Simulating Acrylate Polymerization Reactions: Toward Improved Mechanistic Understanding and Reliable Parameter Estimates

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Summary: It is well accepted that free-radical acrylate polymerizations are governed by a complex coupled kinetic mechanism consisting of propagation, termination and inter-molecular transfer to small species such as monomer or modifiers, together with intra- and inter-molecular transfer reactions to polymer. Propagation, β-scission or termination of the transient secondary/tertiary radicals formed following transfer to polymer is possible. This reaction cascade strongly affects the micro-structural characteristics of the polymer and its application properties. Individual parts of this mechanism have been discussed on many occasions. However, a general approach for determining the rate coefficients for the full kinetic scheme has been missing. Such an approach is developed in this communication.

Keywords: branched; degradation; kinetics (polym.); modeling; radical polymerization; simulations

Introduction

Free-radical acrylate polymerizations have been studied for quite some time. Severe problems in acquiring consistent results for kinetic rate coefficients over an extended range of reaction conditions have been encountered. E.g., pulsed laser polymerization (PLP) experiments and subsequent analysis of the polymer by size exclusion chromatography (SEC)[1,2], which has emerged as the standard technique for determining the propagation rate coefficient k_p, have been performed successfully for butyl acrylate only at temperatures below 20 °C.[3,4] For the same monomer, the activation energy for the rate coefficient of transfer reactions to monomer that is based on measurements at low temperatures[5] could not be used to successfully extrapolate the rate coefficients necessary for describing the number average molecular weight M_N found for high-temperature polymerization above 150 °C. This has lead to speculation that impurities may

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cause enhanced transfer.[6] However, the required rate coefficient for transfer being derived on the base of this presumption was extremely high and could only be thought of as phenomenological in nature. Both the failure of PLP-SEC experiments and the high phenomenological transfer coefficients required to model such results indicates that the kinetic schemes of initiation, propagation, termination and transfer reactions to monomer are incomplete. Support for this fact was found by Lovell et. al.[7], who detected significant amounts of side branches in the polymer formed at high conversion in butyl acrylate polymerizations. This initiated an intensive debate about the polymerization mechanism including transfer reactions to polymer and its consecutive reactions.[8,9,10,11,12,13] Scheme 1 shows the general mechanism for inter-molecular transfer to polymer. A free radical abstracts a hydrogen atom from a dead polymer chain with a probability that is proportional to the length of this chain (a). As a result the initial free radical is converted into a dead polymer chain, and the previously dead polymer chain into a chain with a secondary or tertiary radical function depending on the molecular structure.

Scheme 1: General kinetic scheme of inter-molecular transfer reaction to polymer and its consecutive reactions.

$$R_s + P_r \xrightarrow{k_{tr,pol} \cdot r} P_s + R_{r,\mathrm{sec/tert}} \qquad (a)$$

$$R_{s,sec/tert} \xrightarrow{k_\beta} P_{s-r} + R_r \qquad (b)$$

$$R_{s,sec/tert} + M \xrightarrow{k_{p,sec/tert}} R_{s+1} \qquad (c)$$

This secondary/tertiary radical (for the sake of simplicity it will be denominated from now on as secondary) can either undergo a β-scission reaction forming a dead polymer chain and a terminal radical (b) or propagate forming a side branch (c). This propagation is thought to be significantly slower than the propagation of a terminal radical since the radical function may be stabilized by its neighborhood. Villermaux[14] proposed this reaction sequence for α-olefin polymerizations in the 1970s. It can take place either as an inter-molecular transfer to polymer (Scheme 1), or as an intra-molecular reaction (see Scheme 2 for the kinetic mechanism and Scheme 3 for mechanistic aspects). In the intra-molecular transfer to polymer, a preferably 6-membered transition state is formed. Upon further propagation, the propagating chain end becomes the backbone and the former chain end is left as a short side branch. In α-olefin polymerizations this is traditionally denoted as a short chain branch (SCB) having a formal chain length of C_4.

Scheme 2: General kinetic scheme of intra-molecular transfer reaction to polymer and its consecutive reactions

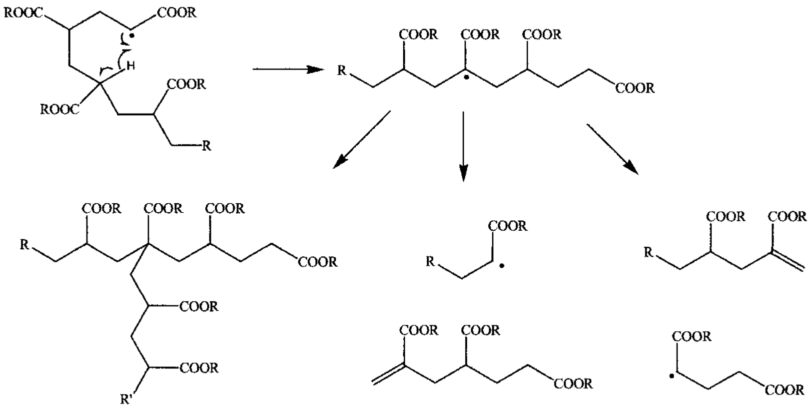
$$R_s + P_r \xrightarrow{k_{bb}} P_s + R_{r,sec/tert(bb)} \qquad (a)$$

