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III. Heterogeneous Polymerization

Modeling of Emulsion Polymerization, Will It Ever be Possible ? Part-2: Determination of Basic Kinetic Data Over the Last Ten Years

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Summary: Modeling of Emulsion polymerization processes is based on the knowledge of fundamental kinetic and thermodynamic parameters. The most important kinetic parameters are propagation and termination rate coefficients. Ten years ago a paper has been published with the title ''Modeling of Emulsion Polymerization, will it ever be possible?''. The paper expresses serious doubts whether the different kinetic parameters will ever be available for general industrial recipes containing several monomers. In this paper the developments in the last 10 years regarding pulsed initiation polymerization (PIP) and other techniques regarding the determination of especially the kinetic parameters will be discussed. Amongst the areas where progress can be seen is the understanding of acrylate systems and water soluble monomers. New techniques like MALDI-ToF MS and time resolved electron spin resonance have strongly contributed to the area. Also the puzzling effect of chain length dependent propagation is discussed. Finally an answer will be given to the title question.

Keywords: emulsion polymerization; kinetics of polymerization; modeling; pulsed laser polymerization; size exclusion chromatography

Introduction

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.

Ten years ago a rather grim picture of the possibilities of complete modeling of emulsion copolymerization was given.[1] The purpose of this paper is to review the developments over the last 10 years in the understanding of the fundamental aspects of free radical polymerization and emulsion (co)polymerization, necessary to be able to model emulsion polymerization. In this paper a special emphasis is given on the work that has been done in the context of the European Graduate School on Microstructural Control in Radical Polymerization, a collaboration between groups of the University of Amsterdam, the Eindhoven University of Technology, the University of Clausthal and the Georg August University in Göttingen.

An excellent overview on the kinetics of emulsion polymerization can be found in

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the book of Gilbert.[2] A more general overview on emulsion polymerizations, including characterization and production can be found in the book of Lovell and El-Aasser.[3]

A textbook describing the essentials of emulsion polymerization in a relatively easy way was released in 2005.[4]

Recently Gilbert was suggesting that most of the outstanding problem in emulsion polymerization were solved.[5] Although this might be a too bold statement, indeed some major steps have been made and the possibilities of modeling have greatly improved.

One of the most difficult parts to model but also to experimentally reproduce is particle nucleation. This paper will not deal with this difficult issue because in many cases seeded emulsion polymerization is used, in which case only particle growth has to be described.

First of all the basic kinetic equations governing emulsion (co)polymerization rate and development of molecular weight should be made explicit to get an overview of the kinetic parameters needed in modeling these processes.[4]

Particle growth in emulsion homopolymerization is determined by the following equation:

$$R_p = -\mathrm{d}[M]/\mathrm{d}t = k_p[M]p\,\tilde{n}\,N_p/N_A \qquad (1)$$

where R_p is the rate of growth, k_p the (average) propagation rate constant, $[M]_p$ the monomer concentration in the particles, $\tilde{n}$ 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 local monomer concentrations can be determined by swelling experiments. The propagation rate coefficients are determined with pulsed laser polymerization. The number of particles can be determined by determining particle size. Several techniques are available but most commonly used are dynamic light scattering and electron microscopy.

N_p is determined in the nucleation stage. In the case of micellar nucleation the flux of radicals generated during the nucleation stage and the number of micelles present determines the number of particles at the end of the nucleation stage.

The average number of radicals per particle is determined by the rate of entry of radicals, the rate of exit of radicals (often dominated by transfer to monomer processes) and the termination rate coefficients.[4]

In the case of an emulsion <u>co</u>polymerization and applying the pseudo-homopolymerization rate approach, the rate of growth is given by:

$$\begin{aligned} R_p &= -\mathrm{d}[M]/\mathrm{d}t \\ &= \langle kp\rangle[M]_{p,tot}\,\tilde{n}\,N_p/N_A \qquad (2) \end{aligned}$$

where $\langle k_p\rangle$ is the average propagation rate constant and $[M]_{p,tot}$ the total monomer concentration in the particles. 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. In the case of an emulsion copolymerization there is an additional effect of monomer partitioning on the composition drift. When the water solubility of the two monomers differs, one of the monomers is held back in the aqueous phase which can result in an enhancement of the composition drift. In some special cases (where the more reactive comonomer is also the more water-soluble comonomer) the water solubility can partially compensate composition drift. So if reactivity ratios are obtained by analysis of emulsion copolymerizations one can either use the concept of apparent reactivity ratios or introduce the monomer partitioning equilibria and use the reactivity ratios obtained in homogeneous media.[4]

The quality of the predictions of kinetics and microstructure has improved very much due to the improvement of the methods of obtaining kinetic and thermodynamic parameters relevant to homogeneous and heterogeneous polymerizations. This development will also have its impact on the possibilities of designing intelligent process strategies aimed at obtaining well-defined products with better properties.

In this paper some of the problematic aspects and their developments in the past ten years of modeling emulsion copolymerizations will be discussed. Five of these problems are highlighted under separate headings.

Important Parameters in Emulsion Copolymerization Modeling; Some Developments in the Past Ten Years

Chain Length Dependent Propagation Rate Coefficients

The propagation rate coefficient is one of the most important parameters in modeling both homogeneous and heterogeneous radical polymerizations. The Pulsed Laser Polymerization (PLP) method followed by size exclusion chromatography (SEC) has led to a tremendous improvement of obtaining propagation rate coefficients.[6,7] Still some problems with the method exist. One of them was that, although usually unreported, the propagation rate coefficients showed a slight dependence on the laser frequency and thus seemed to be chain length dependent. At least part of this effect now seems to be linked to the SEC method as will be described in this paragraph.

