p)$ . The emulsion copolymerization of styrene (S) and methyl acrylate (MA) is known to often produce highly heterogeneous copolymers<sup>23</sup> and is generally a low  $\bar{n}$  system ( $\bar{n} < 0.5$ ).<sup>24</sup> In this paper an investigation is presented on the preparation of a homogeneous S-MA emulsion copolymer by applying seeded semicontinuous emulsion copolymerization.

Rather than a large difference between reactivity ratios as for VAc and MA, the large difference between the water solubilities of S and MA is the main problem here. In addition to <sup>1</sup>H NMR which determined the average chemical composition of the copolymer formed, further analysis was necessary in order to evaluate the results. High performance liquid chromatography (HPLC) was used to obtain more detailed microstructural information (viz., chemical composition distribution, CCD) of the copolymer formed. Such detailed information is a necessity, because the chemical composition measured by means of <sup>1</sup>H NMR is only an average value of the cumulative copolymer composition, and an accurate view of the composition of the newly formed copolymer is obscured by the copolymer formed earlier in the process and by the copolymer of the seed latex particles. The effect of the latter is the main reason why, in this investigation, very small seed latex particles have been used.

## EXPERIMENTAL

Monomer partitioning, reactor equipment, and emulsion copolymerization procedures have been comprehensively described elsewhere.<sup>24</sup> The seed latex was prepared at 92°C under starved conditions according to the recipe given in Table (I). n-dodecyl mercaptan was used as chain transfer agent (NDM) and sodium dodecylsulfate as emulsifier (SDS). After filtration in order to remove coagulum, the seed latex was used without further purification. The seed latex particle size was measured by means of dynamic light scattering. The obtained z-average diameter was approximately 30 nm and the weight-average diameter was about 17 nm. The final solid content of the latex amounted to 7.8 wt %. The recipes for the constant addition rate experiments and the optimal addition rate experiment are given in Tables (II) and (III), respectively. All semicontinuous experi-

**Table I** Recipe Used for Preparing the Seed Latex

Reagent	Initial Charge (g)	Discontinuous Addition (g) every $\frac{1}{2}$ h	Continuous Addition (g/h) during $4\frac{1}{2}$ h
H <sub>2</sub> O	990	—	—
MA	—	—	17.638
S	—	—	7.112
NDM	—	—	0.25
SDS	4.20	—	—
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	2.31	0.15	—
NaHCO <sub>3</sub>	0.77	0.05	—

**Table II** Recipe Used in the Unseeded Starved Reactions with Constant Feed Rate

Reagent	Initial Charge (g)	Feed (g) during 4, 8, 32 h
H <sub>2</sub> O	600	—
MA	—	85.5
S	—	34.5
NDM	—	1.2
SDS	2.0	—
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.20	—
NaHCO <sub>3</sub>	0.067	—

ments were carried out at  $50 \pm 0.2^\circ\text{C}$ . In the case of the experiments leading to the optimal addition rate profile, all ingredients, except for a part of the styrene, were initially charged into the reactor. The remaining styrene was continuously added into the reactor according to one of the calculated monomer addition profiles. The overall monomer ratio was monitored by means of on-line GLC and the conversion was determined by means of dry solid content analysis. The total volume of all samples taken during the entire course of the reaction was always less than 4% of the total volume. The appropriate corrections were made in the calculation of the conversion. The volume of the samples taken from the reactor causes a slight error in the monomer addition profile. Although it is possible to adjust the monomer addition profile for the decrease in mass of the emulsion (when samples are taken with constant mass at fixed intervals), this minor effect was neglected in all experiments. Particle size measurements were carried out by means of dynamic light scattering and TEM. The determination of the copolymer composition distribution (CCD) by means of gradient HPLC has been described elsewhere.<sup>25</sup> The CCD measurements were performed on a homemade reversed phase column (Lichrosorb RP-C18 with a particle size of  $5 \mu\text{m}$ ; length = 10 cm, ID = 4.0 mm, Knauer, Berlin, FRG) at 313 K. A linear elution gradient with a flow rate of  $0.8 \text{ mL} \cdot \text{min}^{-1}$  was applied starting with a mixture of 80% THF, 15% methanol, and 5% water and ending, after 16 minutes, with pure THF. It has to be mentioned that S-MA copolymer with a styrene content of say less than 10 mol % cannot be quantitatively detected, since UV detection was used. The content of PMA and/or very MA rich copolymer molecules in the total copolymer sample can be calculated from <sup>1</sup>H NMR data in a straightforward manner. The intramolecular microstructure of the copolymer was analyzed by means of 100 MHz <sup>13</sup>C NMR.<sup>26</sup>

## RESULTS

The possibility of preparing homogeneous copolymers by means of a convenient semicontinuous process has been investigated. The primary aim is to prepare a homogeneous high conversion emulsion copolymer [25 mol % S and monomer to water ratio  $[(M/W)_0] = 0.2 \text{ (g/g)}$ , i.e., ca. 17 wt % solid in the final latex]. A latex with the same average chemical composition and solid content prepared in batch, is known to be very heterogeneous in chemical composition.<sup>23</sup> In the semicontinuous experiments a seed latex has been used to ensure reproducibility. As can be seen in Table (III), the amount of copolymer charged as seed copolymer latex particles into the reactor is negligible.

