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Safety and Quality Aspects of Acrylic Monomers

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Summary: Acrylic monomers are important intermediates for the chemical industry. Especially acrylic acid (AA) is the basis for various reactions, such as polymerizations and esterifications and is, therefore, responsible for high product diversity. Spontaneous polymerization is a safety problem during the transportation and storage of acrylic monomers. In the production process, polymerization leads to blockages in the apparatus. For the prevention of these issues, special stabilizer systems are used such as hydroquinone monomethyl ether (MeHQ)/oxygen and phenothiazine (PTZ). The reactions of these stabilizer systems are not well understood at the moment. Therefore a lot of expertise and experience are necessary to guarantee safe handling. In this paper some methods for the investigation of stability related reaction kinetics are presented. A better comprehension of the mechanism of the polymerization inhibition is generated by the kinetic simulation with these data.

Keywords: acrylic; kinetic; quality; safety; stability

Introduction

Acrylic monomers (AM) and in particular acrylic acid (AA) are important intermediates of the chemical industry. The worldwide production capacity of AA is about 4 mio. t/a.[1] Many products made of AA are part of our daily life. The reason for the high demand on AA and its derivatives is the variety of applications of even the simplest carboxylic acid. The bi-functional compound discloses the synthesis of various interesting plastics with different properties by homo- and copolymerization with other monomers. They are used as binding, flocculating and dispersing agents in colorants, adhesives, detergents, industrial coatings, cosmetics, drugs, papermaking, textiles, leather processing, sewage and water treatment and are also used in oil production as flocculants and drilling fluids. Another important application is the manufacturing of super absorbent polymers which - as an example - are used in diapers.[1–3]

The high reactivity of AA which is appreciated for the polymer synthesis causes problems during the production, transportation and storage of the monomers. The unintended polymerization causes economic losses by decreasing quality and product deterioration on one hand, and can turn into a safety problem in case of runaway polymerization on the other hand. Therefore the monomers have to be stabilized against free radical polymerization. Well-established stabilizers are hydroquinone monomethyl ether (MeHQ)/oxygen and phenothiazine (PTZ).

The stability of AMs depends on the temperature, the concentration of the dissolved molecular oxygen, the nature and the concentration of the added stabilizer, the byproducts spectrum, the concentration of impurities (such as metal ions[4]) and, in the case of aqueous AM solutions, on the water concentration. The mutual interaction of these parameters

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makes the prediction of the AM stability difficult, particularly if only the influence of one single parameter is taken into consideration.

Another reaction which takes place during the transportation and storage of AA is the formation of diacrylic acid (DiAA) and higher oligomers by Michael addition of AA molecules. In contrast to the radical polymerization this reaction cannot be inhibited. If the AA is handled inappropriately the reaction will lead to a massive loss of product quality and will disturb or even hinder the subsequent processing.

In this paper some results are presented exemplarily to demonstrate the available methods and their capability. They can be grouped by the depth of the resultant information content. The determination of the inhibition period (IP) gives an overall measure on the stability of a monomer at predefined boundary conditions. The IP is the amount of time until spontaneous polymerization starts. The investigation of the kinetics of the inhibition related reactions gives a deeper insight into the chemical happenings during the IP. To approve the interrelation between the separated kinetic information chemical models have to be formulated and simulated.

$$
\begin{aligned}
&I \xrightarrow{k_d} 2\,R\bullet \\
&R\bullet + M \xrightarrow{k_p} R-M_1\bullet \\
&M_n\bullet + M \xrightarrow{k_p} M_{n+1}\bullet \\
&M_n\bullet + M_m\bullet \xrightarrow{k_{tk}} M_{n+m} \\
&M_n\bullet + M_m\bullet \xrightarrow{k_{td}} M_n + M_m
\end{aligned}
$$

Scheme 1.