Size exclusion chromatography is crucial in obtaining kinetic parameters in radical polymerization, examples are; to extract propagation rate coefficients from SEC traces of polymer obtained in pulsed laser polymerization[6,7]; to obtain transfer to monomer rate coefficients[8]; transfer to polymer rate coefficients[9]; termination rate coefficients[10] and information on many other aspects of the polymerization mechanism.

The accuracy of the obtained kinetic parameters relies on the chosen model to link the kinetic parameters to the molecular mass distribution, the calibration of the SEC system and the quality of the obtained SEC separation.

In the extraction of propagation rate coefficients often the low molecular mass inflection point is proposed as the best measure of the propagation rate coefficient[11] although under specific conditions the peak maximum should be taken.[12]

The calibration of the SEC system is often a weak point in the analysis. Often one relies on the published Mark-Houwink parameters for the system studied although also more absolute calibration methods like light scattering or viscosimetric measurements are used. In some cases complications occur because of branching phenomena, both in the polymer samples used to calibrate the system and in the studied samples (see for example the complications with branching in polyacrylates[13]). In the analysis of molecular mass distributions of copolymers the calibration is even more complicated and several possible approaches exist. Davis *et al*.[14] suggested to use a linear interpolation of the calibration curve for the copolymer by using the calibration curve for the homopolymers. This turned out to be a good approximation for the system Sty-MMA. A better and more accurate option would be the use of Mark-Houwink relationships, which relate the average copolymer chemical composition to the hydrodynamic volume.[15,16] However, the determination of this relationship requires well characterized copolymer standards which are not readily available. A third option and perhaps the best with regard to SEC would be the use of a triple detector setup which in principle results in an absolute molar mass determination (only true for ideal statistical copolymers). Calibration of the triple-detector setup however, is tedious and time consuming, but nevertheless the method has been used to evaluate copolymer kinetics for several systems.[17–19]

In the past years the kinetic models have been refined and also the calibration methods gained in quality. However with the increasing amount of detail one tries to obtain from the SEC traces also the quality of the SEC separation itself comes into play.

The point that column broadening is depending on hydrodynamic volume and thus on molecular mass of the polymer is really posing a big problem in detailed analysis of (co)polymers with SEC.

In the past four years a discussion appeared in literature on the extraction of propagation rate coefficients (k_p) from SEC traces obtained with the pulsed laser polymerization method (PLP).[20–24]

The use of MALDI-TOF mass spectrometry in obtaining accurate molecular mass distributions has been investigated by Staal and Willemse.[23] By the proper choice of the matrix in MALDI-TOF MS the effects of mass discrimination can be minimized, also for broad samples.[23]

Mass discrimination is caused by a different tendency of polymer molecules to transfer to the vapour phase. This tendency can be dependent on molar mass and chemical composition of the (co)polymers. If we investigate homopolymers, as is done in this example, we only have to worry about actual mass discrimination. This effect manifests itself most clearly in a tilting of the distribution on one side (usually the low molecular weight side, see Figure 1). In case of an analysis over a small range of molecular weights this effect will usually not show. That is why fractionation of MALDI samples is advised. Sometimes even with broad samples the effect of mass discrimination is limited. The combination of polymer and matrix is crucial in the occurrence of this effect. In the past some puzzling effects of laser frequency on the obtained propagation rate coefficients were observed.[20] We now believe the effect can be attributed to band broadening in SEC. When mass discrimination occurs (like in Figure 1) it can not obscure the difference in the width of the peak between MALDI and SEC because it is not logical that band broadening would lower the intensity of the peak on both sides of the peak maximum to the same extend. Note that in Figure 1 the SEC trace is obtained from a UV(254 nm) active end group. The backbone is not UV active. Under these conditions the SEC and the MALDI represents the same distribution, a number distribution, and can be easily compared.

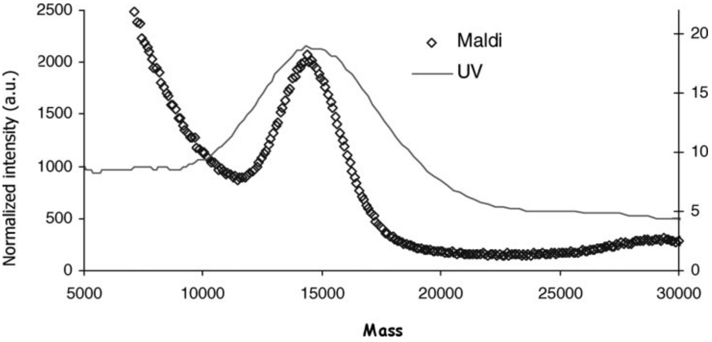

Figure 1.
MALDI-ToF MS spectrum compared to the SEC analysis (UV signal) of the same sample of PMMA obtained in a PLP experiment at 0 °C and 10 Hz in bulk, using benzoin as photoinitiator. MALDI-ToF-MS analysis was carried out on a Voyager DE-STR from Applied Biosystems. The matrix used for the analysis is trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile. The matrix was dissolved in THF at a concentration of 40 mg · ml^{-1}. Silver trifluoracetate (Aldrich, 98%) was used as cationization agent and was added to THF at typical concentrations of 1 mg · ml^{-1}. The polymer was dissolved in THF at appr. 2 mg ml^{-1}. In a typical MALDI-ToF-MS experiment the matrix, salt and polymer solution were premixed in a ratio of 10:1:5. The premixed solutions were handspotted on the target-well and left to dry. All mass spectra were recorded in the reflector mode and are the result of approximately 5000 individual laser shots. Mass spectra were baseline corrected with the advanced baseline correction mode from the Data Explorer© software from Applied Biosystems.