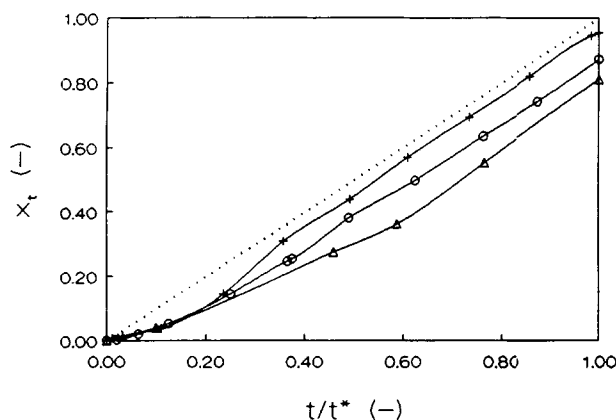
### Semicontinuous Emulsion Copolymerizations with Constant Addition Rates

In the conversion-time plots of Figure 1 it is demonstrated that lower monomer addition rates result in more starved conditions (i.e., higher instantaneous conversions). At the end of the addition time the experiment with the highest addition rate had the lowest conversion. Homogeneous copolymers can only be prepared under extremely starved conditions. Too fast an addition rate leads to inhomogeneous copolymers, as can clearly be seen in Figures 2(a) and 2(b). In this figure the fractional conversions of S and MA are given as a function of time for the 8-h and 32-h starved reactions. Moreover, the instantaneous average cumulative copolymer composition ( $\bar{F}_s$ ) has been plotted versus time. It is clear that the initial copolymer is relatively MA rich.

**Table III** Recipe Used in the Seeded Semicontinuous Experiments with Calculated Addition Profile

Reagent	Initial Charge (g)	Feed (g) According to Calculated Addition Profile
H <sub>2</sub> O	900	—
MA	127.4	—
S	8.0	43.3
NDM	1.4	0.43
SDS	3.0	—
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.30	—
NaHCO <sub>3</sub>	0.10	—
Seed latex <sup>a</sup>	16.7	—

<sup>a</sup> See Table I.



**Figure 1** Effect of monomer addition rate on total conversion ( $x_t$ ) versus normalized time ( $t/t^*$ ) of unseeded semicontinuous S-MA emulsion copolymerizations.  $t^*$  = addition time (reaction time): ( $\Delta$ ) 4 h; ( $\circ$ ) 8 h; ( $+$ ) 32 h; the dotted line ( $\cdots$ ) represents 100% instantaneous conversion.

This can be explained by a nonnegligible amount of polymerization (of MA) in the aqueous phase in the very early part of the reaction, when no latex particles have yet been formed. As soon as particles have been formed, polymerization in the particles will predominate over aqueous phase polymerization. In the particles, relatively S rich copolymer is formed due to the fact that the latex particles are relatively rich in styrene monomer, because a significant part of MA added is dissolved in the aqueous phase, whereas the styrene added is almost completely imbibed by the particles. One additional 8-h experiment was carried out in the presence of seed latex particles. In that case no initial MA rich copolymer was observed indicating the absence of a significant aqueous phase polymerization.

As expected, under starved conditions homogeneous copolymers can only be prepared when applying extremely long feeding times. In the following, a strategy has been described by which this problem can be overcome.

