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Modeling of emulsion copolymerizations Will it ever be possible?

Part III Conclusion

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Abstract

In this paper some of the challenging aspects of modeling kinetics of emulsion copolymerizations will be discussed, giving a retrospective and a perspective on the area. In order to describe the fundamental processes in emulsion polymerization, like entry of radicals, many basic kinetic and thermodynamic coefficients are needed but still lacking. The important parameters in modeling emulsion copolymerizations will be discussed and some of the latest progress in the area will be highlighted.

Introduction

Latex particles have a broad field of application including paints, coatings and adhesives. An interesting specialty area of application is that of controlled drug release and diagnostics using latex particles. In the production of latex particles almost exclusively the emulsion copolymerization technique is used. In
understanding the properties of these latex particles the understanding of the formation of the chains and the particles is of crucial importance\textsuperscript{1, 2}. Modeling emulsion polymerization is important for this understanding but the purpose of modeling emulsion copolymerizations can be manifold. First of all, modeling of polymerization processes can be used to save time in modern polymer production processes. By being able to reduce the number of experiments in order to investigate the effects of changes in reaction parameters one can save time and money. Furthermore the understanding of the mechanisms involved in the particular polymerization process is reflected in the models and through an iterative process modeling in itself is a tool to elucidate the mechanisms behind emulsion copolymerizations. Finally in process control polymerization models are often an integral part of the control system. The discussion on the possibilities of modeling emulsion (co)polymerization has been summarized periodically in the first two papers in this series\textsuperscript{1, 2}.

A comprehensive description of the emulsion (co)polymerization process can be found in the book of Gilbert\textsuperscript{3}. Recently an addendum in the form of a State of the Art article was published\textsuperscript{4}. A more general overview on emulsion polymerizations, including characterization and production can be found in the book of Lovell and El-Aasser\textsuperscript{5}. Textbooks on emulsion polymerization also exist\textsuperscript{6a, b}, showing that the area is definitely mature, despite the fact that still a lot of aspects are not fully understood.

The three stages of an ab-initio batch emulsion polymerization are; stage I, the particle nucleation, stage II, constant number of particles and more or less constant rate and stage III, decreasing rate because of reduction of the monomer concentration in the latex particles. Of these three stages mainly stage II and stage
The particle nucleation stage is the most difficult stage to model and not much new developments in literature are reported with the exception of the work of the group of Tauer which is discussed later in this paper.

Three aspects of the emulsion polymerization process are very important: the rate of polymerization, the produced molecular weight distribution and the composition distribution of the copolymer. On top of that the particle size distribution and morphology are of great importance, modeling of morphology of latex particles is outside the scope of this paper but an excellent description is available\textsuperscript{7}. The parameters that are important for these first three aspects are indentified in the following paragraph:

The rate of an emulsion polymerization is given by the following equation:

\[ R_p = -\frac{d[M]}{dt} = k_p [M]_p \bar{n} N_p/N_A \]

where \( R_p \) is the rate of growth, \( k_p \) the (average) propagation rate coefficient, \([M]_p\) the monomer concentration in the particles, \(\bar{n}\) the average number of radicals per particle, \(N_p\) the number of particles per unit volume of aqueous phase and \(N_A\) Avogadro’s number.

The degree of polymerization for linear systems in an emulsion polymerization is given by:

\[ DP = k_p [M]_p t_{growth} \]
where $t_{\text{growth}}$ is the average time of growth of a polymer chain in a latex particle, which in turn is determined by the rate of entry of radicals from the aqueous phase.

In case branching occurs and one wants to describe gel formation and branching densities in detail one has to resort to Monte-Carlo simulations.

In case we use two monomers we are dealing with copolymerization and a minimum of four different propagation steps can be identified

\[
\begin{align*}
-M_1 \cdot + M_1 & \rightarrow M_1 \cdot \\
-M_1 \cdot + M_2 & \rightarrow M_2 \cdot \quad r_1 = \frac{k_{11}}{k_{12}} \\
-M_2 \cdot + M_2 & \rightarrow M_2 \cdot \\
-M_2 \cdot + M_1 & \rightarrow M_2 \cdot \quad r_2 = \frac{k_{22}}{k_{21}}
\end{align*}
\]

(3)

Where $k_{ij}$ is the propagation rate coefficient for the radical of type $i$ with monomer $j$ (I and j being 1 or 2) and the reactivity ratios $r_1$ and $r_2$ are defined as the homopropagation rate coefficient divided by the crosspropagation rate coefficient for radicals of type 1 and type 2 respectively.

