

Emulsion Co- and Terpolymerization of Styrene, Methyl Methacrylate and Methyl Acrylate. II. Control of Emulsion Terpolymer Microstructure with Optimal Addition Profiles

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SYNOPSIS

An optimal addition profile for the preparation of a chemically homogeneous emulsion terpolymer of styrene, methyl methacrylate, and methyl acrylate was determined using a recently developed model for describing composition drift in emulsion co- and terpolymerizations, TRISEPS, described in Part I of this series. The model uses recently published simplified equations to describe monomer partitioning and the terminal model for describing terpolymer composition. The optimal addition *rate* profile was determined from the calculated optimal addition profile with a purely empirical and iterative method. With gradient polymer elution chromatography (GPEC®) the homogeneity and/or heterogeneity of the terpolymers prepared in the iterative series of experiments could be determined and compared to the heterogeneity of the corresponding batch terpolymer described in Part I. It was shown that a homogeneous terpolymer could be obtained indicating that the simplified equations for monomer partitioning and the terminal model for terpolymer composition describe the system adequately. It was also shown that GPEC® was useful in the determination of the optimal addition *rate* profile. © 1996 John Wiley & Sons, Inc.

Keywords: emulsion terpolymerization • control of microstructure • monomer addition profile • chemical composition distribution • gradient polymer elution chromatography

INTRODUCTION

In Part I of this series¹ we presented a computer model (TRISEPS) to describe composition drift and co- and terpolymer microstructure in emulsion co- and terpolymerization. The batch emulsion copolymerizations of styrene (S) and methyl acrylate (MA) and of MA and methyl methacrylate (MMA) and the emulsion terpolymerization of these three monomers were investigated theoretically with the model TRISEPS and experimentally with ¹H-NMR and gradient polymer elution

chromatography (GPEC®). Good quantitative agreement was found between experimental and predicted cumulative terpolymer composition as a function of conversion and of terpolymer microstructure, including the three-dimensional chemical composition distribution (CCD). In all cases considerable composition drift was observed. In this article this computer model will be applied to control composition drift and to prepare a homogeneous emulsion terpolymer of S, MMA, and MA with semi-continuous emulsion terpolymerization. It will also be checked if GPEC® for terpolymers can be used for the determination of the homogeneity or heterogeneity of the polymers produced and for the determination of the optimal addition *rate* profile. Furthermore, the feasibility of finding an addition profile and of the convergence of the iteration procedure needed for the determination of the optimal addition *rate* profile will be discussed.

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CO- AND TERPOLYMER COMPOSITION CONTROL

In literature various methods have been presented to control composition drift in emulsion copolymerization and to obtain emulsion copolymers that have specific chemical composition distributions. Composition drift can be controlled by controlling the monomer concentrations in the main locus of polymerization, i.e., the polymer particles. The monomer concentrations can be effectively controlled by adjusting the monomer addition rates in semi-continuous reactions. Many researchers have studied semi-continuous emulsion copolymerization, which involves the addition of the monomers to the reaction mixture during the course of the reaction, in contrast to continuous polymerizations, where product is at the same time removed from the reactor. The easiest way to control the composition drift is to add the monomer mixture (pure or pre-emulsified) at a constant, low rate (starved conditions).²⁻⁸ If the polymerization takes place under starved conditions, the monomer concentrations are very low and this leads to low polymerization rates and long reaction times. A more advanced method was given by Hamielec et al.⁹ In this method the overall monomer ratio in the reactor is kept constant by adding the more reactive monomer (or both monomers) after charging all of the less reactive monomer and part of the more reactive monomer. Guyot et al. applied this method using on-line gas chromatography amongst others to the emulsion copolymerization of butadiene and acrylonitrile.¹⁰ In this way the reaction rate is not necessarily low, because the monomer concentrations can be higher. However, the overall monomer ratio in the reactor being constant does not necessarily lead to a constant copolymer composition over the whole conversion range. However, if one or both of the comonomers has a relatively high water solubility this method cannot be applied in a straightforward manner, because a constant overall monomer ratio in the reactor does not necessarily imply a constant monomer ratio in the locus of polymerization, the polymer particles. Arzamendi and Asua^{11,12} proposed a method to make homogeneous copolymers in emulsion at high monomer concentrations by adding the more reactive monomer via an optimal addition rate profile to the reaction mixture containing all of the less reactive monomer using a set of thermodynamic equations to calculate the actual monomer ratio within the polymer particles. Asua and co-workers applied this method to several emulsion copolymerizations.¹¹⁻¹⁴ The method was also applied by Van Doremale et al.⁷ to the emulsion copoly-