$$R_{s,sec/tert(bb)} \xrightarrow{k_\beta} P_{s-r} + R_r \quad (r = 2 \lor r = s-3) \qquad (b)$$

$$R_{s,sec/tert(bb)} + M \xrightarrow{k_{p,sec/tert}} R_{s+1} \qquad (c)$$

From intensive investigations in α-olefin polymerizations it is known that the structures may become much more complex due to the fact that such intra-molecular transfer to polymer (backbiting) may take place twice in direct sequence or with only one propagation step in-between.[15,16,17,18] The dominating structures are of chain-length C_2 and C_4 and ethyl-hexyl chain ends. However, it is common to classify all these individual structures as SCB, defined as branches shorter than C_6, while any longer side branch is attributed to long-chain branches (LCB) originating from inter-molecular transfer to polymer. In inter-molecular transfer to polymer any position of the chain may be attacked; if the intermediate secondary radical propagates, a long side branch is formed.

Scheme 3: intra-molecular transfer to polymer and consecutive reactions



Returning to the discussion of the reactions subsequent to intra-molecular transfer, the β-scission reaction channel remains to be inspected. The result is a long chain (right bottom part of Scheme 3) that is either a propagating macroradical, or a dead polymer chain carrying a terminal double bond. The accompanying species formed is either a trimer with a terminal double bond, or a dimer radical, respectively. If information about the concentration of the oligomers or the terminal double bonds that are formed is unavailable, the effect of this reaction cascade on the molecular weight distribution (MWD) is very similar to that for transfer to monomer. The more frequently this reaction path is taken, the more the MWD is shifted toward low molecular weights. It should be noted that information exclusively about the overall concentration of terminal double bonds would not be sufficient to generate additional kinetic information, since chain terminating dissociation reactions generate double bonds, and transfer to monomer generates a chain leaving the double bond functionality of the monomer unit untouched. In fact, information about the special chain end structure that results from such β-scission reactions would be necessary for such a purpose. Because these two reaction paths appear to be indistinguishable in α-olefin polymerizations, the reaction sequence of intra-molecular transfer to polymer and further propagation are combined into a single backbiting reaction, and the reaction sequence of intra-molecular transfer to polymer and β-scission are omitted. The effect on the MWD is implicitly contained in the values of the rate coefficient for transfer to monomer, since these have been determined based on the Mayo method.[19] This method assumes a kinetic mechanism restricted to initiation, propagation, termination and transfer to monomer together with infinitesimal initiation and conversion. As unimolecular reactions, backbiting and consecutive β-scission take place in the same manner under all reaction conditions; consequently the rate coefficient for transfer to monomer based on M_N using the Mayo method implicitly includes contributions of intra-molecular transfer to polymer and consecutive β-scission.

The situation is different for the inter-molecular variant of this reaction cascade. Inter-molecular transfer to polymer followed by propagation produces long-chain branches. Such transfer followed by β-scission has a significant impact on the dispersion of the MWD. Since inter-molecular transfer to polymer involves 'statistical' attack of the dead polymer chain, the reaction path for β-scission shows a symmetrical probability of fragment formation along the chain-length axis, in contrast with those following intra-molecular transfer. In α-olefin polymers SCBs and LCBs are distinguishable by quantitative ^{13}C-NMR spectroscopy; moreover, the dispersity as well as the full shape of the molecular weight distribution, which can be characterized by SEC, turns out to provide good measures for characterizing the β-scission rate coefficient. For these reasons there exists neither motivation nor basis for a simplification; in fact, it is better to estimate the rate coefficients using modeling-based data interpretation and a model formulation based on coupled reaction steps.

In the intra- as well as the inter-molecular reaction path, the extent of consecutive propagation of the transient secondary radical species is subject to speculation. The stabilization of the radical function by its neighborhood should cause propagation to be significantly slower compared to a terminal radical. This is based on ab-initio calculations[20] and comparison with model substances — both provide good evidence that the propagation of a macroradical with a secondary/tertiary radical function should be slower.[9] The extent of this effect is estimated to range from one to three orders of magnitude; however, there exists no direct measure for this quantity. The transient macroradical cannot be observed directly, nor can conversion be used as a quantitative measure. The latter is affected by multiple microscopic processes, such as the efficiency of initiation, the dependence of the termination rate on the system viscosity ("conversion dependence") and the retardation of propagation by transient species. For this reason it is often assumed as a clear approximation that the propagation of these species is similar to that of a terminal radical in order to remove one uncertain degree of freedom from the model. Otherwise any kinetic information derived on the basis of such a model or modeling result might itself depend on the estimate that is made for this retarded propagation. In α-olefin polymerization this approach works reasonably well.