In order to look at chain length dependent effects, a series of polystyrene standards was measured, both with MALDI-TOF and SEC. From the comparison it is clear that the broadening effects are molar mass dependent (Figure 2). If one uses the low molecular mass inflection points from both SEC and MALDI, the difference increases with increasing molar mass.

It turns out that MALDI-TOF MS is very powerful in obtaining absolute molar mass distributions without any broadening effects. Nevertheless is has to be stressed that mass discrimination with MALDI needs careful checking for each and every individual case. In comparing the two techniques it turned out that SEC introduces artifacts in the form of molecular mass (chain length) dependent column broadening. If we look at Figure 2 we have to realize that in the extraction of k_p data from the distributions the low molecular weight inflection points are used. It can be clearly seen that a difference occurs. The differences are negligible if the maximum if the distribution is used (which in some cases is done). This effect has initially been overlooked in the extraction of propagation rate coefficients from PLP/SEC data, which in turn has led to strange frequency effects

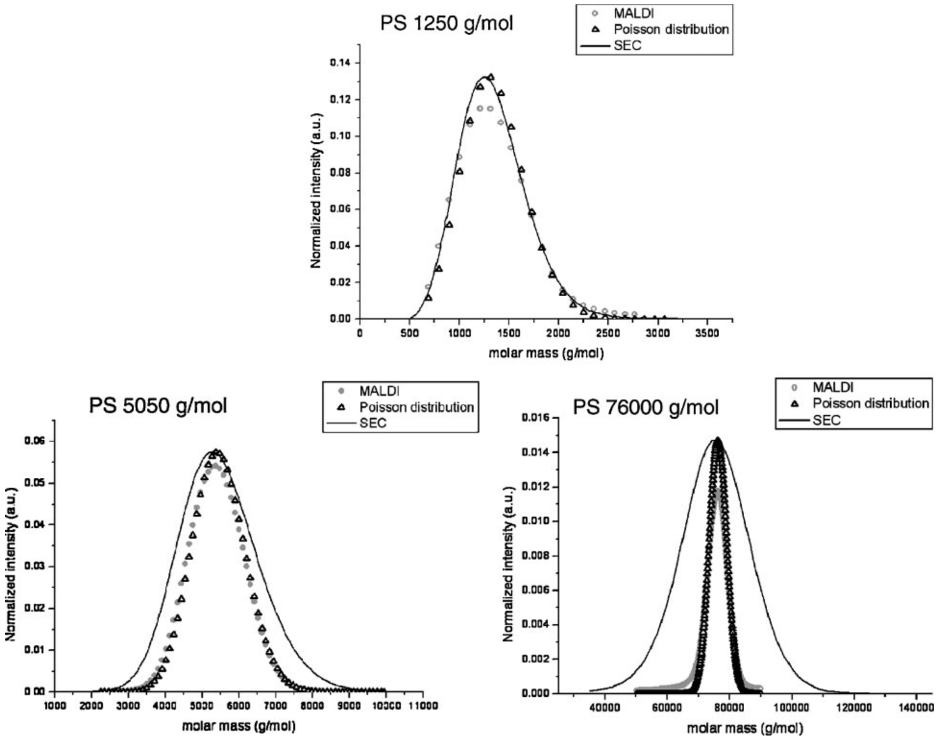

Figure 2.

Comparison of molar mass distributions of polystyrene obtained with MALDI and SEC, showing the increase in broadening as a function of molar mass. Also shown is a Poisson distribution that is describing the expected molar mass distribution of these samples very well. PS is the molar mass at the peak maximum. SEC analysis was carried out on a Viscotek Triple-SEC setup consisting of a Gynkotek pump and four mixed-B columns (Polymer Laboratories) with THF (Biosolve, Ar-stabilised, 99.8%) as solvent running at 1.0 ml · min^{-1}. Calibration curves were constructed using both polystyrene (Figure 2, PS, molar mass range from 580 to 1.10^{6} g · mol^{-1}) and polymethylmethacrylate (Figure 1, PMMA, molar mass range from 650–1.5.10^{4} g · mol^{-1}) standards (Polymer Laboratories) of narrow polydispersity. For evaluation of the molecular weight distributions the differential refractive index was used as a concentration detector for polystyrene. In Figure 1, for PMMA the UV signal (254 nm) was applied. The polymer was dissolved in THF at typical concentrations of 2 mg · ml^{-1}.

in the pulsed laser polymerization experiments.[20] Also this frequency dependence was interpreted as a chain length dependency of the propagation rate coefficient.[21,22] By using the MALDI-TOF data the chain length dependency at higher chain lengths more or less disappears (Figure 3) This has been shown for Sty and MMA in a temperature range from −20 °C up to 60 °C.[23]

Also recently for copolymerization a similar conclusion was reached in terms of chain length independency of reactivity ratios (at higher chain lengths).[24]

From Figure 2 it can clearly be seen that the extend of column broadening is molar mass dependent. This forms the basis of the introduced artifact in terms of apparent frequency dependence of the propagation rate coefficient, also interpreted as a chain length dependent k_p- value[21,22] (see Figure 3). After the MALDI-TOF publication[23] the group of Olaj corrected for the column broadening.[25] Initially they used a constant column broadening factor ($\sigma = 0.05$), leading to the same conclusions as before. Later Schnöll-Bitai introduced a method to correct for chain length dependent broadening. The correction reduced the extend of chain length dependence of k_p but it did not completely disappear.[26] Of course the correctness of the broadening function is the determining factor. Also other authors used a constant broadening factor for correction of PLP data.[27,28]

It has to be noted that the extend of column broadening depends on the quality of the SEC equipment and in particular the quality of the column or column set. The frequency dependence of k_p was noted in many laboratories but the extend may differ because of the use of different columns. We were able to reproduce the effects seen by Olaj with several of our column sets but even with an optimized set of columns the effect remains.