merization of styrene and methyl acrylate. This method and the starved conditions method were used to produce chemically homogeneous and controlled heterogeneous styrene-methyl acrylate emulsion copolymers.¹⁵ The effect of the monomer addition policy on the chemical composition distribution and therefore on the mechanical properties of these copolymers was investigated as well.¹⁶

Arzamendi et al.¹⁷ published results of simulations of reactions with optimal addition rate profiles for homogeneous terpolymers of styrene-methyl methacrylate-ethyl acrylate (S-MMA-EA). Urretabizkaia et al.^{18,19} calculated the optimal addition rate profile of the emulsion terpolymerization vinyl acetate-MMA-butyl acrylate (VAc-MMA-BA) on the basis of an analysis of results obtained from kinetic experiments under starved conditions and a kinetic model. Urretabizkaia et al.²⁰ also applied this technique to the emulsion copolymerizations of ethyl acrylate and MMA and also to terpolymerizations VAc-MMA-BA where the amounts of unreacted monomer in the reactor were monitored on-line with gas chromatography. By following a procedure similar to that needed for the calculation of an addition profile, the addition rates of the more reactive monomers could be adjusted on-line. Although this method allows more flexibility (because inhibition can in principle be detected⁹ and because the actual rate of polymerization does not need to be predicted, which is necessary in situations where the conversion is not monitored on-line), this method is not used here.

In absence of on-line control the optimal addition rate profile for a chemically homogeneous emulsion terpolymer can be determined with one of the four methods described below.

Methods for Determination of the Optimal Addition rate Profile

In all methods all of the less reactive monomer is added to the reactor before the start of the polymerization (or added at a predetermined, more or less arbitrary rate¹⁷), and also part of the more reactive monomer, such that the initially formed copolymer already has the desired composition. The remaining part of the more reactive monomer is then added at a rate such that the ratio of both monomers in the main locus of polymerization is kept constant. It is this addition rate that is unknown and that has to be determined.

All methods start out by calculating the optimal addition profile [amount of monomer i to be added as a function of conversion, $A_i^* = g_i(x_{\text{inst}})$] on the basis of monomer partitioning relations, reactivity ratios and mass balances. [An addition profile is the amount of more reactive monomer(s) to be added

as a function of conversion; an addition *rate* profile is the amount of more reactive monomer(s) to be added as a function of time; an asterisk* indicates that an addition (*rate*) profile is optimal.] This optimal addition profile has to be combined with the polymerization rate. If the correlation between conversion and time [$x_{\text{inst}} = f(t)$] or polymerization rate is known, the optimal addition *rate* profile [amount of more reactive monomer to be added as a function of time, $A_i^* = h_i(t)$] can be calculated. One of the main differences between the approach used by Asua and co-workers^{11-14,17,20} and the one used by Van Doremale et al.⁷ and Schoonbrood et al.¹⁵ is the method with which the optimal addition *rate* profile or conversion-time correlation is determined. There are four general possibilities:

Method 1. Completely empirical/iterative. This method was adopted by Van Doremale et al.⁷ and by Schoonbrood et al.¹⁵ The optimal addition *rate* profile is obtained via a short iteration procedure of semi-continuous experiments with addition *rate* profiles that become more and more optimal. The first addition *rate* profile is "guessed." The polymerization rate data obtained in the iteration procedure are not correlated to a physical quantity (this method is outlined in more detail below).

Method 2. Semi-empirical/iterative. This method was first applied by Arzamendi and Asua.^{11,12} After an initial guess of the rate of polymerization, a semi-continuous experiment is carried out, the rate (or more precisely the average number of radicals per particle, \bar{n}) of which is correlated with some physical quantity such as the volume fraction of polymer in the particles or the particle diameter. This correlation is then combined with the optimal addition profile to determine the optimal addition *rate* profile. It should be noted that the value of \bar{n} is mostly determined by more than one physical parameter including the monomer ratio in the polymer phase and in the aqueous phase. This means that this method still requires some iteration.