That such extended kinetic schemes do not apply exclusively to α-olefin polymerization, or to the polymerization of acrylates, is demonstrated by Campbell et al.[21,22] for high-temperature styrene polymerizations. It is quite interesting to note that these authors find that the full scope of reactions that have been discussed above are relevant for styrene polymerization. This is especially interesting because styrene polymerization was formerly used as the classical example to be treated by a simple kinetic scheme of initiation, propagation, termination and transfer to monomer. They found they could compile a significant number of the required kinetic rate coefficients from other polymerization techniques. The agreement between experimental data and simulation runs is remarkably good.

For acrylate polymerization such a favorable situation does not exist. Moreover, parts of the extended polymerization mechanism appear to be operational only under certain reaction conditions and the analytical information that is accessible is not as differentiated. E.g. the branching density is only available as overall branching density and is not differentiated with respect to SCBs and LCBs. For these reasons, often only portions of the mechanism are considered mechanistic discussions. Lovell et al.[7] attributed the branching to LCBs because of the dispersion of the observed MWDs and because the backbiting process has no effect on the dispersion. In contrast Asua et al.[8,10,11], using the rheological properties of the polymer as an argument, attributed the branching exclusively to SCBs, since polymers with such a high long-chain branching index (I_{LCB}) should have properties like a gel. In ethene acrylate polymerizations Hutchinson[23] couldn't find indications for branching structures that originate from backbiting of acrylate chain ends.

Solution may be found in an investigation by Charleux et al.[24] who performed controlled radical acrylate polymerizations at moderate temperatures and conversion. They found only one nitroxyl end group on the polymer, but significant branching densities. This is only explainable when backbiting generates the branches and the reactivation of dead polymer species by inter-molecular transfer is excluded. The moderate polymerization temperatures in combination with the high activation energy for the β-scission reaction may explain the absence of any indication for β-scission here. The absence of multiple nitroxyl end groups that would be expected from inter-molecular transfer may be explained by the low polymer concentration resulting in a low probability for this bimolecular reaction. However, the dispersion of MWDs from polymer synthesized at high conversion in bulk or solution indicates that in principle inter-molecular transfer is as probable as intra-molecular transfer.

Hutchinson[25] found by means of mass spectroscopy high quantities of double bond terminated chain ends that result from the β-scission mechanism for polymer from high-temperature acrylate polymerizations. As ethene copolymerization may take place under even more elevated reaction temperatures, such high scission probabilities indicate the reason why previous investigations of ethene copolymerizations found no indications of acrylate chain end structures from backbiting. As discussed earlier, by shifting the MWD to lower values of molecular weight, backbiting followed by β-scission has an impact on the MWD that is similar to the impact of transfer to monomer or other modifier agents. This may explain the inconsistent measurements of these values using the Mayo method over extended temperature ranges, since the Mayo method presumes that the kinetic scheme is limited to initiation, propagation, termination and transfer reactions to small species.

All this together indicates that in acrylate polymerizations, the full mechanism of intra- (based on the results of Charleux) and inter-molecular transfer to polymer (because of the dispersion of the MWD) together with subsequent β-scission (see Hutchinson) is present. Propagation of the transient secondary macroradical species following transfer to polymer is very likely retarded.

Unfortunately, when discussing kinetic effects, only parts of this scheme are considered. Of course this is due to the limited information that is available and to the fact that depending on the experimental conditions, only parts of the mechanism are really obvious. Asua[8,11] focused on the effect of backbiting with retarded propagation but omitted the β-scission channel and inter-molecular branching that might over-emphasize some contributions. In a theoretical study about PLP-experiments for α-olefins, Busch[9] omitted the β-scission channel after backbiting as is usually done in α-olefin polymerization schemes. However, in so doing, the effect of the retarded propagation of transient secondary radicals on PLP polymer structure may have been underestimated. It was found that significant degradation of the PLP polymer occurs when propagation of the secondary species is a factor 20 to 50 slower than the propagation of terminal radicals. As a consequence the combined effect of retarded propagation and transfer to small species was claimed to be responsible for degradation of the PLP polymer. Given the current state of knowledge, the hypothesis of transfer to small species may have to be replaced by β-scission following backbiting.

From all this it is clear that it is highly desirable to find a method for deriving a consistent set of rate coefficients for the proposed kinetic scheme. Preferably, for each rate coefficient an independently determined experimental quantity (sensor) should be used for estimating its value. However, allowing for the complexity of the kinetic scheme, it is clear that this will not necessarily be possible. Moreover, the fact that the branching indices I_{SCB} and I_{LCB} cannot be determined separately does not improve the situation. However, SEC traces of polymer formed under high temperature synthesis conditions show significant amounts of oligomers. These may provide additional information that is useful.