The mechanism of the radical polymerization. I: initiator, R$\bullet$: primary radical, R-M$_n\bullet$, M$_n\bullet$, M$_m\bullet$: alkyl radicals, M: monomer, M$_n$, M$_m$, M$_{n+m}$: polymers.

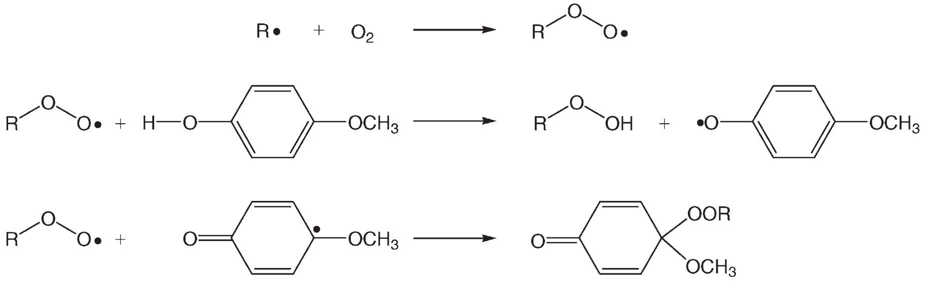
State of the Art

Already in 1956 Henrici-Olivé et al. [5] presented a mechanism for the stabilizing effect of dissolved molecular oxygen (in methyl methacrylate). Here, an alternating copolymerization between oxygen and monomer takes place, which can be explained by the ratio of the rate constants. Although the rate of the radical polymerization is high ($k_p \approx 10^2$ mol L^{-1} s^{-1}, Scheme 1), the rate of oxygen addition to primary or alkyl radicals is much higher ($k_{copo,ox} \approx 10^8$ mol L^{-1} s^{-1}, Scheme 2). The addition of another oxygen molecule to the formed peroxy radical is useless, as the resulting tetroxy radical would be unstable. The addition of monomer molecules to peroxy radicals, which is the consecutive step, is relatively slow ($k_{copo,m} \approx 10^{-1}$-10 mol L^{-1} s^{-1}, Scheme 2). Therefore, if enough oxygen is dissolved in the monomer, the radical reactions are slowed down and the polymerization is prevented. During the IP the oxygen is successively consumed. In a simplified approach the oxygen consumption in monomers can be described by a pseudo-zero-order kinetic relation.[7] If the critical oxygen concentra-

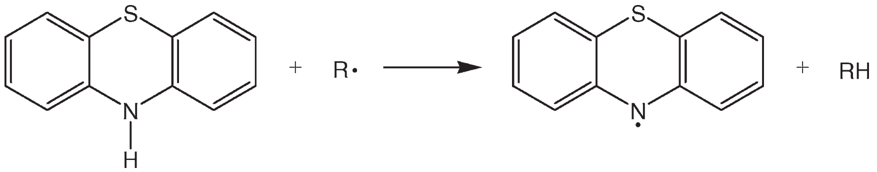
$$
\begin{aligned}
&I \xrightarrow{k_d} 2\,R\bullet \\
&R\bullet + O_2 \xrightarrow{k_{copo_{ox}}} R-O_2\bullet \\
&R-O_2\bullet + M \xrightarrow{k_{copo_m}} R-(O_2-M)_1\bullet \\
&R-(O_2-M)_n\bullet + O_2 \xrightarrow{k_{copo_{ox}}} R-(O_2-M-)_n O_2\bullet \\
&R-(O_2-M)_n\bullet + R-(O_2-M)_m\bullet \xrightarrow{k_{t1}} \text{polymer} \\
&R-(O_2-M-)_n O_2\bullet + R-(O_2-M)_m\bullet \xrightarrow{k_{t2}} \text{polymer} \\
&R-(O_2-M-)_n O_2\bullet + R-(O_2-M-)_m O_2\bullet \xrightarrow{k_{t3}} \text{polymer}
\end{aligned}
$$

Scheme 2.