### Semicontinuous Emulsion Copolymerization with Optimal Addition Profile

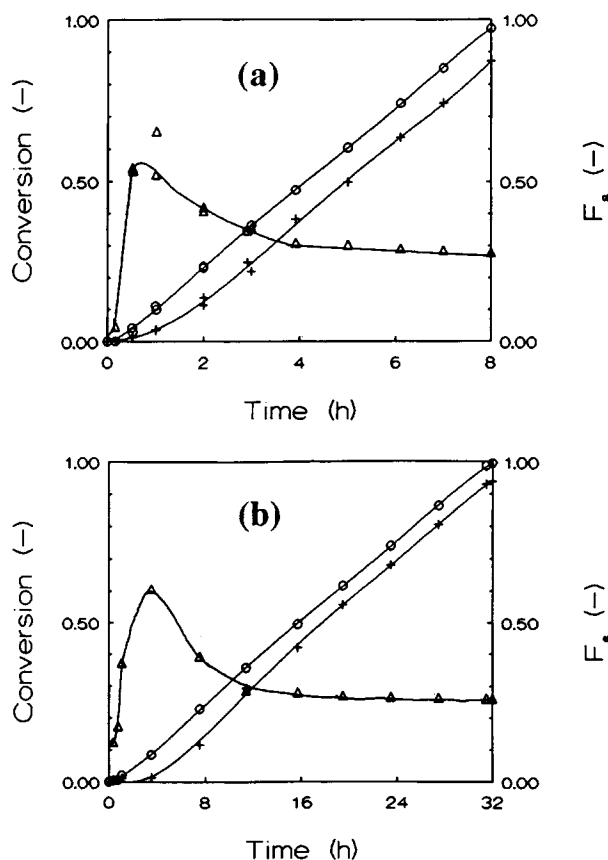
#### Strategy Followed to Achieve Optimal Addition Profile

All ingredients are charged into the reactor, except for a part of the most reactive monomer (i.e., styrene). The model Simulation EMulsion COPolymerization (SIEMCO),<sup>24</sup> the reactivity ratios ( $r_s = 0.73$  and  $r_m = 0.19$ ), and the monomer partitioning

data<sup>24</sup> (see appendix) are used to calculate the amount of the most reactive monomer to be charged initially into the reactor in order to obtain the desired local monomer ratio  $q_p = (S/MA)_p$  inside the latex particles. This particular ratio is related to the copolymer of the desired chemical composition ( $\bar{F}_s$ ) according to the instantaneous copolymer equation [eq. (1)]. In this case  $\bar{F}_s = 0.25$ , corresponding to  $q_p = 0.087$  (mol/mol).

$$\frac{\bar{F}_s}{1 - \bar{F}_s} = \frac{r_s q_p + 1}{r_m / q_p + 1} \quad (1)$$

A first estimation of the semicontinuous (co-)polymerization rate is made by SIEMCO assuming an arbitrarily chosen value of  $\bar{n}(t)$  (e.g., 0.5) throughout the reaction, while the most reactive monomer (S) is added at a time-dependent rate in order to maintain the optimal monomer ratio inside the particles. Three functions are calculated (fitted



**Figure 2** Fractional conversions of ( $\circ$ ) S and ( $+$ ) MA, and ( $\Delta$ ) the average copolymer composition ( $\bar{F}_s$ ) calculated from GLC data of an unseeded semicontinuous emulsion copolymerization with a constant feed rate.  $(S/MA)_{\text{feed}} = 0.33$  (mol/mol) and  $(M/W)_0 = 0.2$  (g/g) process time: (a) 8 h; (b) 32 h.

with polynomials); the subscripts indicate the number of iteration steps:

1. Instantaneous molar conversion ( $x_{\text{inst}}$ ) versus time [dependent on  $\bar{n}(t)$ ],

$$x_{\text{inst}} = f_0(t) \quad (2)$$

The first estimation of the conversion–time plot has subscript 0, and the first experimentally obtained conversion–time plot has subscript 1.

2. Calculated ideal amount of added styrene ( $A_s^*$ ) versus instantaneous molar conversion,

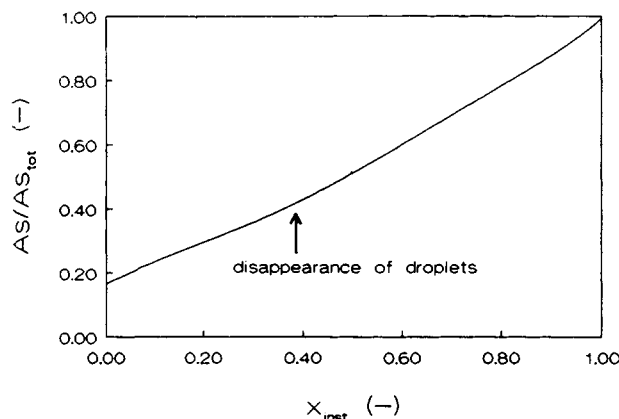
$$A_s^* = g(x_{\text{inst}}) \quad (3)$$

This function is only dependent on reactivity ratios and monomer partitioning and is depicted in Figure 3. The bend corresponds to the disappearance of the monomer droplets. The offset at 0% conversion represents the initially charged styrene.