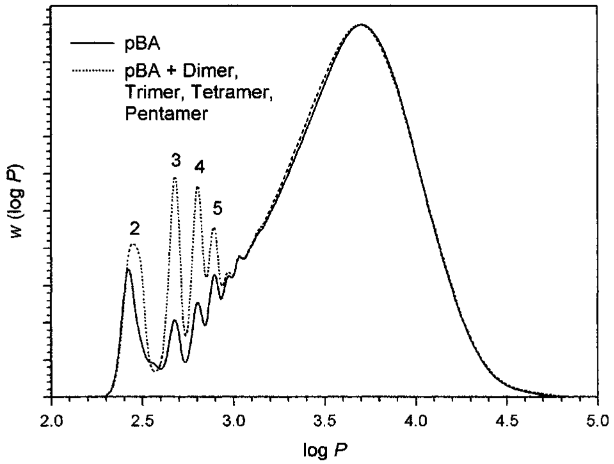


Figure 1: Molecular weight distribution of poly-butyl acrylate produced under high-temperature conditions. The distribution has been measured twice, once with added quantities of dimer, trimer, tetramer and pentamer model substances.

Figure 1 shows such a MWD; in order to verify the presence of oligomers, model compounds of the individual oligomers were added in one SEC trace. This verification works well. In combination with Scheme 3 the obvious question is: do the enhanced quantities of dimers and trimers provide kinetic information about the β-scission reaction that occurs subsequent to intra-molecular transfer to polymer? Given this picture, one might go so far as to predict that a major amount of the transient species end with a dimer radical whose termination is favored because of the chain-length dependent termination that is known to exist in acrylate polymerizations.

Sensitivity study

Modeling is an ideal tool to test such hypotheses. For this purpose the kinetic scheme is implemented in PREDICI and the rate coefficients are varied systematically. The experimental sensors that are used to estimate these rate coefficients are tracked to see whether they show systematic variation as well as cross sensitivity to variation of the other rate coefficients. In a favorable situation the latter is not observed.

Scheme 4: Kinetic scheme considering initiation, propagation, termination and transfer reactions to monomer

$$
\begin{array}{lcll}
I_2 & \xrightarrow{k_i} & I\cdot + I\cdot & \\
I\cdot + M & \xrightarrow{k_p} & R_1 & \\
R_s + M & \xrightarrow{k_p} & R_{s+1} & \\
R_s + M & \xrightarrow{k_{tr,M}} & P_s + R_1 & \\
R_s + R_r & \xrightarrow{k_t} & P_{s+r} & \vee \quad P_s + R_r
\end{array}
$$

However, if cross sensitivity is observed, parameter estimation will still be possible if the sensitivities differ in their magnitude. In this case coupled estimation has to be performed. In the first step of this process, a kinetic scheme is introduced that considers initiation, propagation, termination and transfer reactions to monomer as shown in Scheme 4. For reaction conditions that are typical for high-temperature, high-pressure acrylate polymerizations, such as 170 °C and 200 bar, the resulting MWD is shown in Figure 2. The coefficients are provided in Table 1 and have been documented by Müller[26], or are derived from α-olefin polymerizations assuming similar relative reactivities for species types (indicated by a star).

Table 1: Rate coefficients for modeling butyl acrylate homopolymerization at 170 °C and 200 bar. (* these coefficients have been estimated based on relative reactivities from α-olefin polymerizations)

coefficient	value	
k_p	$1.67\cdot10^5$	$L\cdot mol^{-1}\cdot s^{-1}$
k_t	$1.10\cdot10^7$	$L\cdot mol^{-1}\cdot s^{-1}$
$k_{tr,M}$	$1.81\cdot13^5$	$L\cdot mol^{-1}\cdot s^{-1}$
k_{bb}	$2.13\cdot10^4$	$s^{-1\,(*)}$
$k_{tr,P}$	$5.00\cdot10^3$	$L\cdot mol^{-1}\cdot s^{-1\,(*)}$
k_β	$6.28\cdot10^4$	$s^{-1\,(*)}$

The calculation is done for a chemically initiated solution polymerization of butyl acrylate (Busch et al.[27,28]). As is to be expected, the MWD is featureless having a dispersion (M_W / M_N)

of two. In contrast, experimental work shows that under these conditions the dispersion is significantly higher. As a consequence, the kinetic scheme is expanded by inter-molecular transfer reactions to polymer and its consecutive reactions such as propagation and β-scission as shown in Scheme 5.

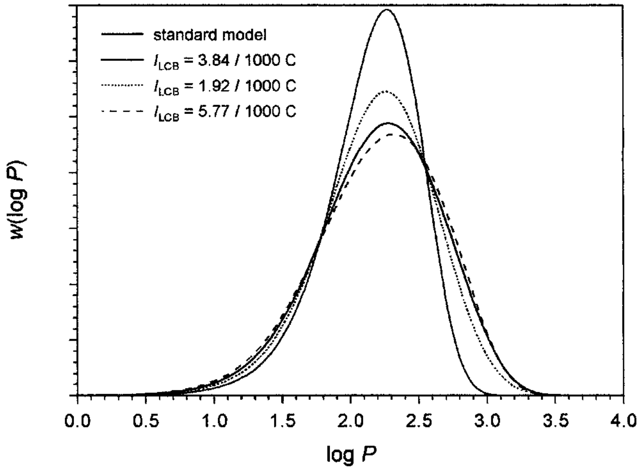


Figure 2: MWDs calculated for butyl acrylate solution polymerization at 170 °C and 200 bar considering either the ideal polymerization kinetics (indicated as standard) or additional inter-molecular transfer to polymer with subsequent propagation or β-scission of the transient macroradical species. For the latter case the rate coefficient of inter-molecular transfer to polymer $k_{tr,P}$ has been varied by ±50% (last two topics of legend).