The mechanism of the inhibition by oxygen. I: initiator, R$\bullet$: primary radical, M: monomer, R—O$_2\bullet$: peroxy radical, R-O$_2$-M$\bullet$, R-O$_2$-M-O$_2$-M$\bullet$: alkyl radicals, R-R, R—O—R: polymers, R—O$_2$—O$_2$—R: (unstable) tetra oxide polymer.



Scheme 3.
The inhibition mechanism of $MeHQ/O_2$.



Scheme 4.
The inhibition mechanism by PTZ.

tion $w(O_2)_{krit.,AA} \approx 0{,}5\,ppm^1$ $(g\,g^{-1})$ is reached the polymerization starts.[5–7]

During the polymerization the previously formed peroxides are cracked by the reaction temperature and new radicals are liberated. This again causes an increase of the polymerization rate and an accelerated heat development.

To prevent the formation of O_2-M-copolymers additional stabilizers are used. A well-tried stabilizer for AMs is hydroquinone monomethyl ether (MeHQ). MeHQ traps most peroxy radicals before they react with monomer molecules. Since MeHQ alone is not able to trap primary and alkyl radicals the presence of sufficient oxygen is always necessary. Here, MeHQ acts as a secondary stabilizer (Scheme 3). For storage and transportation conditions $MeHQ/O_2$ is suitable[8] because MeHQ does not change the color of the monomer and if the polymerization is desired in a consecutive processing step it can be induced by simply stripping the monomer with nitrogen.

In the production process the stabilization with $MeHQ/O_2$ fails, due to the high temperatures (>100 °C) and the anaerobic atmosphere, in which case phenothiazine (PTZ) is used instead. In the PTZ inhibition reaction (Scheme 4) the hydrogen, which is bound to the nitrogen atom, is transferred to a free radical. The resulting PTZ radical is stabilized by mesomerism. Levy assumed that the inhibition by PTZ does not depend on dissolved oxygen and therefore PTZ should react with peroxy radicals as well as with primary and alkyl radicals.[11]

The reaction of DiAA formation which cannot be inhibited is described as a 1,4-Michael addition (Scheme 5). This reaction is catalyzed by protons. If AA is diluted with water it has a higher dissociation degree. Hence, more protons are set free. This in turn leads to an increase of the DiAA formation rate.

DiAA can react again with AA molecules and form triacrylic acid and higher oligomers. The investigation of the formation rate of DiAA showed a second order reaction kinetics.[10] The formation of higher oligomers was also observed, but

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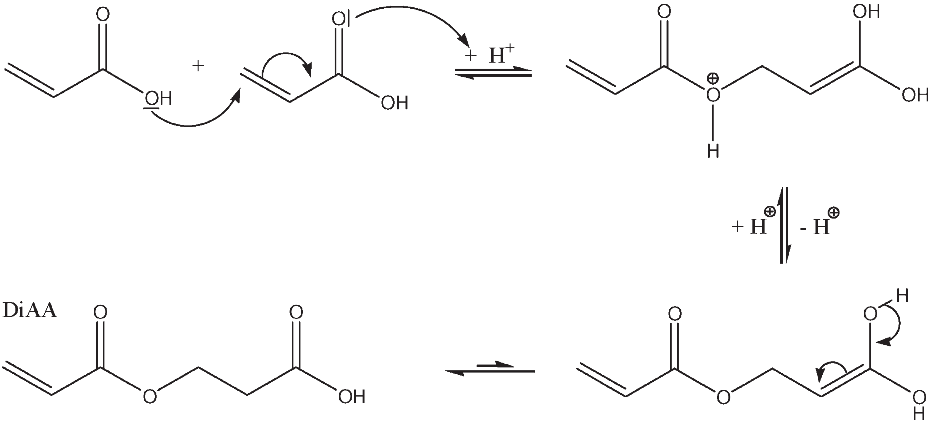
[1] ppm and % are always given in $(g\,g^{-1})$ unless otherwise specified.