3. Estimated amount of styrene to be added during the first experiment as a function of time,

$$A_s = g(f_0(t)) = h_1(t) \quad (4)$$

It should be noticed that the semicontinuous emulsion copolymerization has an optimal addition profile when styrene is added according to  $A_s = A_s^* = g(x_{\text{inst}})$ . However, at this stage of the procedure polymerization rate is not known and cannot be reliably calculated beforehand. First of all, the time-



**Figure 3** Normalized optimal addition profile of styrene versus the instantaneous conversion giving the desired homogeneous emulsion copolymer (25 mol % S, solid content of latex  $\approx$  17 wt %).  $A_{s_{\text{tot}}}$  = total amount of styrene to be added (g).

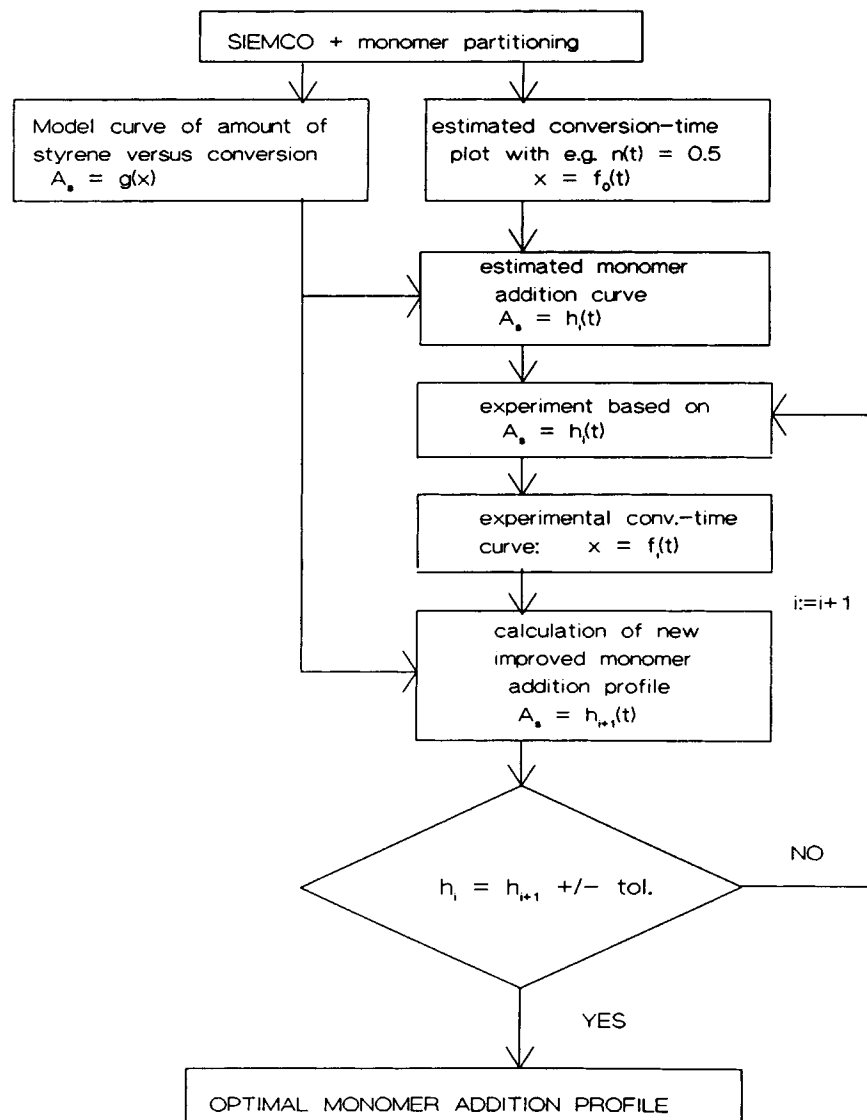
dependent polymerization rate under the experimental conditions must be determined in order to obtain this optimal addition profile. This is accomplished by applying an iteration procedure [Fig. (4)].

The first semicontinuous experiment is carried out by applying the calculated styrene addition profile based on an estimated (constant) value of  $\bar{n}(t) = 0.5$ . Generally speaking, it would be highly fortuitous if this first estimated addition profile would be optimal, because the average number of radicals will generally deviate from its first estimation (i.e.,  $\bar{n} = 0.5$ ), and may also depend on conversion (monomer concentrations in the particles).