Scheme 5: Kinetic scheme for considering inter-molecular transfer reactions to polymer with consecutive propagation or β-scission of the transient secondary macroradical

$$\mathrm{R_s} + \mathrm{P_r} \xrightarrow{k_{tr,P}\cdot r} \mathrm{P_s} + \mathrm{R_{r,tert\,(trP)}}$$

$$\mathrm{R_{s,tert\,(trP)}} + \mathrm{M} \xrightarrow{k_{p,tert}} \mathrm{R_{s+1}} + \mathrm{LCB}$$

$$\mathrm{R_{s,tert\,(trP)}} \xrightarrow{k_{\beta}} \mathrm{P_{s-r}} + \mathrm{R_r}$$

Inter-molecular transfer to polymer reactivates polymer species to macroradicals. If these propagate further, the MWD becomes broader, while β-scission shifts it to smaller values. Overall, β-scission dampens the broadening of the MWD. This is due to two effects: first, the longer chain-lengths have higher probability of being attacked by inter-molecular transfer to polymer since this probability increases with chain-length. The probability of β-scission also increases, since it is a first order consecutive reaction. Second, with increasing polymer concentration (conversion) the probability of inter-molecular transfer to polymer, which is a bimolecular process, increases, but since β-scission is a unimolecular reaction, it is favored over further propagation of the transient species, which is a bimolecular reaction that is disfavored because of decreasing monomer concentration. Figure 2 shows that by including these reactions the MWD becomes broader. This effect is progressive, increasing with increasing values of the rate coefficient $k_{\mathrm{tr,P}}$ for the inter-molecular transfer reaction to polymer. Simultaneously, the long-chain branching index I_{LCB} increases. (In the following for such variations the legend is organized in that way that the reference case is mentioned first, followed by the result for the smaller and larger value in this sequence.)

Variation of the rate coefficient for β-scission k_β has a dominant effect on the MWD, while I_{LCB} remains more or less unaffected. The higher the values for k_β are, the lower the dispersion index of the MWD is. For the sake of brevity, this is not demonstrated here by a separate illustration, but it is well known from modeling work on α-olefin polymerizations.[28,29] Up to this point an overall distribution can be generated that agrees in shape and dispersion with the characteristics of the MWD of high-temperature, high-pressure acrylate polymerization as shown in Figure 1; however, the characteristic oligomer structure cannot be generated.

Scheme 6: Kinetic scheme for considering intra-molecular transfer reactions to polymer with consecutive propagation or β-scission of the transient secondary macroradical

$$\mathrm{R_s} \xrightarrow{k_{\mathrm{bb}}} \mathrm{R_{s,tert\,(bb)}}$$

$$\mathrm{R_{s,tert\,(bb)}} + \mathrm{M} \xrightarrow{k_{\mathrm{p,tert}}} \mathrm{R_s} + \mathrm{SCB}$$

$$\mathrm{R_{s,tert\,(bb)}} \xrightarrow{k_\beta} \mathrm{P_{s\text{-}r}} + \mathrm{R_r} \qquad (r = 2 \;\vee\; r = s - 3)$$

For this reason the kinetic scheme is expanded another time by the reaction sequence that results from intra-molecular transfer to polymer and is depicted in Scheme 6. Figure 3 compares the reference case of Figure 2 (here, top of legend; there, second item of legend) with MWDs that are calculated by including the reaction sequence for intra-molecular transfer to polymer and its consecutive reactions. Due to the β-scission channel, the MWD is shifted to lower molecular weights as would also be expected for transfer reactions to small species. This is predominantly controlled by the value of k_β. As it is a simple shift of position, this variation is not shown here. However, it has been demonstrated by Busch et al.[27,28]

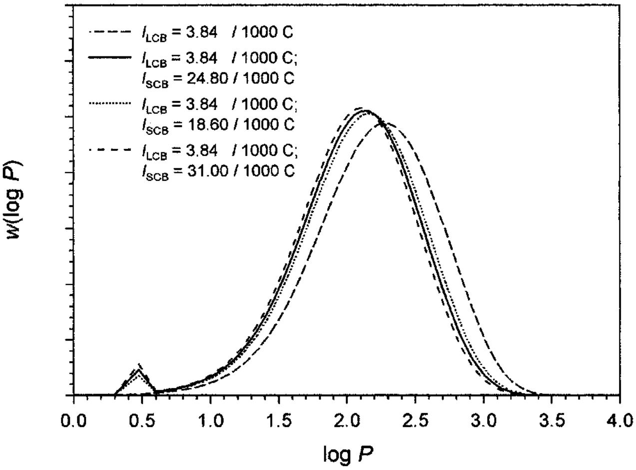


Figure 3: MWDs calculated for butyl acrylate solution polymerization at 170 °C and 200 bar considering either a kinetic scheme summarized in Scheme 4 and Scheme 5 (dashed line at top of legend referring to the second item of the legend of Figure 2) or additional intra-molecular transfer to polymer with subsequent propagation or β-scission of the transient macroradical species (see Scheme 6). For the latter case, the rate coefficient of intra-molecular transfer to polymer k_{bb} has been varied by ±25%.