Scheme 5.
The mechanism of the DiAA formation via Michael addition.

can be neglected because of the slow reaction rates.[11]

Experimental Part

For all experimental work and the related apparatus the following requirements have to be considered:

(1) No contamination of monomers with any impurities
(2) No metal containing materials in any equipment that has contact with the monomer
(3) Gas (oxygen) impermeable piping and apparatus
(4) Adjustable oxygen concentration in the feed
(5) No use of initiators
(6) No direct comparison between monomers of different production lots
(7) Storage of monomers in a dark and cold place (−18 °C)

Determination of the Stability via Isoperibolic Reactors (IPR)

The stability of acrylic monomers is measured by novel isoperibolic reactors (40 mL). The reactor system consists of twelve reactors each with temperature control and registration. A special construction allows experiments under similar conditions as in a production plant. With an application of one-way elements and by the external placing of the thermocouple elements bulk polymerizations can be carried out without cleaning procedures. This guarantees the same starting conditions. The determination of the IP is done by measuring the temperature profile. During the IP the temperature stays at the chosen initial temperature. When spontaneous polymerization starts, the temperature rises rapidly. The parallelization enables the simultaneous performance of four separate experiments each under triple determination.[12]

Kinetic Investigations

Depending on the desired boundary conditions and on the reaction which has to be studied, different reactors are used. In general, batch and CST reactors are used.[7,13] All reactors are run in an isothermal operation mode. In contrast to the IPRs the reactors for kinetic investigation are not designed for the polymerization reaction. Thus, the experiments have to be stopped before the end of the IP.

The MeHQ, PTZ and DiAA concentrations are analyzed via HPLC. The oxygen concentration is either detected by a clark cell,[7] after stripping the dissolved oxygen out of an AA sample, or via an in-situ sensor[13] which uses the principle of fluorescence quenching.

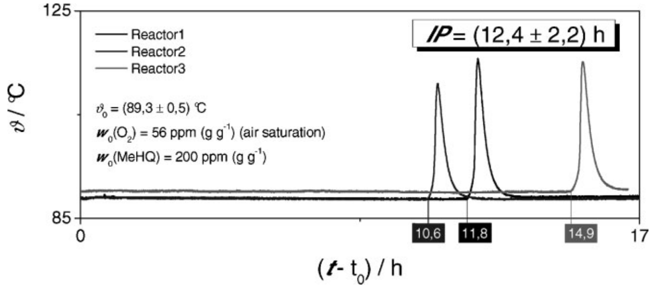


Figure 1.
The result of an IPR experiment for the determination of the stability of AA (200 ppm MeHQ) at 90 °C initial air saturation.

Results

Stability Investigations - Acrylic Acid

The determination of the IP gives an overall information about the stability of the monomer under the chosen conditions (temperature, oxygen concentration, stabilizer, ...). The result of an IPR experiment with AA (200 ppm MeHQ) at 90 °C and initial air saturation is shown as an example in Figure 1. Each curve describes the temperature profile in one of the three reactors. The beginning of the peak shows the end of the IP and the start of the polymerization. The average IP is then calculated.

By variation of one parameter the dependence of the IP from this parameter is systematically ascertained. Figure 2 shows the measured IPs at different temperatures.

The IP can be considered as a kinetic parameter. It describes the duration in which all inhibition related reactions take place. According to that the reciprocal IP is a measure for the overall reaction rate of all chemical events during the IP. Thus, an Arrhenius-like relationship is found by plotting the logarithm of the reciprocal IP against the reciprocal temperature (Figure 3). The resultant Arrhenius parameters can be used for inter- and extrapolation of the IP. By this way the monomer stability can be estimated under storage and transportation conditions.