Furthermore, particle number and average propagation rate constant may deviate from the values assumed to be valid in the calculations. From the experimental conversion–time data of this first experiment a new conversion time curve is fitted:  $x_{\text{inst}} = f_1(t)$ . Subsequently, for the next experiment an addition profile closer to (generally not exactly equal to) the optimal one is calculated by taking  $A_s = g(x_{\text{inst}}) = g[f_1(t)] = h_2(t)$ . In this manner  $x_{\text{inst}}$  is eliminated by combining the experimental conversion–time curve with the ideal curve of monomer addition versus conversion. So in fact, a number of parameters for which the values are uncertain (including  $\bar{n}$ , particle number, and average propagation rate constant as a function of time) do not have to be known. The next semicontinuous emulsion copolymerization then is carried out by applying this second addition profile of S. The entire procedure is continued until the final monomer addition profile conforms to the subsequently calculated monomer addition profile within a chosen tolerance region to be applied in the following experiment ( $h_i = h_{i+1} \pm \text{tolerance}$ ). This condition implies that during the final experiment S was optimally added according to  $A_s = g(x_{\text{inst}})$  and consequently the experimental conversion time curves must also be equal ( $f_i = f_{i+1} \pm \text{tolerance}$ ). Due to the fact that  $\bar{n}$  depends on the local monomer ratio inside the particles and that the monomer ratios may differ at equal conversions of the successive iteration steps, the number of required iteration steps is generally larger than one. The present system converges rapidly, only four iterations being required in S–MA emulsion copolymerization to arrive at (visibly) indistinguishable monomer addition versus time curves of the two latest successive iteration steps.

### Experimental Application of the Developed Procedure

The very rapid convergence of the iterative procedure is depicted in Figure 5 showing the conversion–

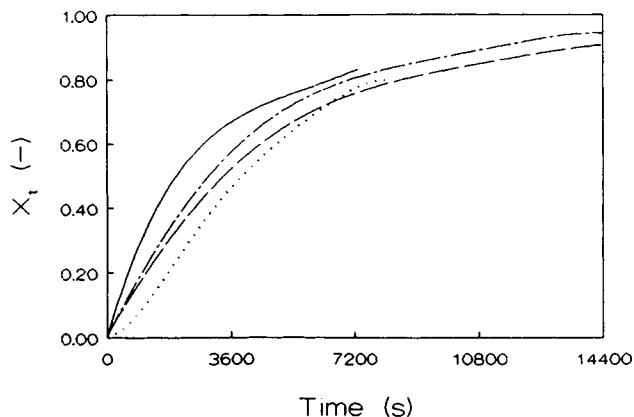


**Figure 4** Outline of the semiempirical iteration procedure for developing the optimal monomer addition profile.

time plots at successive iteration steps. Only four steps were necessary to achieve the criterion that the monomer addition profile is essentially constant with successive iteration steps, i.e., the optimal monomer addition profile has been reached. According to the optimal addition profile, styrene has to be added very slowly toward the very end of the polymerization due to the buffering behavior of water for methyl acrylate. However, in order to reduce process time, this phenomenon had to be neglected and after 4 h addition time all remaining styrene was added at once and polymerization was allowed to continue during one more hour, resulting in a 5-h reaction time. The optimal addition profile ob-

tained for styrene is given in Figure 6. Applying this optimal monomer addition profile, two experiments have been carried out: one experiment with and another one without an intentionally created induction time. In Figure 7 the conversions and average copolymer composition of both experiments have been plotted versus time.

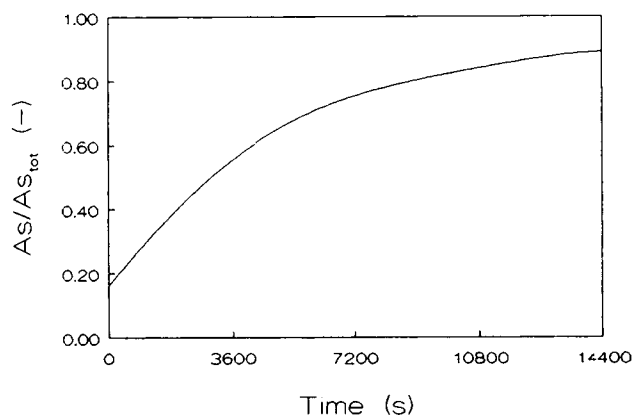
Finally, as a draconian test of the homogeneity of the copolymer formed, the copolymer CCDs of both reaction products were measured by means of gradient HPLC. As can be clearly seen in Figure 8, the copolymer formed in the optimal experiment is very homogeneous up to high conversion, whereas the copolymer formed in the experiment with the