Also in Figure 2 a consistent picture emerges where the molar mass distributions obtained with MALDI-TOF closely follow a Poisson distribution. Although some mass

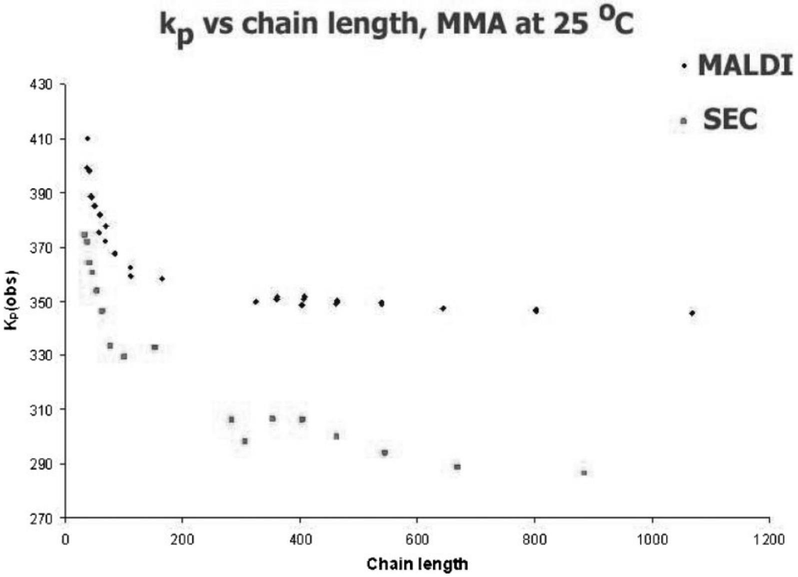

Figure 3.
Propagation rate coefficients of methyl methacrylate at 25 °C obtained through pulsed laser polymerization in combination with MALDI-TOF MS and SEC (DRI) showing that k_p is constant at high chain lengths (MALDI) and that SEC introduces an apparent chain length dependence at high chain lengths due to the chain length dependent broadening effects present in SEC (after reference 23).

discrimination effects can not be excluded, it is impossible to imagine that for each polymer standard a mass discrimination effect would lead to a symmetrical narrowing, a depression of the flying tendency, both on the high molecular mass side of the peak and on the low molecular side, as discussed before.

Having observed the effect of a molar mass dependent column broadening, the question is whether other data support this view.

If we look at the different methods to correct for column broadening several broadening functions are put forward. For example Tung[29] introduced as one of the first a column broadening function, later Hamielec[30] introduced an improved expression. There are many examples in literature where column broadening was studied over a wide range of molar masses and where the column broadening factor has shown to be molar mass dependent. For example Nguyen[31] observed that the axial dispersion constant for polystyrene samples on μStyragel columns increased with smaller elution volume (thus higher molar masses). Omorodion and Hamielec observed molar mass dependent dispersion coefficients for aqueous SEC on Dextran standards,[32] again more column broadening at higher molar masses. Several other examples of molar mass dependent column broadening effects can be found in literature.[32]

Theoretically it is expected that column broadening is molar mass dependent.[33]

Column broadening is supposed to be consisting of several contributions including the diffusion coefficients of the polymer sample which obviously depends on the polymer molar mass.[34] The extend of column broadening and sometimes even the direction of the molar mass dependency of column broadening depends on many factors like flow rate, column quality, extracolumn broadening, contribution of adsorption effects etc.[34] For that reason column broadening has to be determined for each individual SEC set-up and in case of broad molar mass samples or when using a wide range of molar masses as is the case in studying molar mass effects (on k_p for example), also as a function of molar mass.

The main discussion resulting from the issue of chain length dependent column broadening in PLP experiments was focusing on long chain effects, the chain length dependence of propagation rate coefficients at short chain lengths is an undisputed phenomena, a recent overview of these effects is given in reference.[35]

In 2006 and 2007 several papers from other groups appeared discussing the abovementioned effects.[36–42]

Whether one can rely on MALDI-ToF MS as the method of choice for the determination of molar mass distributions and the extraction of kinetic data is still a matter of debate but the number of consistent results with respect to kinetic constants[23,24] and reactivity ratios[43] determined with this technique is growing fast.

The two options to circumvent the above described problems are either to correct for chain length dependent band broadening in SEC according to methods described by several authors[39–41] or resort to the use of MALDI-ToF MS, possibly in combination with SEC where fractions of the SEC are analyzed with MALDI in order to get the information and the amounts of chains of a particular length by the mass detectors in SEC (for example practiced in the group of Kowolik in Karlsruhe, describes elsewhere in this volume).

Transfer to Polymer in Acrylate Polymerizations

All PIP results for acrylates at temperatures of 30 °C and higher show broad featureless molecular weight distributions, frequency dependent inflection points and concentration dependent solution PLP results.[44] The PLP experiments of acrylic acid show similar problems.[45] At the higher temperatures (>30 °C) in some cases also an effect of pulse energy and photoinitiator concentration was observed.[44] There were many speculations about the origin of the problems. Speculations included transfer to monomer and transfer to polymer.

Lovell[46] showed that transfer to polymer both by inter- and intramolecular chain transfer to polymer occurs extensively at the higher temperatures and especially in solution. In solution, because of the ratio monomer to polymer in the coil, intramolecular transfer is favoured.[46] The reactions that can occur are summarized in Figure 4.