Stability Investigations - Acrylates

In earlier works we have already shown that the AA-esters are much more stable than AA itself, and that they also show a lower oxygen consumption rate.[13] We have proved this result with the help of the

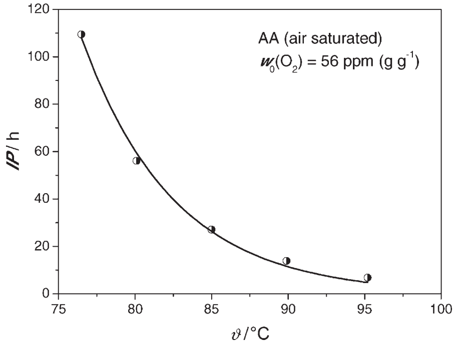


Figure 2.
The IP of AA (200 ppm MeHQ) at different temperatures and initial air saturation.

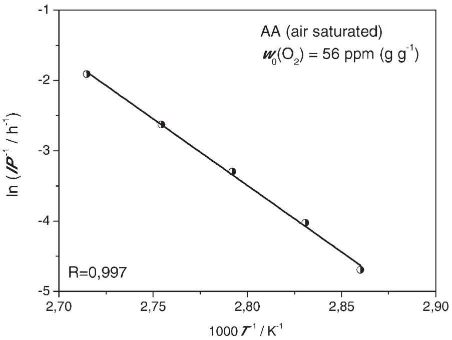


Figure 3.
The Arrhenius plot of the IP of initially air saturated AA (200 ppm MeHQ).

IPRs. The stability of the acrylates correlates directly with the size of the molecules. 2-ethyl hexyl acrylate is more stable than butyl acrylate and this again is more stable than methyl acrylate. It can be explained by an intramolecular dilution of the double bond concentration. In addition to the longer IP, the IPR experiments demonstrate that the polymerization rate must be lower, because the temperature peaks are much smaller and, thus, the heat production rate must be lower, too.

Kinetic Investigations - Part I: Diacrylic Acid Formation

The diacrylic acid (DiAA) formation takes place even at room temperature in significant amounts. Hence, the knowledge of the DiAA formation kinetics is important for quality aspects. On the laboratory scale DiAA formation can be prevented by storage of AA in the frozen state (e.g. −18 °C). At industrial scale freezing is not possible. Hence, it is necessary to find out how long AA can be stored under given conditions, without the product quality suffering.

The data published by Wampler already show that a higher temperature and the presence of water accelerates the DiAA formation.[10] Our experiments confirmed these results. As demonstrated in Figure 4 the DiAA curve at 3% water is above the 1,5% curve. The higher number of data points enables us to see that the assumed second order reaction kinetics cannot be true. With regard to the reaction scheme (Scheme 5) the DiAA formation seems to be a bimolecular elementary reaction. At the beginning the DiAA formation proceeds slowly and accelerates successively. This curve progression can be explained by a consecutive reaction via an intermediate chemical species. At the end the curves start to flatten out, which is related to the TriAA formation. S-shaped curves result by this.

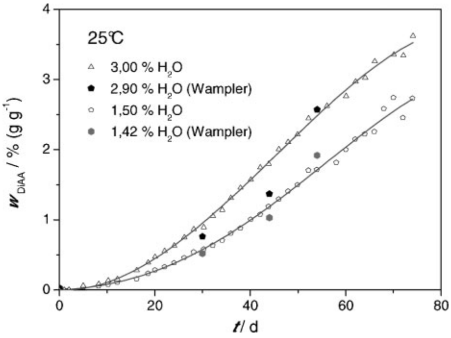


Figure 4.
DiAA formation in AA at 25 °C and water concentrations of 1,5 and 3%. To compare our data with those published by Wampler[10] these are also shown in the diagram (filled symbols).

After 60 days at 25 °C and a water concentration of 1,5%, about 2% of DiAA has built up in AA. At 35 °C it reaches even 6% DiAA. In this case the subsequent processing steps are already disturbed and the resultant products can not yield the desired quality and properties.