Method 3. Semi-empirical/noniterative. The rate of polymerization is determined in a series of independent seeded low-

conversion batch experiments, conditions of which correspond to various stages of conversion, and these rates are then combined to give the polymerization rate as a function of conversion and thus the conversion-time curve, which can then be combined with the optimal addition profile. This method was applied to the emulsion polymerization of styrene (S), methyl methacrylate (MMA), and methyl acrylate (MA), but the profile was not properly tested.²¹

Method 4. Completely theoretical. In this case the rate of polymerization is predicted beforehand on the basis of some kinetic model. In view of the "state of the art" in predicting the polymerization rate of a given emulsion polymerization system, this method is not generally applicable. Urretabizkaia and Asua^{18,19} applied this method, but, although their terpolymer seems to be homogeneous, from their experimental results with gas chromatography (GC) one cannot obtain information about the sensitivity of the homogeneity to errors in the addition *rate* profile or kinetics. Van Doremale et al.⁷ used high-performance liquid chromatography (HPLC) to show that small errors in the optimal addition *rate* profile can lead to heterogeneities [bimodal chemical composition distribution (CCD)] that cannot be picked up easily from cumulative co- and terpolymer composition data obtained with GC, ¹H-NMR, or differential scanning calorimetry (DSC), whereas it is very well possible with HPLC or gradient polymer elution chromatography (GPEC®, see part I¹). The fact that these techniques are not generally used is the reason why not much attention has been paid to the sensitivity of the optimal addition method to errors in the optimal addition *rate* profile. Related to this is the question whether slight errors, resulting in slight heterogeneities in the chemical composition distribution, have any effect on final product properties.¹⁶ Analysis with DSC of a bimodal copolymer of S and

MA by Van Doremale et al.⁷ revealed that this copolymer had exactly the same glass transition as the homogeneous product. In this work GPEC®/ELSD is used to check the homogeneity of the terpolymers.

Methods 3 and 4 have the advantage that they can be applied to systems that do not converge (easily) in an iteration procedure to find the optimal addition *rate* profile. Here method 1 will be applied to prepare a homogeneous emulsion terpolymer of S, MA, and MMA. The method is outlined in more detail below.

In a (emulsion) terpolymerization of S-MA-MMA, S and MMA are far more reactive than MA (see Part I¹) and have to be added according to a calculated addition profile so that the monomer composition in the polymer particles can be kept constant, while parts of these monomers and all of the less reactive monomer MA are added to the reactor before the polymerization starts. The procedure is as follows:

1. The amounts of S and MMA that are needed to produce the right terpolymer at the beginning of the reaction are calculated, and the optimal addition profile for both monomers is determined: $A_i^* = g_i(x_{\text{inst}})$, $i = \text{S, MMA}$. This correlation is unique and only depends on reactivity ratios and monomer partitioning. Only if the reaction is carried out in such a way that the experimental dependency of added amount of monomer i on instantaneous molar conversion corresponds exactly to the optimal calculated dependency $A_i^* = g_i(x_{\text{inst}})$, the fractions of all monomers in the particles will be constant and have the desired value, and the terpolymer will be homogeneous. To meet this condition one needs to find the optimal addition *rate* profile [$A_i^* = h(t)$]. An initial guess is used as a start.
2. The next step is to carry out a reaction with the addition *rate* profile and to determine the conversion-time curve, $x_{\text{inst}} = f(t)$. The conversion-time curve is then fitted with a polynomial.
3. The fitted, experimental conversion-time curve is combined with $A_i^* = g_i(x_{\text{inst}})$ to give a new addition *rate* profile $A_i = h(t)$. This new addition *rate* profile is then used in step 2), and the new conversion-time curve is fitted again, and combined with $A_i^* = g_i(x_{\text{inst}})$ until the new profile is not significantly different from the previous one.

The optimal addition profiles of the more reactive monomers are linked to the conversion, which means that they are linked to each other as well. So, if one of the monomer addition profiles is optimal, the other is as well and if the optimal addition *rate* profiles are determined with an iteration procedure, only one procedure is needed, and not two.