Most of the side reactions will render smaller apparent k_p values at higher temperatures giving a downwards deviation from the Arrhenius plot as indeed is observed.[44] In addition it can not be excluded that proton abstraction by initiator derived radicals can occur which would explain the effect of pulse energy and initiator concentration previously reported for methyl acrylate.[44]

Slow reinitiation of the backbone radical is the dominating effect and is affecting the overall kinetics of propagation. This last explanation is in line with the work of Asua et al.[47,49] because they needed a lower average k_p value to describe their actual polymerization kinetics of butyl acrylate in emulsion polymerization. The transfer to polymer process renders a very stable radical that affects the overall propagation rate although the final number of branches is only modest (usually a few percent). The EPR experiments of Yamada on methyl acrylate also support this explanation. He was able to show the occurrence of the mid-chain radical and also the occurrence of β-scission[50–52] in the temperature range 40–85 °C. So a non-linear Arrhenius plot can be explained by the contribution of the slow reinitiation of the backbone-derived radical at higher temperatures.

This however means that the results of PLP experiments at higher temperatures will depend on the radical pulse frequency. This is because a smaller fraction of the chains will be subject to transfer to polymer at higher frequencies. Recently experiments were done at 200 Hz with a pulsed lamp (normally the PLP experiment does

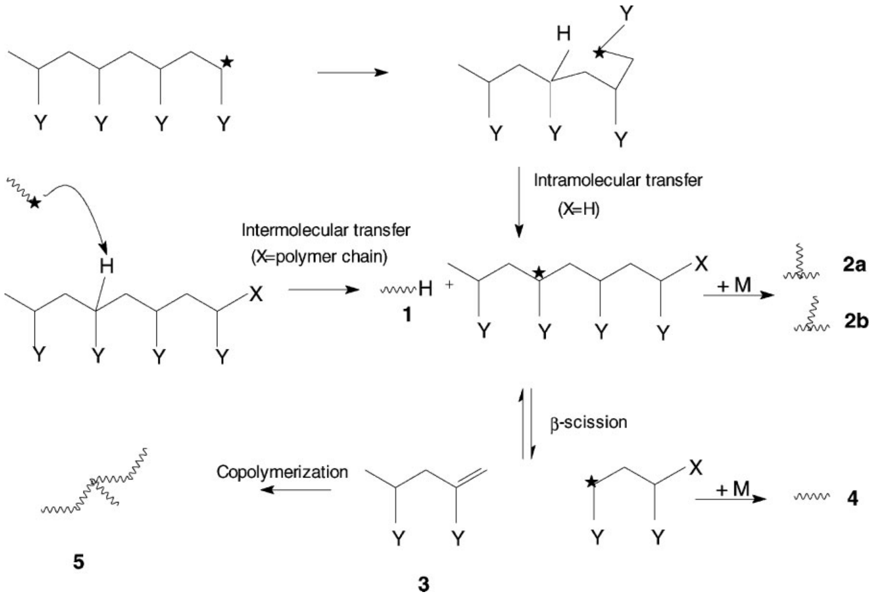

Figure 4.
Reactions that can occur during a pulsed initiation experiment with acrylates. Y is an acrylate ester side group (or the acid itself). Intramolecular transfer to polymer leads to a branched chain (2a). Intermolecular transfer to polymer results in a shorter chain (species 1) and reinitiates a dead polymer chain and results in branched chain 2b. The backbone radical can undergo β-scission that results in two shorter chains (species 3 and 4). The unsaturated species 3 can undergo copolymerization resulting in species 5 (after ref. 13).

not go above frequencies of 100 Hz), which show that the linearity of the Arrhenius plot can indeed be stretched to higher temperatures.[49]

This explanation is now fully covering the problems that were addressed in the first paper in this series,[1] showing that great progress has been made in the area of understanding acrylate radical polymerizations.

The pulsed laser polymerization of cyclohexyl acrylate[53] can now be fully understood with the proposed mechanism,[13] showing that also fragmentation of the mid-chain radical species can occur under PLP conditions.

Finally with the introduction of the coupling of PLP and EPR direct evidence for the occurrence of the mid-chain radicals during PLP experiments has been found.[54]

In 2004 reliable IUPAC values for the propagation rate coefficients of butyl acrylate were published.[55]

Termination Rate Coefficients as a Function of Chain Length and Conversion

In 1986[56] with the advent of powerful UV lasers a new method was introduced which is capable of determination of the propagation rate coefficient (k_p) and the termination rate coefficient (k_t); time resolved pulsed laser polymerization (TR-PLP). In this method the conversion of the monomer is followed as a function of time (t), for example with a near-infrared detector after the generation of radicals with a short laser pulse. The monomer concentration C_M as a function of time t is given by (k_t chain length independent):

$$\frac{C_M}{C_M^0} = (2 \cdot k_t \cdot C_R^0 \cdot t + 1)^{\frac{-k_p}{2 \cdot k_t}} \tag{3}$$

with C_R^0 the radical concentration immediately after laser pulse absorption which can be calculated from the absorbed laser energy if the quantum yield is known. With known C_R^0 the value for k_t and thus for k_p can be inferred. A combination of the obtained ratio k_p/k_t with independently determined k_p data, for example obtained with the PLP/SEC method gives k_t values.

In principle if k_t is chain length dependent, the traces obtained with the TR-PLP method should contain this information. In general it was observed that the fits of eq. 3 to the traces showed a trend in the residuals.