In the case of an emulsion copolymerization, the phenomenon of composition drift can occur. This means that the feed composition and the ratio in which the two monomers are incorporated in the copolymer are not equal. This can result in a drift in the monomer ratio in the reactor and therefore also a drift in the composition of the formed copolymer which can result in heterogeneous copolymers. The reactivity ratios (3) are combined with the local monomer concentrations in the latex particles to describe composition drift. One of the few
areas in emulsion polymerization that can be regarded as a more or less closed chapter is the theoretical and experimental description of monomer partitioning for the water insoluble monomers$^{3-6a,b}$. This is not true for the more water-soluble monomers. In that case, besides copolymerization inside the latex particles also aqueous phase copolymerization can take place simultaneously. This aqueous phase copolymer can affect entry, the surface composition of the latex particles and it can also remain in the aqueous phase affecting the reology of the complete latex. Increased interest exists in water phase copolymerization, using the more water soluble monomers, next to polymerization in the particles.

For the rate, molecular weight and chemical composition of emulsion copolymers therefore the following parameters are important: the propagation rate coefficients, the monomer concentrations inside the latex particles and entry of radicals (determining both $\bar{n}$ and $t_{\text{growth}}$). Besides these parameters also the rates of termination and transfer (both to monomer and to polymer) are important.

In this paper some of the problematic aspects of modeling kinetics of emulsion copolymerizations will be discussed, giving a retrospective and a perspective on the area. Emphasis will be given on the important general kinetic parameters like the propagation rate coefficients ($k_p$), the termination rate coefficients ($k_t$) and the transfer coefficients ($k_{tr}$), reactivity ratios and the different aspects of entry in emulsion (co)polymerization. At the end some new approaches in modeling emulsion (co)polymerization are discussed.

1. Propagation rate coefficients
It is now well established that in most cases the propagation rate coefficients that are obtained from solution or bulk polymerization experiments can be used in emulsion polymerizations. Also transferring reactivity ratios (the ratios of propagation rate coefficients) from e.g. bulk to emulsion systems is in general possible (when taking the monomer partitioning into account of course).

In our previous paper in this series we already reported on the artifacts that can result from GPC column broadening. These findings have now also been confirmed by an extensive theoretical study. This means that the propagation rate coefficients are chain length dependent only up to a limited chain length of maybe up to 10-20 units and not extending till very long chains. The chain length dependence of $k_p$ values is reviewed in combination with chain length dependent termination rate coefficients.

For the group of acrylate monomers always complications arise when applying pulsed laser polymerization in combination with SEC. Higher frequency lasers and the application of MALDI-ToF MS in determining molecular weight distributions without band broadening have helped in obtaining more and more accurate values for the propagation rate coefficients.

For water soluble monomers like acrylic and methacrylic acid also reliable data are available now. However with water soluble monomers complications arise because the $k_p$ values not only depend on pH but also on the monomer and polymer concentration in the aqueous solutions. A historic account of the developments in the understanding of acrylate kinetics has recently been published in a special issue of Macromolecular Rapid Communications, completely devoted to acrylate chemistry.
In conclusion, over the last 20 years an enormous improvement has been made in obtaining accurate propagation rate coefficients, even at short chain lengths. Improvement in the instrumentation and developments of better techniques have led to the situation that for modeling in emulsion copolymerizations the $k_p$ values are the least problematic parameters, at least for the long chain limit values. For the description of oligomer formation in the aqueous phase still many challenges remain (see paragraph on entry in emulsion copolymerization).

2 Termination rate coefficients

As is well established\textsuperscript{10} the termination rate coefficients are both conversion and chain length dependent. The methods to obtain these parameters have been rather indirect, however with the development of time-resolved EPR in combination with a laser pulse (SP-PLP-ESR), the decay of the radical concentration as a function of time can be directly observed, leading to the most accurate way of determining $k_t$ values\textsuperscript{17}. The detailed results obtained so far for diluted systems provide strong support for the composite model\textsuperscript{18}, in which termination rate coefficients, starting from small radicals, first considerably decrease, for example, with a power-law exponent of 0.5, and subsequently, for example, at chain lengths above 100, decrease to a weaker extent, for example, with the theoretically predicted power-law exponent of 0.16\textsuperscript{17}. So although for each system and set of conditions different $k_t$ values should be used, in effect good methods exist that can give these parameters and also the theoretical understanding of the termination process is as such that in modeling emulsion polymerizations this variable value of $k_t$ can be correctly taken into account. The rates of diffusion in the interior of a latex particle are of course much
lower and definitely a challenge lies in studying termination in highly viscous systems.