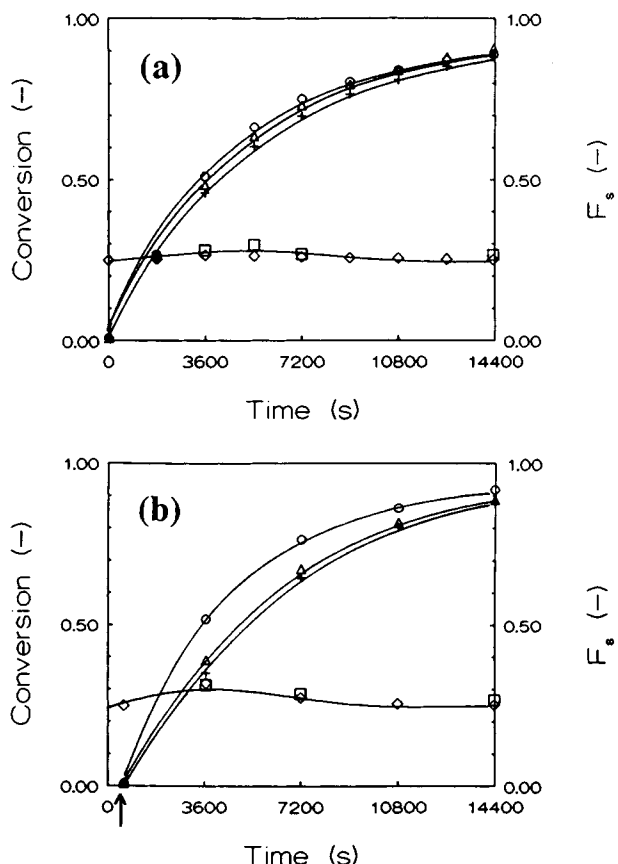
**Figure 5** Experimental conversion-time curves of four seeded semicontinuous emulsion S-MA copolymerizations at four successive iteration steps: —, 1st; ·····, 2nd; - · - · - ·, 3rd; - - - -, 4th and optimal.

induction time was not completely homogeneous. Instead, this copolymer exhibited bimodality. At low conversion a copolymer has been formed more rich in styrene than that at high conversions. This must be attributed to too high a concentration of styrene in the reactor at the beginning of the experiment due to the delay in the start of the polymerization; as a result there is too low a styrene concentration at high conversions. This bimodality in the CCD cannot be easily observed from average cumulative chemical composition data obtained, for instance, by means of  $^1\text{H}$  NMR (Figure 7). HPLC, on the other hand, provides high resolution information about copolymer CCDs and proves to be a powerful tool in this type of investigation.

Although the difference in chemical composition of the two parts of the CCD [Fig. 8(b)] shows up



**Figure 6** Optimal monomer addition profile, for the described semicontinuous emulsion copolymerization, obtained after 4 iteration steps.

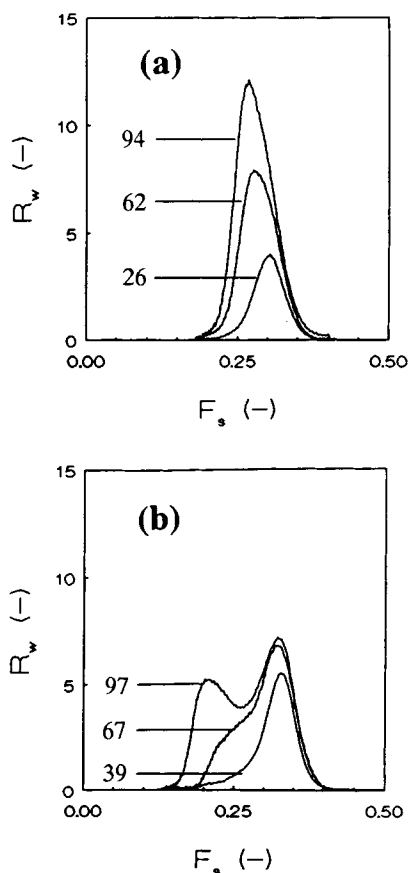


**Figure 7** Conversion of copolymer prepared according to the optimal addition profile and  $\bar{F}$  average cumulative chemical composition determined from GLC data: ( $\diamond$ ), and by means of  $^1\text{H}$  NMR ( $\square$ ), (a) no induction time; (b) induction time of 600 s (indicated by arrow). Key: ( $\Delta$ ) experimental total molar conversion, (+) partial conversions of MA, and ( $\circ$ ) S.

significantly in the powerful HPLC method, it is too small to result in phase separation of the product, as indicated by the occurrence of only one glass transition temperature [Figure 9(b, c)].