For this method a seed latex has to be used, in this case with the same overall composition as the terpolymer ($F_{\text{S}}, F_{\text{MMA}}, F_{\text{MA}} = 0.2, 0.3, 0.5$) that will be polymerized onto it. The particle diameter is very small, so that its contribution to the homogeneity/heterogeneity at the end of the reaction is negligible.

EXPERIMENTAL

The optimal addition profile [amount of a monomer i to be added as a function of conversion, $A_i^* = g_i(x_{\text{inst}})$] was determined with the model TRI-SEPS, described in Part I.¹ The input parameters are as given therein.

The experimental procedures and conditions are as follows. All experiments were carried out in a 1.3 dm³ stainless-steel reactor equipped with a turbine impeller.²² During the semi-continuous reactions the monomer feed (not emulsified) was added with two Dosimats 665 (Metrohm), which were computer controlled (Atari 1040 ST). The impeller speed was 250 rpm and the reactions were carried out at 50°C. The total amount of monomers added was such that all latices had a final solids content of 17%. The reagents used were: styrene (S), methyl methacrylate (MMA), methyl acrylate (MA) (the monomers were distilled under reduced pressure before use), sodium persulfate (SPS, initiator), *n*-dodecyl mercaptan (NDM, chain transfer agent), sodium bicarbonate (SB, buffer) (all p.a.), sodium dodecyl sulfate (SDS, emulsifier, 99%). Recipes: water 900 g; SDS 10 mmol/dm³; SPS 1 mmol/dm³; SB 1 mmol/dm³; S + MMA + MA (including polymer in the seed latex) 180 g ($F_{\text{S}}, F_{\text{MMA}}, F_{\text{MA}} = 0.2, 0.3, 0.5$); NDM 0.5 w % of monomers. A corresponding part of the NDM was added with the monomer feed. Conversion was measured gravimetrically. After each sample withdrawn from the reactor the decrease of the reacting mass was calculated and the addition rate of the monomers was corrected accordingly *during* the experiment. The seed latex had the same composition as the desired terpolymer and was prepared at 80°C under starved conditions.

RESULTS AND DISCUSSION

Determination of an Optimal Addition *rate* Profile with Method 1 for the System S-MMA-MA with $F_S = 0.2$, $F_{MMA} = 0.3$, and $F_{MA} = 0.5$

In Part I¹ the batch emulsion terpolymerization of S, MMA, and MA with F_S , F_{MMA} , $F_{MA} = 0.2, 0.3, 0.5$ and $M/W = 0.2$ was extensively studied with various techniques including ¹H-NMR and GPEC®. The model predictions with TRISEPS were in agreement with the experimental data. It was clearly shown that MA was by far the least reactive monomer. In this section results will be shown of an attempt to control the composition drift occurring in that system: by calculating the optimal addition profile with help of TRISEPS and determining the optimal addition *rate* profile with an iteration procedure with method 1. Furthermore, the general feasibility of obtaining an optimal addition profile with method 1 will be discussed.

In Figure 1 the elution chromatograms of the terpolymers produced in four consecutive iteration runs are depicted. For comparison, the elution chromatogram of the corresponding batch terpolymer [see Part I, Fig. 11)] is included. As can be seen, the third and fourth runs already give terpolymers that are homogeneous in comparison to the batch product and to the terpolymers of the first and second runs, although it should be noted that it is strictly impossible to tell from such a chromatogram whether a terpolymer is truly homogeneous, as outlined in Part I.

In Figure 2 the consecutive addition profiles of S are shown. The addition profiles of S and MMA are

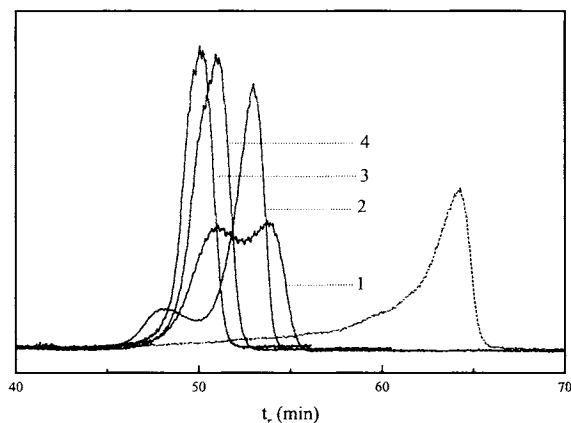


Figure 1. Elution chromatograms of terpolymers produced in consecutive iteration runs for the determination of the optimal addition *rate* profile (—) with the run numbers indicated, and of the corresponding batch terpolymer (· · ·, see also Part I, Fig. 11), as determined with GPEC®/ELSD. For experimental details, see Part I.