3 Transfer rate coefficients

In emulsion polymerizations transfer to monomer is an important process because it affects the number of radicals per particle. Transfer to polymer affects the structure of the produced polymer chains but also can affect the rate of reaction through slow re-initiation from the mid-chain radical. It is possible to take all these effects as a result of transfer to polymer in acrylates into account but one has to resort to Monte-Carlo simulations. Going back to the initial discrepancies regarding kinetic parameters in acrylate emulsion polymerizations the understanding of acrylate chemistry has dramatically improved. When modeling acrylate chemistry however, one has to take into account much more detailed kinetic steps therefore. The use of Monte-Carlo simulations is a very good option for including many reaction steps and with the ever increasing calculation speed of computers it still remains feasible to do these calculations typically in minutes.

4 Copolymerization parameters

In describing the chemical composition and sequence distribution of (emulsion) copolymers the ultimate model is generally accepted (see equation 3). Although it is relatively simple to determine the two reactivity ratios for such a system, using the correct statistical methods remains of great importance. For describing the average $k_p$ in copolymerizations, the penultimate unit model is
usually needed. In the penultimate model also the penultimate unit in the chain determines the reactivity of the radical and eight different propagations steps can be distinguished leading to six reactivity ratios. In emulsion copolymerizations often the aqueous phase polymerization is also important, especially when using more water soluble monomers like acrylic of methacrylic acid. Because we are usually dealing with oligomers, the long chain limit approximations for the copolymerization equations are no longer valid and preferential addition to the first initiator derived radical and chain length dependent propagation rate coefficients come into play. Also here Monte-Carlo simulations can be used. As has been mentioned before, the propagation rate coefficients of acrylic and methacrylic acid depend on pH and concentrations of both monomer and polymer. For this reason it is expected that also reactivity ratios applying to these monomers will depend on concentrations, conversion and feed ratios. A conventional way of determining reactivity ratios is to vary the feed composition and measure the copolymer composition at low conversion. Another way is to follow the feed composition as a function of conversion. In both cases it is likely that the data cannot be described with one set of reactivity ratios but instead a continuous change in reactivity ratios over the data might occur, rendering accurate determination of these parameters impossible. Recently a new method to determine reactivity ratios has been developed and experimentally tested. In this method the full chemical composition distribution (CCD) of the copolymer obtained at one feed composition is used to obtain reactivity ratios. Because the r-values are obtained from a single experiment the influence of for example the feed composition on r-values can be studied with this method. Both Huijser et al. and Daswani also used this method to study the influence of chain length on
(apparent) r-values by analyzing the CCD at each chain length. The method is
developed for the long chain limit of copolymerization. Huijser did not find a
chain length dependence of the r-values from chain lengths 15 and higher for
copolymerizations between styrene and butyl acrylate and other combinations\textsuperscript{22}. At shorter chain lengths Daswani did find chain length dependent apparent r-
values and also radical specificity for certain monomers\textsuperscript{21}. In this case we are
dealing with apparent r-values because the long chain limit equations are applied
to short chains.

It can be concluded that reactivity ratios usually can be determined easily and that
more data are needed for the first steps in the formation of oligomers, particularly
relevant for the processes that take place in the aqueous phase in emulsion
polymerizations. In order to describe the propagation kinetics the penultimate
model is needed, which requires PLP experiments and more complicated
molecular weight determinations. It turns out that the pulsed laser polymerization
method is more difficult to apply to copolymerizations because of GPC-
calibration problems and that because of the structure of the equations not all the
reactivity ratios can be obtained from fitting the average \(k_p\) as a function of
conversion\textsuperscript{1}. Also here Monte-Carlo simulations are needed to describe each
individual reaction step with their individual kinetic parameters.

5 Entry in Emulsion Copolymerization

One of the important processes in emulsion polymerization is the entry of radicals
into particles. One of the often applied and more or less generally accepted models
to describe entry is the model of Maxwell and Morrison\textsuperscript{23}. The essence of the
model is that the rate determining step of entry is propagation of oligomers in the aqueous phase up to a certain chain length (z-mer) after which the oligomeric radical irreversibly enters the particle. For entry in emulsion homopolymerization experimental data partly support this model, for emulsion copolymerization not many experimental data are available. In order to model the entry of radical in emulsion copolymerization, a study of the oligomers present in the aqueous phase is necessary. Recently a new method for separation and characterization of the oligomers present in the aqueous phase was developed. MALDI-ToF-MS was found to be a powerful technique in order to characterize the oligomers present in the aqueous phase. It was shown that the methodology works well, even though we are dealing with very small quantities of oligomers and the possibility of mass discrimination in MALDI-ToF-MS. One advantage of the method applied to oligomers in the aqueous phase is that they already have a relatively narrow molecular weight distribution, necessary to limit mass discrimination.