In Figure 10 are depicted the CCDs of three high conversion copolymers prepared by different processes. The one prepared by the conventional batch process [Fig. 10(a)] exhibits bimodality, has two glass transition temperatures [Fig. 9(a)] and has a minimum film formation temperature of  $17^\circ\text{C}$ . Note that the polymethyl acrylate peak has been calculated from  $^1\text{H}$  NMR average chemical composition data and the CCD determined by means of HPLC/UV. Both the copolymer prepared in a semibatch process under starved conditions (32 h) [Fig. 10(b)] and the one obtained in a semicontinuous process while applying the optimal monomer addition strategy (5 h) [Fig. 10(c)] are homogeneous with respect



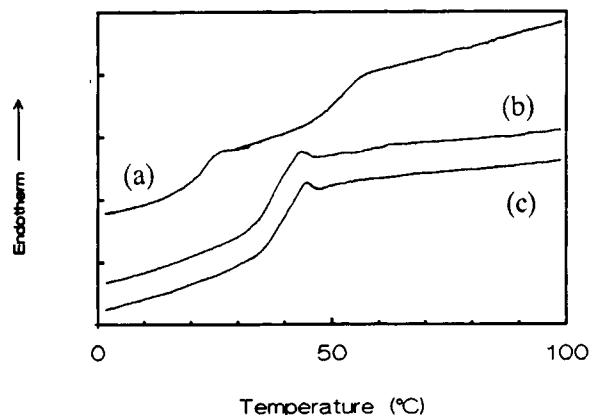


**Figure 8** CCDs (normalized according to conversion and determined by means of HPLC) of S-MA copolymer prepared at successively increasing conversions, according to the optimal additional profile: (a) no induction time; (b) induction time. The total mol % conversion is indicated.

to chemical composition and have a minimum film formation temperature of 27°C. The optimal addition strategy allows the preparation of homogeneous copolymer within a considerably shorter period of time than the strategy of monomer mixture addition at constant rate.

### Intramolecular Structure

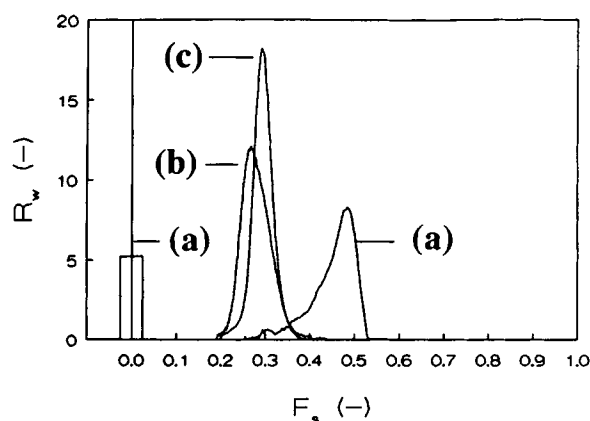
In Table IV the experimentally determined MA-centred triad fractions are given of the two high conversion S-MA emulsion copolymers. Comparison with the theoretical values of a homogeneous copolymer, having the same average chemical composition, also indicates that the optimal method of monomer addition gives a homogeneous copolymer, in contrast to the batch copolymer, which is heterogeneous.



**Figure 9** Differential calorimetric thermograms (10°C/min) of some S-MA emulsion copolymers with  $\bar{F}_s = 0.25$  and  $(M/W)_0 = 0.2$  (g/g): (a) conventional batch process, (b) semicontinuous, optimal monomer addition profile, (c) semicontinuous, nonoptimal addition profile due to induction.

### DISCUSSION

An iterative procedure aimed at determining optimal addition profiles has been successfully applied to semicontinuous S-MA emulsion copolymerization. The applicability (in terms of the required convergence) to other systems with different reactivity ratios and different monomer partitioning behavior has to be investigated. However, it can be argued that this iterative procedure cannot converge to addition profiles forming inhomogeneous copolymers.



**Figure 10** Experimental CCDs of three different S-MA emulsion copolymers, with  $\bar{F}_s = 0.25$  and  $(M/W)_0 = 0.2$  (g/g): (a) conventional batch process (3 h, 92 mol % conversion), (b) semicontinuous, starved conditions (32 h, 95 mol % conversion), (c) semicontinuous, optimal addition profile (5 h, 87 mol % conversion).

**Table IV** Triad Fractions of Various S-MA Emulsion Copolymers Compared with the Theoretical Values of a Homogeneous Copolymer

Method of Preparation	$\bar{F}_s^{a,c}$	MMM <sup>b,c</sup>	MMS <sup>b,c</sup>	SMS <sup>b,c</sup>	SSS <sup>b,c</sup>	SSM <sup>b,c</sup>	MSM <sup>b,c</sup>
Theoretical homogeneous copolymer	25.0	47.3	42.9	9.8	0.4	11.1	88.5
Batch	25.2	60.6	23.7	15.7	5.4	30.0	64.6
Optimal addition	27.5	45.1	43.7	11.2	0.0	18.5	81.5