Independent of whether the transient species originates from intra- or inter-molecular transfer to polymer, for the β-scission reactions, the same rate coefficient should be applied due to the chemical similarity of these processes. Under these circumstances, the value affects both the position of the MWD (superimposed on the effect of transfer reactions to small species) and its dispersion. The effect of k_β on the intensity of the trimer peak is also now observable. However, the effect of the rate coefficient k_{bb} for intra-molecular transfer to polymer on the trimer peak is larger. This is consistent with the sensitivities of $k_{tr,P}$ and k_β to to the long-chain branching index and the dispersion of the MWD, respectively. A trimer peak is clearly observed and its magnitude varies systematically with k_{bb}. (The triangle shape originates in the way the distribution represents the histogram values of discrete species.) However, there is no indication for an excess of dimer species as might be expected from Scheme 3.

Busch et. al.[27,28] demonstrated that even the assumption of a strong chain-length dependence in the termination reaction could not produce such an observation. The reason is found in the fact that even under such conditions, the probability of such a bimolecular reaction of two species at low concentration is low enough to allow for some additional propagation steps. In essence, an overall enhancement in the quantity of oligomeric species could be observed, but no preference for dimers. With this knowledge, the experimental data should be re-inspected.

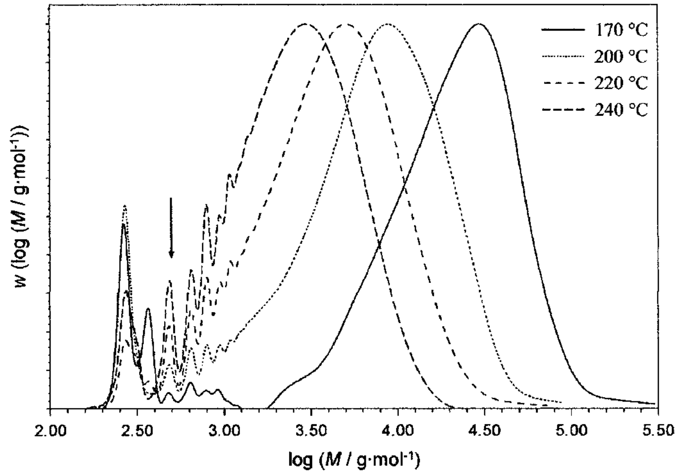


Figure 4: MWDs of poly-butyl acrylate synthesized in solution at 350 bars and varying temperature. The arrow indicates the position of the trimer peak.

Figure 4 shows MWDs of poly-butyl acrylate being produced by solution polymerization at moderate pressure and elevated temperaures. When the temperature is varied over a wide range, and considering the discussion above, it is apparent that only the trimer concentration (indicated by an arrow) seems to provide reliable information. The other oligomers do not vary systematically with changing conditions, or to the same extent. Another hypothesis for the origin of such species is that they are formed by β-scission of transient macroradicals that originate from inter-molecular transfer to polymer. For highly branched macromolecules, such as exist here, chain topology affects the products that result from the β-scission process. Short and long chain-fragments are formed preferably. However, Busch et al.[27,28] could show that such an effect would produce a more or less broad shoulder on the high and low molecular weight side of the MWD, but not a discrete species is favored. Since oligomers other than the trimer cannot be linked with information from simulations and their origin remains unclear, these should not be used for kinetic data interpretation. Only clearly identified, non-speculative sensors should be used for such purposes.

Moreover, it becomes clear that the rate coefficients cannot be determined step by step, since at least some of them affect multiple experimental quantities. When estimation is possible, it will involve the estimation of coupled parameters. To test this, a sensitivity study will be necessary. If the sensitivities of the individual sensors differ significantly, this would be promising for a successful estimation of kinetic coefficients.

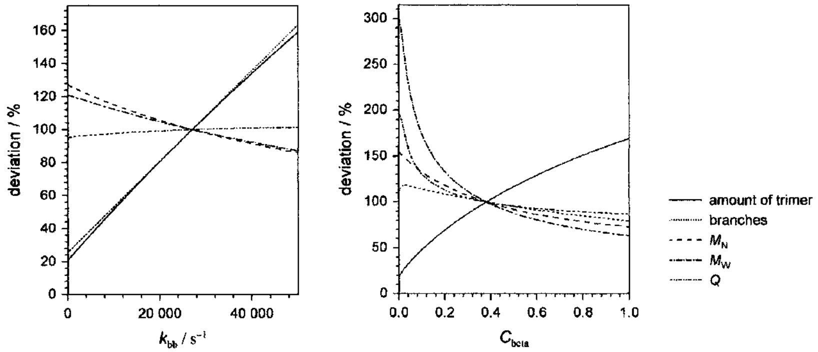


Figure 5: Sensitivity of the individual experimental sensors on the rate coefficient of intra-molecular transfer to polymer k_{bb} and β-scission k_β. The relative deviation referenced to a typical value of these individual coefficients is shown.