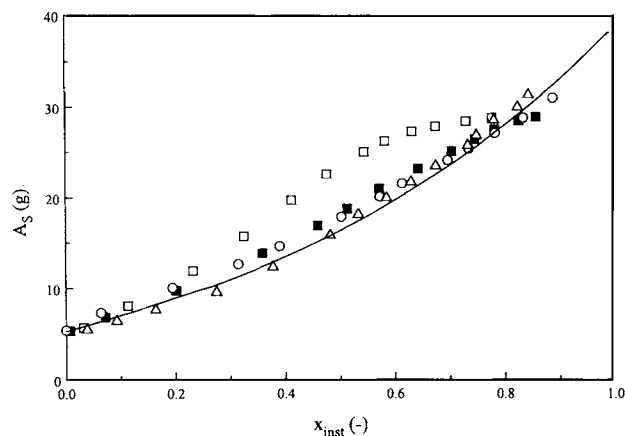


Figure 2. Representation of the consecutive experimental reactions in the iteration procedure to find the optimal addition *rate* profile for the terpolymer (0.2, 0.3, 0.5). Shown are the addition profiles of S [amount of S (A_S) versus instantaneous conversion (x_{inst})]: (□) first run; (■) second run; (○) third run; (△) fourth run; (—) calculated optimal addition profile.

coupled, so showing the addition profiles of MMA gives no additional information. It can be seen that the optimal addition profile is already closely approximated in the second run. Since Figure 1 shows that only the third and fourth runs gave “homogeneous” terpolymers, it can be concluded that GPEC® is a much more appropriate technique for indicating the homogeneity than plotting the addition profiles versus conversion, as in Figure 2.

A further indication for the homogeneity of the optimal addition terpolymer of fourth run is given in Figure 3, which shows the differential scanning thermograms of this terpolymer and the corresponding batch terpolymer. It can be seen that the batch terpolymer has two glass transitions ($T_g = 26$ and 73°C), but the optimal addition terpolymer only one ($T_g = 55^\circ\text{C}$), as expected from the elution chromatograms and the ¹H-NMR data of the batch product.¹

The Feasibility of Finding Addition Profiles and of the Convergence of the Iteration Procedure

The comonomer systems so far investigated in literature with respect to the optimal addition *rate* profile did not give rise to any problems, neither with respect to the feasibility of finding optimal addition profiles (i.e., what monomers should be added?) nor with respect to the feasibility of the iteration procedure to find the *rate* profile (i.e., does this type of iteration procedures always converge?). However, the question rises whether the method is

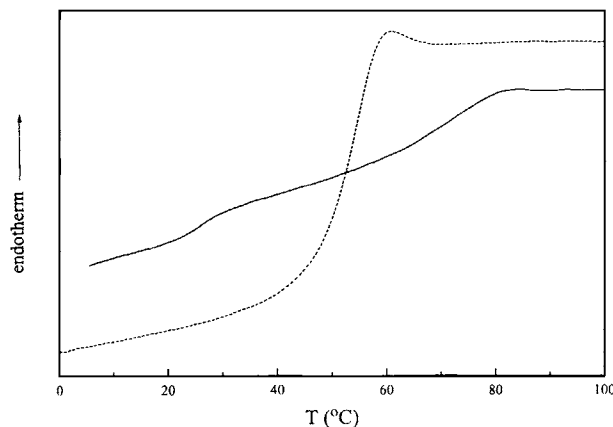


Figure 3. The DSC-thermograms of (—) the batch and (---) fourth-run optimal addition terpolymer.

always so straightforward. The answer is no, as shown below.