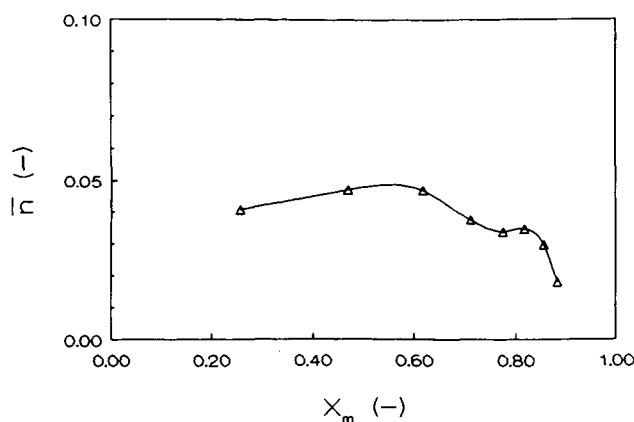
<sup>a</sup>  $\bar{F}_s$  = mole fraction of styrene (determined by 400 MHz <sup>1</sup>H NMR).

<sup>b</sup> Triad fraction determined by <sup>13</sup>C NMR.

<sup>c</sup> Value  $\times 100$ .

Finally  $\bar{n}$  has been calculated during a semicontinuous experiment with the optimal addition profile. By applying a suitable penultimate model,<sup>24</sup>  $\bar{n}$  has been calculated as a function of conversion from experimental conversion time data, the experimentally determined particle number (ca.  $6 \times 10^{17} \text{ L}^{-1}$ ), and the monomer partitioning data (see Figure 11). Its reliability is limited since the values of the parameters used to calculate  $\bar{n}$ , such as the number of latex particles,  $\bar{k}_p$ , and the monomer concentrations in the particles, can only be determined with limited accuracy. However, it is obvious that  $\bar{n}$  is less than 0.5 (i.e., low  $\bar{n}$  system). The apparent decrease in  $\bar{n}$  calculated at high conversion is unlikely, and could be attributed to the diffusion-controlled decrease in  $\bar{k}_p$ .

It is clear that the application of semicontinuous emulsion copolymerizations with optimal monomer addition profiles can be a powerful tool in kinetic investigations. It enables one to obtain accurate kinetic data at various local monomer ratios inside the particle that are constant during each individual experiment.



**Figure 11** Calculated  $\bar{n}$  as a function of instantaneous conversion from semicontinuous S-MA copolymerization with the optimal monomer addition profile.

## CONCLUSION

Homogeneous S-MA emulsion copolymers can be prepared by applying a constant addition rate of the monomer mixture, provided extremely low addition rates are being used. Unfortunately, this results in very long process times. A considerably shorter process time can be obtained by calculating the optimal S (i.e., the most reactive monomer) addition profile, when all MA has initially been charged to the reactor. The time-dependent rate of addition of S can be computed by an iterative procedure involving reactivity ratios, accurate monomer partitioning data, and a limited series of strategic experiments. The homogeneity of the copolymer formed was confirmed by means of gradient HPLC.

## APPENDIX MONOMER PARTITIONING EQUATIONS

The monomer concentrations in each phase were calculated with the appropriate mass balance equations and the experimentally determined equilibrium monomer partitioning equations (A. 1-3).<sup>24</sup>

The concentration of monomer  $i$  in the latex particles  $[M_i]_p$  ( $\text{mol} \cdot \text{L}^{-1}$ ) and its concentration in the aqueous phase  $[M_i]_w$  ( $\text{mol} \cdot \text{L}^{-1}$ ) have been determined as functions of the mole fraction ( $f_i$ ) of monomer  $i$  in the monomer droplets:

$$[M_i]_p = Kp_{1,i} f_i + Kp_{2,i} f_i^2 \quad (\text{A. 1})$$

$$[M_i]_w = Kw_i f_i \quad (\text{A. 2})$$

In the absence of monomer droplets the monomer partitioning behavior is calculated by equation (App. 3) obtained by combining equations (A. 1) and (A. 2):

$$[M_i]_p = (Kp_{1,i}/Kw_i)[M_i]_w + (Kp_{2,i}/Kw_i^2)[M_i]_w^2 \quad (\text{A. 3})$$

The following values were used to describe the monomer partitioning in the copolymer lattices:  $Kp_{1,s} = 6.89$ ,  $Kp_{2,s} = 1.18$ ,  $K_{w,s} = 0.003$ ,  $Kp_{1,m} = 8.94$ ,  $Kp_{2,m} = -2.83$ , and  $K_{w,m} = 0.61$  ( $\text{mol} \cdot \text{L}^{-1}$ ). The values of these equilibrium parameters fulfill the condition of equal monomer ratios in both organic phases.

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Received April 1, 1991

Accepted August 30, 1991