Chain length dependent termination coefficients could cause the observation that eq. 3 does not gave a satisfactory fit. Equation 3 has been derived in a way that a constant k_t is assumed. If a chain length dependent and thus time dependent k_t is introduced in the derivation a much more complicated equation results but it is possible to solve this problem. From eq. 3 also trends in k_t should be visible by fitting parts of the traces with different k_t values. Unfortunately the quality of the signals is not really sufficient to obtain reliable data; in order to obtain termination rate coefficients the second derivative of the curve of monomer concentration vs time needs to be analyzed. This leads to a noise problem. De Kock realized this and developed a new method where the molecular mass distribution of the polymer formed in a single pulse PLP experiment is analysed.[57] Because at that time the intrinsic problems with chain length dependent broadening in SEC were not realized (see paragraph 1) the obtained data might be unreliable. A combination with MALDI-ToF MS might prove to lead to very reliable data.

One of the improvements to these methods is to account for the fact that the photoinitiator derived radicals are not always equally reactive.[58] Avoiding this effect improved the fits of the TR-PLP traces with equation 3.

The measurement of chain length and conversion dependence of the termination rate coefficients has dramatically improved with the introduction of the ESR technique in monitoring the radical concentrations in the single laser pulse polymerisations.[59] Both in the work of De Kock and in the work of the group of Buback a composite behavior was observed for the chain-length dependence, in that the chain length dependence is more pronounced for shorter than for longer radicals.

Transfer to Polymer Influencing Entry and Exit in "Hairy" Particles

The elucidation of the important effect of transfer to polymer in acrylates (see paragraph 2) also has led to an improvement of the understanding of modeling acrylate containing recipes of emulsion polymerisations.[47,49]

Recently the effect of chain transfer to polymer in hairy particles has been discovered. Particles electrosterically stabilized with polyacrylic acid (PAA) chains seems to show deviating kinetic behaviour. The proton abstraction on the PAA chain is leading to a mid-chain radical which is slow to propagate but quick to terminate and thus is leading to an additional radical loss mechanism causing deviating kinetics.[60]

Additional to that is the possible occurrence of β-scission (see Figure 4) that could lead to secondary particle formation.[61] One remark to be made at this point is that the described experiments are done at 323 K. It remains to be questioned whether extensive β-scission occurs at this temperature.[62]

The described effects are not only claimed for PAA stabilized systems but also for poly(ethylene oxide) containing lattices. As such the importance of this effect for may industrial emulsion polymerization recipes could be envisaged and is claimed.

Recently it was shown in a convincing way that as soon as chain transfer agents are added many of the described effects in paragraph 2 dissapear.[63] The reason for that is that chain transfer agents are capable of reacting with the mid-chain radicals and thus taking over radical activity, rendering a more reactive radical and a terminated (mid chain radical) chain. As such the occurrence of β-scission is suppressed by the addition of chain transfer agents and even the rate of reaction increases because of replacement of the slow mid chain radical by a more reactive transfer agents radical.[64]

This would mean that in industrial recipes where acrylic acid is used in combination with chain transfer agents, the effects of paragraph 2 and paragraph 4 are not really visible!

(meth)acrylic Acid Containing Emulsion Polymerization Recipes

As mentioned in the previous paragraph many industrial emulsion polymerization recipes contain acrylic of methacrylic acid. In the case of acrylic acid many problems in modeling these systems can be envisaged because of the need to take into account all the reactions in Figure 4, plus the additional reactions with chain transfer agents as described in paragraph 5.

Additional to that, in general, when more water soluble monomers are present in the recipe, also the description of entry in emulsion copolymerization poses a problem. Although several models exist[65–67] for the description of entry in emulsion copolymerization, direct experimental verification is lacking. The Maxwell Morrison model for entry in emulsion homopolymerization[68] is validated by the determination of the length of the oligomers existing in the water phase. Techniques like isotachophoreses and liquid chromatography[69] have been used.

In the recipes containing more water soluble monomers like (meth)acrylic acid also other aspects play a role, for example the quantification of the incorporation of these monomers inside the particles, on the surface (creating hairy particles) or forming water phase polymer.[70,71]

Especially in this area still a lot of knowledge needs to be gained This information is very relevant for modeling but also for practical applications, as entry of radicals in latex particles not only determines molecular mass of the formed polymer chains but can also affect the morphology of the latex particles. The issue of water phase polymer formation is another aspect where fundamental knowledge is lacking. Only in the past few years reliable data for propagation of acrylic and methacrylic acid in water has been acquired,[72] showing that already homopolymerization in aqueous solution is influenced by many factors like pH, ionic strength and monomer concentration. Last but not least, in acquiring kinetic data from PLP experiments, especially for rapidly reacting monomers like the acrylates, the temperature during the experiment itself should be carefully monitored and controlled in order to prevent additional artefacts.[73]

Conclusion

In the past ten years several steps were made in the area of obtaining basic kinetic data to improve on the modeling of emulsion polymerization.

- The introduction of MALDI-ToF MS in the area has led to more understanding, especially on the end groups of polymer chains related to the polymerization mechanisms.
- The awareness that SEC suffers from chain length dependent broadening has brought more understanding to some previously unclear observations, amongst others in PLP experiments.
- The general acceptance of chain transfer to polymer in acrylate polymerizations has led to many improvements in understanding and modeling acrylate containing emulsion polymerization reactions, both in the kinetics and product characteristics. Also the theories around entry, exit and secondary nucleation in hairy particles has benefited a great deal from this knowledge.
- The development of the direct measurements of radical concentration versus time with EPR is a major step forward in obtaining reliable data on termination rate coefficients as a function of chain length and conversion

In order to describe the fundamental processes like entry and exit of radicals in emulsion copolymerizations many basic kinetic and thermodynamic parameters are needed but still lacking.