Figure 5 shows part of such a sensitivity study. Each rate coefficient is varied and the response of each experimental sensor to this variation is observed. Moreover, by modifying the other coefficients, potential cross-sensitivities can be discovered. As shown in Figure 5, in order to provide a unified picture, the values of the individual sensors are normalized to a value that is determined for a specific rate coefficient. Figure 5 demonstrates the fortunate situation where the sensitivity of each individual experimental sensor differs from the others. It is expected that the sensitivities of M_N and M_W to variation of k_{bb} are more similar than the other sensors, but as these quantities are not used to estimate this rate coefficient, this is not important. Proceeding with this study one can learn that there exist cross-sensitivities as expected from the discussion above. However, comparison of the variation of the sensitivities shows that parameter estimation should be possible. Table 2 summarizes qualitatively the sensitivities of the experimental quantities that may be used for estimation of the rate coefficients of the kinetic model. The overall branching index will be used to fix $k_{tr,P}$ while the trimer quantity provides access to k_{bb}. C_β, the ration of the rate constant of β-scission over that of propagation (k_β/k_p) will be varied until the dispersion of the MWD as well as the trimer quantity is matched.

Table 2: Sensitivity of experimental sensors on the variation of kinetic parameters

		influece on	
parameter	trimer	branches	MWD
C_{beta}	strong	medium	weak
$k_{tr,P}$	weak	strong	medium
k_{bb}	strong	strong	medium

A problem what is unsolved up to this point is the proposed slower propagation of the transient secondary macroradical. A value of k_β would be dependent on the choice of $k_{p,sec}$. However, a solution for this might be to refer k_β to $k_{p,sec}$ in terms of a rate constant ($C_\beta = k_\beta / k_{p,sec}$), since these two reaction paths are in direct competition. This is a common formulation that is also used to quantify and transfer rate coefficients, independent of the choice of the propagation rate coefficient k_p.

For butyl acrylate solution polymerization at 200 °C and 350 bars, Figure 6 shows how the determination of rate coefficients is affected as the extent of retardation, formulated as $k_p/k_{p,sec}$, is varied. Corresponding to a certain ratio of retardation $k_p/k_{p,sec}$, the value of the rate coefficients that are derived based on modeling based data interpretation are rated over that value that is derived considering $k_{p,sec} = k_p$. When using relative rate constants, the values vary by less than 10% for changes of more than three orders of magnitude in $k_p/k_{p,sec}$. Considering other experimental uncertainties, this might be acceptable. Since no direct information about $k_{p,sec}$ is available, it seems justified to use as approximate value for k_p and refer k_β to this value. As soon as there exists more information about $k_{p,sec}$, or if another assumption is made about this value, the model will automatically adapt since it is formulated to use $C_{beta} = k_\beta / k_{p,sec}$ and recalculate k_β from this considering the information about $k_{p,sec}$.

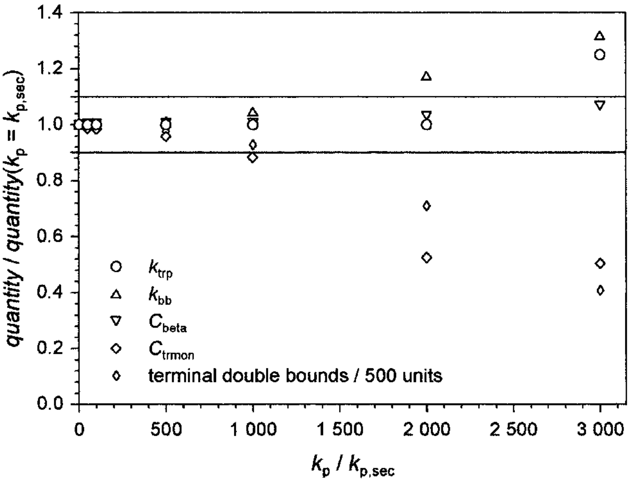


Figure 6: Effect of retarded propagation of the transient macroradical species that results from intra- or inter-molecular transfer to polymer on the overall parameter estimation. Each parameter is normalized to its value determined with no retarded propagation present. The lines indicate a limit of ±10% relative to this value.

Moreover, into this figure the ratios for values of the computed number of terminal doubled bounds originating from the β-scission reaction are included. Again, the respective numbers are referenced to that value that is computed assuming $k_p/k_{p,sec} = 1$. As for the derived rate coefficients the variation is less than 10% for a variation of $k_p/k_{p,sec}$ over three orders of magnitudes. With this also for the values of structural characteristics that are computed based on this model the uncertainty will lie within acceptable accuracy.