The nature of the addition profile is determined by the reactivity and the thermodynamic partitioning of the monomers, the two factors determining composition drift. If instead of S-MA-MMA the system S and MA with butyl acrylate (BA) instead of MMA is chosen, the iteration procedure is not as straightforward. In the latter monomer system S is the most reactive monomer and BA and MA are the least reactive monomers. In the binary copolymerization BA and MA are equally reactive: $r_{BA} = r_{MA} = 1$.²² BA is slightly less reactive towards S than MA (BA-S: $r_{BA} = 0.18$, $r_S = 0.95$,²³ MA-S: $r_{MA} = 0.19$, $r_S = 0.73$), but it is almost as water-insoluble as S. As argued in Part I, reactivity ratios mostly have a greater effect on composition drift than partitioning. In this case this is not true. For a recipe with a final solid content of 17% and $F_{MA} = F_{BA} = F_S = 0.33$ the result is that more MA than BA needs to be charged initially, because more MA is retained in the aqueous phase and therefore less MA is present in the polymer particles. However, if all of the MA is charged initially and BA and S are charged only partly, the calculated addition rate of BA is negative, because MA is slightly more reactive in the terpolymerization than BA. The conclusion is that neither BA or MA can be charged completely in the beginning. This seems to be a general phenomenon in cases where the more reactive monomer is also the more water-soluble monomer: if reactivity and partitioning counteract each other, it is possible that no monomer is simply the least "reactive" monomer (taking into account monomer partitioning).

The convergence of the iteration procedure according to method 1 after the optimal addition profile has been calculated seems to depend mainly on

the relation between monomer addition—and therefore composition of the monomer mixture in the reactor at any time—and rate of polymerization. The iteration procedure converges in a particular system (with monomer A as the more reactive monomer; more reactive means more reactive in copolymerization, so ignoring monomer partitioning effects), because the instantaneous conversion drops when more of A is added at a given conversion than should be added according to the optimal addition profile. The measured instantaneous conversion is then lower than it should be, the next calculated *rate* profile will be slower and the addition rate of A will be lower. So in the next run the overall concentration of A at any time will be lower, i.e., the addition *rate* profile becomes more optimal. The iteration procedure does *not* converge, if the rate of polymerization increases strongly when too much A is added, because then the next calculated addition *rate* profile will be even faster. Although A is the more reactive monomer, its propagation rate constant k_p may still be lower than that of the less reactive monomer, and in fact, that seems to be the rule of thumb in the most common comonomer systems: the higher the propagation rate constant of a monomer, the less reactive it is in copolymerization. This is the case for S with methacrylates, S or methacrylates with acrylates, S or methacrylates with vinyl esters. It was also shown to be true in the terpolymer system S-MMA-MA.²⁴ One exception to the rule is MA with VAc. Here MA is far more reactive,¹¹ but at temperatures below 54°C the homopropagation rate constant of MA²⁵ is higher than that of VAc.²⁶ Another interesting exception is the system MMA-VAc for which the average propagation rate coefficients were measured by Ma et al.²⁷ Although $k_{p,MMA} \ll k_{p,VAc}$ and the average propagation rate coefficient \bar{k}_p decreases strongly with f_{MMA} when $0 < f_{MMA} < 0.04$, it increases with f_{MMA} when $f_{MMA} > 0.04$. If the \bar{k}_p is the main factor determining the rate of polymerization, the above mentioned rule of thumb tells us that the behavior of the \bar{k}_p will favor convergence in most cases, since \bar{k}_p drops by adding more of the more reactive monomer.

CONCLUSIONS

A homogeneous emulsion terpolymer of styrene, methyl methacrylate and methyl acrylate was prepared with an optimal addition *rate* profile. The *rate* profile was determined by combining a simple model for monomer partitioning and the terminal model for describing the composition of co- and terpolymers. The method applied here was a completely

empirical/iterative method based on an iterative series of experiments. With this method the optimal addition rate profile could be determined fairly quickly and a homogeneous terpolymer could be prepared. The homogeneity/heterogeneity of the semi-continuous terpolymers prepared during the iteration procedure and the corresponding batch terpolymer were verified with gradient polymer elution chromatography (GPEC®). By using a simple example it was shown that finding the optimal addition profile is not always straightforward, especially if the effects of reactivity and monomer partitioning counteract each other.

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