It is shown that there are still many outstanding problems on many facets of modeling emulsion copolymerizations. Especially the nucleation stage will be very hard to model and this will probably only be successful for a particular reactor setup where many experimental data form the basis of a semi-empirical predictive model.

Since the first paper with the same title,[1] at least in the area of propagation rate coefficients, we are no longer dealing with discrepancies of a factor of 50 but are now debating effects of 20% or so. This shows that indeed major improvements are made and modeling has become feasible, especially for the well studied monomers

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[1] A. M. van Herk, A. L. German, *Macromol. Theory Simul.* **1998**, *7*, 557.
[2] R. G. Gilbert, *'Emulsion polymerization: A Mechanistic Approach'*, Academic Press, London **1995**.
[3] P. A. Lovell, M. S. El-Aasser, Eds., *'Emulsion polymerization and Emulsion polymers'*, John Wiley & Sons, Chichester, England **1997**.
[4] A. M. van Herk, Ed., *'Chemistry and Technology of emulsion polymerization'*, Blackwell publishing, Oxford, **2005**.
[5] S. C. Thickett, R. G. Gilbert, *Polymer* **2007**, *48*, 6965.
[6] S. Beuermann, M. Buback, *Progr. Polym. Sci.* **2002**, *27*, 191.
[7] A. M. Van Herk, *Macromol. Theor. Simul.*, **2000**, *9*, 433.
[8] P. A. Clay, R. G. Gilbert, *Macromolecules* **1995**, *28*, 552.
[9] R. Balic, C. M. Fellows, A. M. van Herk, *Macromolecular Research* **2004**, *12*, 325.
[10] J. B. De Kock, B. Klumperman, A. M. van Herk, A. L. German, *Macromolecules* **1997**, *30*, 6743.
[11] O. F. Olaj, I. Bitai, F. Hinkelmann, *Makromol. Chem.* **1987**, *188*, 1689.
[12] J. Sarnecki, J. Schweer, *Macromolecules* **1995**, *28*, 4080.
[13] A. M. van Herk, *Macromol. Rapid communications* **2001**, *22*, 687.
[14] T. P. Davis, K. F. O'Driscoll, M. C. Piton, M. A. Winnik, *Journal of Polymer Science, Part C: Polymer Letters* **1989**, *27*, 181.
[15] M. Buback, A. Feldermann, C. Barner-Kowollik, I. Lacik, *Macromolecules* **2001**, *34*, 5439.

[16] R. A. Hutchinson, J. H. McMinn, D. A. Paquet, Jr., S. Beuermann, C. Jackson, *Ind. Eng Chem Res.* **1997**, *36*, 1103.

[17] M. L. Coote, M. D. Zammit, T. P. Davis, G. D. Willett, *Macromolecules* **1997**, *30*, 8182.

[18] R. A. Sanayei, K. F. O'Driscoll, B. Klumperman, *Macromolecules* **1994**, *27*, 5577.

[19] L. H. Yee, J. P. A. Heuts, T. P. Davis, *Macromolecules* **2001**, *34*, 3581.

[20] M. Jung, E. M. S. van Hamersveld, T. Julien, A. M. van Herk, *Macromol. Chem. rapid communications* **2001**, *22*, 978.

[21] O. F. Olaj, P. Vana, M. Zoder, A. Kornherr, G. Zifferer, *Macromolecular Rapid Communications* **2000**, *21*, 913.

[22] O. F. Olaj, P. Vana, M. Zoder, *Macromolecules* **2002**, *34*, 1208.

[23] R. X. E. Willemse, B. B. P. Staal, A. M. van Herk, S. C. J. Pierik, L. Klumperman, *Macromolecules* **2003**, *36*, 9797.

[24] R. X. E. Willemse, A. M. van Herk, *J. Am. Chem. Soc.* **2006**, *128*, 4471.

[25] O. F. Olaj, M. Zoder, P. Vana, A. Kornherr, I. Schnöll-Bitai, G. Zifferer, *Macromolecules* **2005**, *38*, 1944.

[26] I. Schnöll-Bitai, C. Mader, *Macromol. Symp.* **2007**, *248*, 33 in *Radical Polymerization: Kinetics and Mechanism*. Edited by M. Buback, A.M. van Herk.

[27] M. Buback, M. Busch, R. A. Lamel, *Macromol. Theory Simul.* **1996**, *5*, 845.

[28] B. O'Shaughnessy, D. Vavylonis, *Macromol. Theory Simul.* **2003**, *12*, 401.

[29] L. H. Tung, *J. Appl. Polym. Sci.* **1966**, *10*, 375.

[30] S. N. E. Omorodion, A. E. Hamielec, *J. Liquid. Chrom.* **1989**, *12*, 1131.

[31] T. Q. Nguyen, H.-H. Kausch, *J. Chromatography* **1988**, *449*, 63.

[32] Y. Ishida, *Shimadzu Hyoron* **1971**, *28*, 287.

[33] M. E. van Kreveld, N. van den Hoed, *J. Chromatography* **1978**, *149*, 71.

[34] W. W. Yau, J. J. Kirkland, D. D. Bly, *Modern Size-Exclusion Chromatography*, John Wiley & Sons, New York **1979**.

[35] J. P. A. Heuts, G. T. Russell, G. B. Smith, A. M. van Herk, *Macromol. Symp.* **2007**, *248*, 12.

[36] A. Kornherr, O. F. Olaj, I. Schnöll-Bitai, G. Zifferer, *Macromol. Theory Simul.* **2006**, *15*, 215.