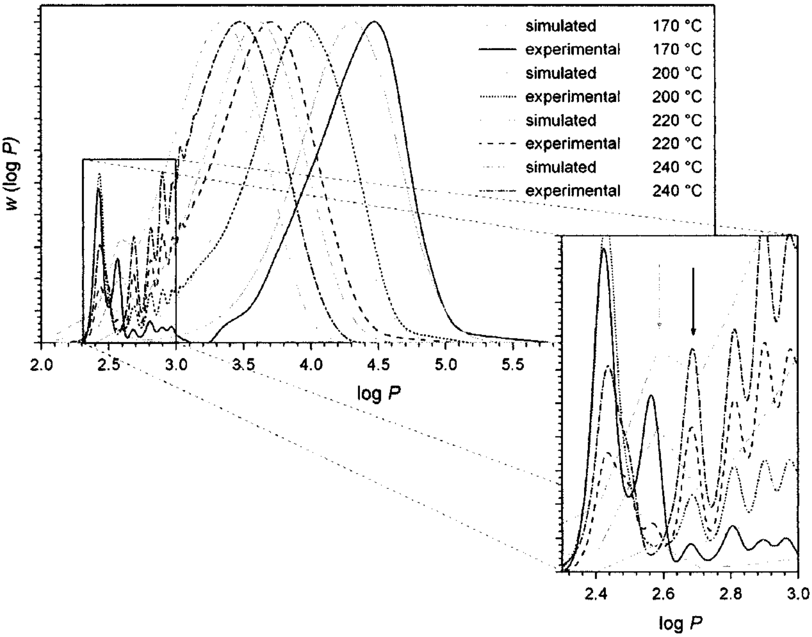


Figure 7: Comparison of experimental MWDs (black lines) with adapted simulation (grey lines). The offset in molecular weight for the experimental data in the oligomer range originates in the calibration of the setup. For this reason, the arrows in the insert indicate position of the trimer, respectively.

There now exists a well-defined approach for estimating the rate coefficients k_{bb}, $k_{\mathrm{tr,P}}$ and k_{β} that are necessary to model polymer properties. The rate coefficients for the rest of the polymerization mechanism, such as k_{p}, k_{t} and $k_{\mathrm{tr,mon}}$[26], are taken from the literature. Due to some calibration issues, the trimer peak in the experimental data is not found exactly at $3 \cdot M$ (M is the molar mass of the monomer unit) – this is overcome by using the ratio of the trimer peak to the main peak of the distribution.

Figure 7 compares experimental results for butyl acrylate solution polymerizations at 350 bars and varying temperature with results of simulation runs using adapted rate coefficients. The elevated reaction conditions together with the wide variation of the reaction temperature have been chosen considering the discussed aspects of the introduction. A wide variation of temperature at elevated values should assure to see a significant variation for the β-scission probability. Both intra- and inter-molecular transfer to polymer should take place at significant reaction rates at high-temperature conditions. Choosing a polymerization in solution will limit the system viscosity on the one hand and reaction rates on the other. Especially, there are reaction conditions accessible with high monomer conversion but moderate polymer concentration. This limits the rate of inter-molecular transfer to polymer but pronounces the β-scission reaction channel as a consequence of inter-molecular transfer due to the low monomer concentration. The main focus of these specially designed experiments was directed toward the properties of the polymer. For this reason, and for simplicity, thermally induced conversion in the individual experiments was accommodated by adjusting the initiator efficiency.

The overall characteristics of the MWDs are well matched for all experiments. The magnification area shows that the peak height of the trimer peaks is also well described. Due to the calibration issue mentioned above, the experimental trimer appears at slightly higher values. The correct and verified positions are indicated by the arrows. The mismatch between the experimental and simulated positions of the main peak, which increases slightly with temperature, is apparent. However, it should be recalled that extrapolated data from independent experiments were used to estimate the rate coefficients for transfer to monomer. When estimating these coefficients, the effect of intra-molecular transfer to polymer and β-scission was not considered in the kinetic scheme. As these effects were present in these experiments, the estimated values would be too large. A reinvestigation of these data considering the full, consolidated kinetic scheme as provided here, is necessary. This investigation is underway and is the reason why a full set of rate coefficients is not provided here circulation of such preliminary values should be avoided. However, the values do organize well on an Arrhenius plot. This, together with the good agreement between experiment and simulation, provides a demonstration of the potential value of numerical simulation for obtaining useful kinetic information from complex reaction schemes. Already Figure 7 shows that the full MWDs together with the some of the special characteristics of the low molecular weight fraction can be well described over a wide rage of reaction conditions.

Conclusions

It has been demonstrated that acrylate polymerization follows a complex kinetic scheme including propagation, termination, transfer to monomer and intra- as well as inter-molecular transfer to polymer with subsequent β-scission or propagation of the respective transient macroradical species. Instead of applying only parts of the kinetic scheme, the complete set of elementary reactions has been used to formulate a simulation-based, experimental strategy for determining the required rate coefficients. This strategy has been analyzed with respect to parameter sensitivities and applied to experimental results. The agreement between simulations and experimental results provides added motivation to refine the method in order to eliminate the cross-sensitivity of M_N, which is controlled by transfer to monomer (using rate coefficients from the literature) and the effect of intra-molecular transfer to polymer followed by β-scission. Progress is encouraging — at the end of this refinement a consistent kinetic data-set that provides predictive potential for modeling high-temperature butyl acrylate polymerizations will be available.

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