Kinetic Investigations - Part II: Stabilizer Consumption (MeHQ)

The knowledge of the oxygen consumption kinetics is of great importance, particularly for the storage and transportation of AA. Assuming that the oxygen depletion takes place linearly, the end of the IP can be estimated by simple extrapolation. The state of the art is a pseudo-zero order reaction kinetic.[14] However, in Figure 5 the oxygen consumption curves for pure and aqueous AA (200 ppm MeHQ) do not progress linearly. In pure AA and with 5% water even negative reaction orders can be observed ($n < 0$). Thus, the oxygen consumption is accelerated. This means that the IPs estimated in the past were too long, because the oxygen reservoir is consumed earlier than the linear extrapolation would predict. If more water is added (10%) the oxygen consumption reaction order changes and becomes positive.

Because of the safety aspects, i.e. to avoid a polymerization in the laboratory reactors, in the earlier work all experiments were stopped a long time before the IP ended. Now, experiments with long residence times enabled us to measure the non-

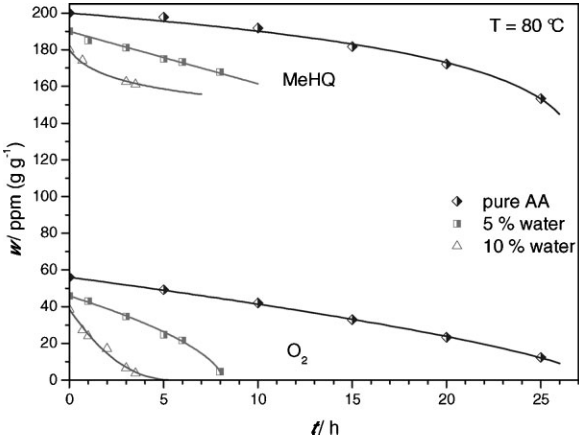


Figure 5.
The result of a CSTR experiment for the determination of oxygen and MeHQ consumption kinetics in pure AA (diamonds) and in aqueous AA (squares, triangles) at 80 °C and initial air saturation.

linear oxygen and MeHQ consumption curves. It can also be seen that the MeHQ is not totally consumed. Oxygen must then be the limiting stabilizer. The simultaneous determination of the MeHQ concentration serves as a control for the oxygen measurement.

As already shown in Scheme 3 the oxygen and MeHQ consumption are directly coupled to each other. This is why in Figure 5 an identical qualitative image concerning the MeHQ consumption curves can be observed.

Kinetic Investigations - Part III: Stabilizer Consumption (PTZ)

So far, the PTZ consumption also, which is important for the stabilization during the production process, is supposed to be a pseudo-zero-order reaction.[15] The result shown in Figure 6 is not in accordance with this state of the art. In fact, the PTZ consumption shows an exponential progress with a positive overall reaction order. Here, once again, the deviation from linearity has been ascertained by a higher experimental effort.

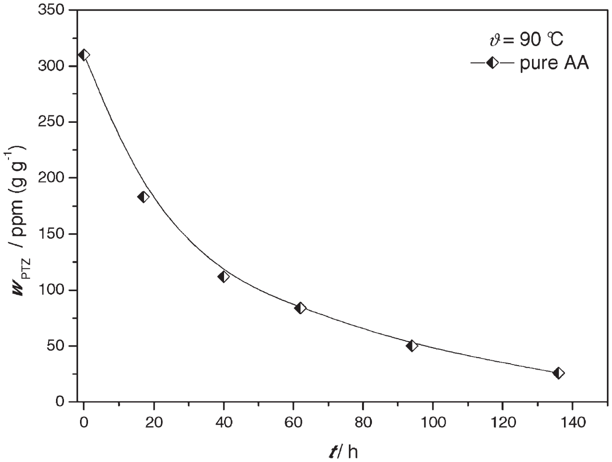


Figure 6.
The result of a batch experiment. PTZ consumption in AA at 90 °C and initial oxygen saturation.