[37] A. Kornherr, O. F. Olaj, I. Schnöll-Bitai, G. Zifferer, *Macromol. Theory Simul.* **2004**, *13*, 560.

[38] I. Schnoll-Bitai, T. Hrebicek, A. Rizzi, *Macromol. Chem. Phys.* **2007**, *208*, 485.

[39] I. Schnoll-Bitai, J. Vega, C. Mader, *Anal. Chimica Acta* **2007**, *604*, 9.

[40] I. Schnöll-Bitai, C. Mader, *J. Chromatogr. A* **2006**, *1137*, 198.

[41] M. M. Yossen, J. R. Vega, G. R. Meira, *J. Chromatogr. A* **2006**, *1128*, 171.

[42] G. Meira, M. Netopilik, M. Potschka, I. Schnoll-Bitai, J. Vega, *Macromol. Symp.* **2007**, *258*, 186.

[43] S. Huijser, G. D. Mooiweer, J. Feenstra, R. Duchateau, C. E. Koning, to be published.

[44] B. Manders, "*Pulsed initiation polymerization. Applications in homogenenous and heterogeneous radical systems*", Thesis, Eindhoven The Netherlands **1997**.

[45] F.-D. Kuchta, A. M. van Herk, A. L. German, *Macromolecules* **2000**, *33*, 3641.

[46] N. Ahmed, F. Heathly, P. Lovell, *Macromolecules* **1998**, *31*, 2822.

[47] C. Plessis, G. Arzamendi, J. R. Leiza, H. A. S. Schoonbrood, D. Charmot, J. M. Asua, *Macromolecules* **2000**, *33*, 4.

[48] J. Chiefari, J. Jeffery, R. T. A. Mayadunne, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1999**, *32*, 7700.

[49] C. Plessis, G. Arzamendi, J. M. Alberdi, A. M. van Herk, J. R. Leiza, J. M. Asua, *Macromol. Rapid Comm.* **2003**, *24*, 173.

[50] K. Tanaka, B. Yamada, R. G. Gilbert, symposium abstract SML'01, Lucca, Italy 3–8 June **2001**.

[51] B. Tanaka, M. Azukizawa, H. Yamazoe, D. J. T. Hill, P. J. Pomery, *Polymer* **2000**, *41*, 5611.

[52] M. Azukizawa, B. Yamada, D. J. T. Hill, P. J. Pomery, *Macromol. Chem. Phys.* **2000**, *201*, 774.

[53] K. Tanaka, B. Yamada, R. X. E. Willemse, A. M. van Herk, *Polym. J.* **2002**, *34*, 692.

[54] R. X. E. Willemse, A. M. van Herk, E. Panchenko, T. Junkers, M. Buback, *Macromolecules* **2005**, *38*, 5098.

[55] J. M. Asua, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, R. G. Gilbert, R. Hutchinson, J. R. Leiza, A. N. Nikitin, J. P. Vairon, A. M. van Herk, *Macromol. Chem. Phys.* **2004**, *205*, 2151.

[56] M. Buback, H. Hippler, J. Schweer, H.-P. Vögele, *Makromol. Chem. Rapid Commun.* **1986**, *7*, 261.

[57] J. B. L. de Kock, B. Klumperman, A. M. van Herk, A. L. German, *Macromolecules* **1997**, *30*, 6743.

[58] M. Buback, M. Busch, C. Kowolik, *Macromol. Theory Simul.* **2000**, *9*, 442.

[59] M. Buback, E. Müller, G. T. Russell, *J. Phys. Chem.* **2006**, *110*, 3222.

[60] S. C. Thickett, M. Gaborieau, R. G. Gilbert, *Macromolecules* **2007**, *40*, 4710.

[61] S. C. Thickett, B. Morrison, R. G. Gilbert, *Macromolecules* **2008**, *41*, 3521.

[62] J. Chiefari, J. Jeffery, R. T. A. Mayadunne, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1999**, *32*, 7700.

[63] T. Junkers, S. P. S. Koo, T. P. Davis, M. H. Stenzel, C. Barner-Kowolik, *Macromolecules* **2007**, *40*, 8906.

[64] T. Junkers, C. Yang, C. Ke, F. Kahee, D.-Q. Yuan, T. Mori, Y. Inoue, *Australian Journal of Chemistry* **2008**, *61*, 565.

[65] M. Zubitur, P. D. Armitage, S. B. Amor, J. R. Leiza, J. M. Asua, *Polymer Reaction Engineering* **2003**, *11*, 627.

[66] G. L. Shoaf, G. W. Poehlein, *Journal of Applied Polymer Science* **1991**, *42*, 1213.

[67] Y. Dong, D. C. Sundberg, *Macromolecules* **2002**, *35*, 8185.

[68] I. A. Maxwell, B. R. Morrison, Donald, H. Napper, R. G. Gilbert, *Macromolecules* **1991**, *24*, 1629.

[69] J. T. Eleveld, H. A. Claessens, J. L. Ammerdorffer, A. M. van Herk, C. A. Cramers, *Journal of Chromatography* **1994**, *677*, 211.

[70] M. Slawinski, M. A. J. Schellekens, J. Meuldijk, A. M. Van Herk, A. L. German, *Journal of Applied Polymer Science* **2000**, *76*, 1186.

[71] M. Slawinski, J. Meuldijk, A. M. Van Herk, A. L. German, *Journal of Polymer Science* **2000**, *78*, 875.

[72] S. Beuermann, M. Buback, P. Hesse, I. Lacík, *Macromolecules* **2006**, *39*, 184.

[73] N. Garcia, P. Tiemblo, J. Guzman, *Macromolecules* **2007**, *40*, 4802.