The chemical composition distribution (CCD) and the molecular weight distribution (MWD) of cooligomers present in the aqueous phase as well as on the particle phase is determined from the MALDI spectra. It turns out that there is not such a sharp boundary between the oligomer distribution in the aqueous phase and that in the particle phase as indicated by the Maxwell-Morrison model but that the results are more in line with the models put forward by Sundberg which deals with partitioning of each of the oligomers present in the aqueous phase towards the particle phase. The produced oligomers (as theoretically described by the Monte-Carlo simulations) will redistribute over the water phase and particle phase. The resulting oligomer distribution in the aqueous phase is now studied. At very short chain lengths all the produced oligomers can be traced back in the
aqueous phase. As the oligomers chain-extend at some point part of the oligomer distribution will become surface active and disappear from the aqueous phase. This can be observed by a change in the average chemical composition (F, this with respect to the theoretical F from the Monte-Carlo simulations). With further increase in chain length the full CCD is surface active (little change in F, this region corresponds to the z-mers in other models), followed by again a part of the CCD being surface active leading to a change in F. Finally with further chain length increase, the oligomers gradually become insoluble (j-crit mers). Basically the changes in F can be described by for example the concept of Hydrophilic Lipophilic Balance (HLB values). The CCD travels through the HLB window, the HLB values where the oligomers are good surfactants. There where only a part of the CCD is adsorbed on the particle surface a change in F can be observed. After this HLB window the region of insolubility sets in\textsuperscript{21}. So with Monte-Carlo simulations the production of oligomeric radicals in the aqueous phase can be modelled and in a next step one could apply partitioning coefficients on these individual oligomeric radicals to describe the entry process. The partitioning coefficients could be based on the HLB values or solubility parameters or on free energy differences as reviewed in ref \textsuperscript{24}.

In the same context\textsuperscript{21} a separate study of influence of pH on ionic monomer combinations was done. It is observed that with increasing the pH, incorporation of acidic monomer in the particles reduced while the critical chain length of the entering cooligomer is increased.

Because the majority of the cooligomers studied were terminated by disproportionation, the oligomer distribution can be regarded more or less to be representative of the radical distribution.
6 New approaches in modeling emulsion polymerizations

Klaus Tauer started a discussion a few years ago whether the common deterministic modeling approach is capable of predicting several phenomena in emulsion polymerizations, for example nucleation and variable lag times\textsuperscript{27}. In this discussion he challenges the deterministic kinetics of emulsion polymerization and he propagates the use of molecular modeling and the application of multiscale integration techniques. He shows several examples of variable lag times depending on temperature where the experiments were all done by the same person in the same reactor. One step further, the reproducibility of emulsion polymerizations should even be improved more if the human factor is ruled out completely and a robot performs the experiment in so-called high throughput synthesis set-ups like the one from Chemspeed\textsuperscript{28}. Also there, variable lag times were observed but could partially be explained by imperfections in the system and inhibition due to different levels of oxygen in the system. In both studies the nucleation stage is the indeterministic part where small gass bubbles, dust and impurities can affect the nucleation stage. Tauer suggests that those systems that have a higher driving force show less scatter.

Conclusions

It has been shown in the previous paragraphs that although the knowledge on basic kinetic parameters has definitely improved over the last 15 years, the complexity has also increased. The approach where the formation of each individual chain and formation and growth of each individual latex particle is
modelled seems to be necessary, requiring indeed multiscale integration techniques. However, too much mystification of these processes is not necessary\textsuperscript{27}, because we have to realize that still a lot of aspects are unknown. In the first paper in this series\textsuperscript{1} molecular weight distributions were predicted correctly with completely wrong (but compensating) kinetic parameters. Despite all the progress and the involvement of the IUPAC working parties in obtaining reliable rate coefficients, still old and incorrect parameters are used in modeling; for example a paper in 2011 on emulsion polymerization of butyl acrylate, where the activation parameters for propagation from 1998 were used\textsuperscript{29} instead of the IUPAC values\textsuperscript{30} and transfer to polymer and the resulting kinetic effects\textsuperscript{19} were completely omitted, still is capable of predicting the rate of polymerisation!

So the answer to the question: 

\textit{Modeling of emulsion copolymerizations, will it ever be possible is ?}: is, yes it will be possible up to very high levels of accuracy if individual chains and particles are modelled. Monte-Carlo simulations seem to be a good option, where Monte-Carlo simulations as the core of a parameter optimization routine (where the Monte-Carlo simulation is done many times within one parameter optimization run) is even possible without running in calculation time problems\textsuperscript{21}. In the models very accurate parameters can be used, where most development is still needed in the understanding of physical phenomena like nucleation and partitioning.

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