$$\mathrm{RP} \xrightarrow{k_d,\ n=0} \mathrm{R}$$
$$\mathrm{R} + \mathrm{M} \xrightarrow{k_p} \mathrm{P}$$
$$\mathrm{P} + \mathrm{M} \xrightarrow{k_p} \mathrm{P}$$
$$\mathrm{R} + \mathrm{Ox} \xrightarrow{k_{copo_{ox}}} \mathrm{ROx}$$
$$\mathrm{ROx} + \mathrm{M} \xrightarrow{k_{copo_m}} \mathrm{ROxM}$$
$$\mathrm{ROxM} + \mathrm{Ox} \xrightarrow{k_{copo_{ox}}} \mathrm{ROx}$$
$$\mathrm{ROxM} + \mathrm{M} \xrightarrow{k_p} \mathrm{P}$$
$$\mathrm{P} + \mathrm{Ox} \xrightarrow{k_{copo_{ox}}} \mathrm{ROx}$$

Scheme 6.
The model for the simulation of the oxygen stabilization. RP: radical precursor, R: primary radicals, M: monomer (AA), P und ROxM: alkyl radicals, Ox: oxygen, ROx: peroxy radicals.

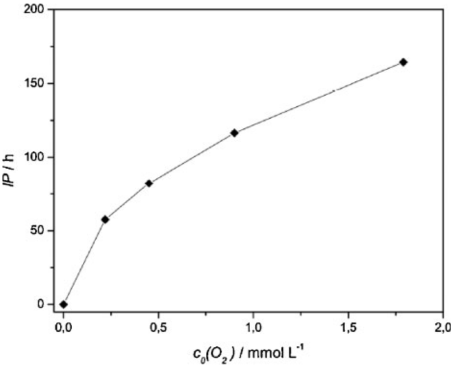


Figure 8.
The simulated IPs at different initial oxygen concentrations calculated by the model shown in Scheme 6.

Simulation

To gain a deeper comprehension of the reaction mechanism during the IP, a kinetic model was developed, which allows the simulation of the oxygen consumption kinetic via Presto-Kinetics®. The chosen reactor model is a simple batch reactor.

At the beginning of the modeling works the maximum chain length of the peroxy radicals was fixed to 20 oxygen and 20 monomer units to keep the model simple. But the variation of the allowed chain length of peroxy radicals showed that a lowering of the chain length leads to significantly extended IPs.

Next, we succeeded in generalizing the copolymerization of monomer and oxygen. Now there is no more distinction possible between the different chain lengths. Furthermore, with this generalized model a non-linear oxygen consumption curve follows, which fits to the previously shown experimental results. The model as described so far is presented in Scheme 6. The simulated conversion curves are shown in Figure 7 (for initial air saturation). After the IP the monomer conversion rises up rapidly to 100% (mol mol^{-1}). This monomer conversion is induced by a simplified polymerization reaction (Scheme 6, third row). The legitimation for such a massive simplification is given by the focus of this research study which lies on the inhibition, not on the polymerization. This reaction step is only implemented to give a signal for the start of the polymerization. Of course, the polymerization curve does not describe the real polymerization.

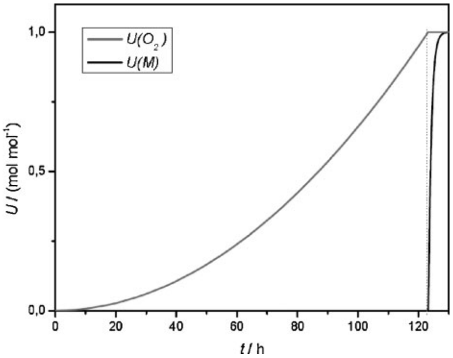


Figure 7.
The simulation result for oxygen stabilization calculated with the model shown in Scheme 6.

The initial oxygen concentration was varied in a theoretical study. Hence, the IP is proportional to the square root of the initial oxygen concentration (Figure 8).

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