Continuous High-Temperature Polymerization of MMA at Pilot Scale

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In the scope of this work, a continuous high-temperature polymerization process for methyl (methacrylate) (MMA) copolymers is developed at pilot scale. At a first instance, the kinetic properties of the reaction system for the given temperature range were determined by DSC and batch experiments. This includes initiation by MMA-peroxides, depropagation of the living chains as well as a high temperature gel effect. All different aspects were included in a general model for the description of the continuous process, allowing the prediction of conversion evolution and molecular weight distributions. This model is established within the software package PREDICI® (CiT, Germany), which is an industrially recognized simulation software for polymerization processes. Finally, the modelled data was compared to data obtained with the continuous pilot plant for verification.

As many other unsaturated compounds, MMA tends to form peroxides with physically dissolved oxygen from air. The latter is usually present in large amounts during monomer storage as it is also indispensable for monomer stabilization, which is commonly achieved by addition of hydroquinone derivatives. The following formation mechanism for MMA peroxides is proposed by [1]:

$$\begin{aligned}
&MMA && \longrightarrow R\cdot \\
&R\cdot && \longrightarrow RO_2\cdot \\
&RO_2\cdot + MMA && \longrightarrow ROOR_1 + R_2\cdot \\
&RO_2\cdot + R\cdot && \longrightarrow ROOR
\end{aligned}$$

The resulting MMA peroxides have a copolymeric character (alternating MMA and O_2) with molecular weights below 10’000 g/mol and they accumulate in the monomer during storage and heating cycles. Figure 1 shows the Arrhenius diagram for several peroxide formation experiments, assuming simplified 1st order kinetics. For these experiments, distilled but air-saturated MMA was heated to various temperatures between 30°C and 90°C and the peroxide content determined by an advanced iodometric method. The formation kinetics can then be determined from the peroxide concentration over time curves.

At temperatures above 100°C, these peroxides decompose quickly into various kinds of radicals, thus initiating polymerization. Figure 2 contains conversion curves for batch experiments at different temperatures without addition of any initiator. The achieved conversions of 30-40% demonstrate the importance of MMA peroxides in high temperature polymerizations. The decomposition kinetics is determined by DSC scanning experiments of the isolated peroxide in solution with constant heating rates. Once again, first order kinetics is assumed for simplification. Values for the formation and decomposition kinetics as used in the model presented in this work are shown in Table 1. More detailed information on the topic of MMA peroxides can be found in [2].

Table 1: Kinetic data for the formation and decomposition of MMA peroxide as used in this work

	Formation	Decomposition
ln k_0 [-]	20.839 ± 2.8 %	26.262 ± 3.8 %
E_A [kJ mol^{-1}]	85.7 ± 1.9 %	108.0 ± 3.1 %

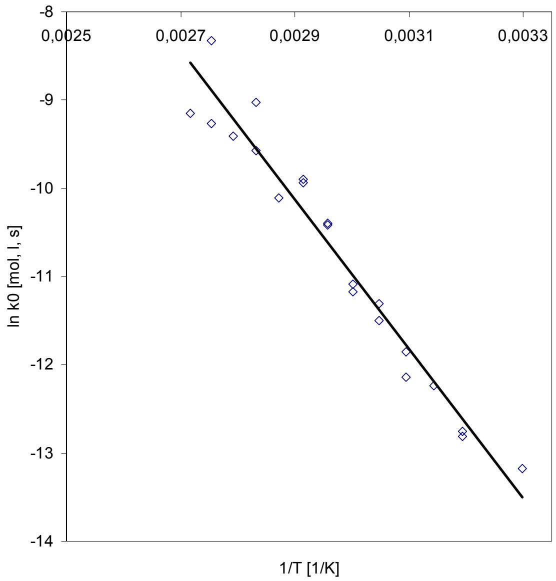

Figure 1: Arrhenius diagram of the MMA peroxide formation

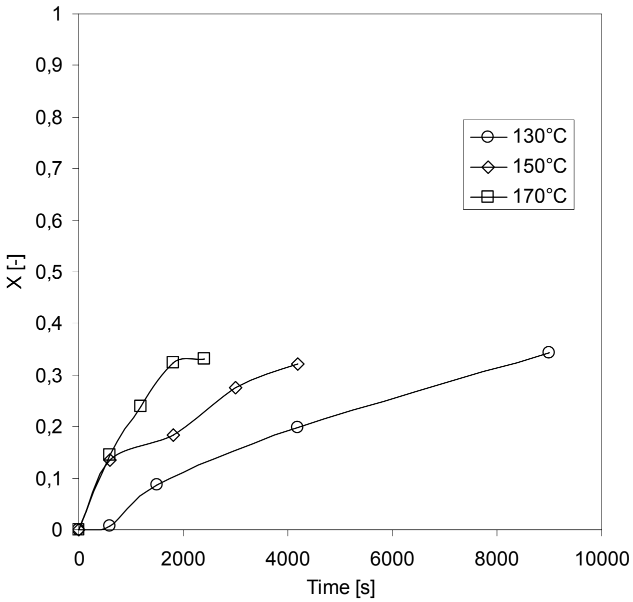

Figure 2: Conversion caused by MMA peroxides in batch experiments

The ceiling temperature, i.e. the thermodynamic equilibrium between propagation and depropagation, is quite low for MMA with approximately 200-220°C, causing a significant limitation of the monomer conversion at reaction temperatures above 150°C. In figure 3, final conversion data from several high temperature batch polymerizations is shown, which demonstrates this effect very well. To take into account the conversion limitation in the model, a depropagation step

$$P_n\bullet \xrightarrow{k_{dp}} P_{n-1}\bullet + MMA$$

is introduced, whose rate constant is determined by an empiric formula that was fitted to experimental data:

$$X^{eq}=1-\exp\left(23.66-\frac{11282.7}{T}\right)$$

$$k_{dp}=k_p\,[MMA]_0\,(1-X^{eq})\,\frac{\rho}{\rho_0}$$

Last but not least, the existing published gel effect models are not suitable for the description of a high-temperature gel effect in a continuous polymerization regulated by a chain transfer agent, since most of them were derived for temperature ranges below the glass transition and/or use initial concentrations for initiator or chain transfer agent (i.e. concentrations at t=0), which for example in a CSTR does not make sense. For these reasons, a new gel effect model is derived, which fulfils the prerequisites of the modelling of the investigated process. To achieve this, the free-volume based model of Chiu et al. [3] is modified by introducing a molecular weight dependency and fitted to experimental data:

$$\frac{1}{k_t}=\frac{1}{k_{t0}}+\frac{\tau(T)}{D(X,M_w)}=\frac{1}{k_{t0}}+\frac{\tau(T)}{D_0\exp\left(\frac{2.3\phi_m}{A(T)+B(T)\phi_m}\right)} \longrightarrow \frac{1}{k_t}=\frac{1}{k_{t0}}+\frac{K\,\tau(T)M_w^{\alpha}}{\exp\left(\frac{2.3\phi_m}{A(T)+B(T)\phi_m}\right)}$$

Figure 4 and 5 show experimental and modelled data for conversion evolution and molecular weight distribution of batch experiments at different temperatures. In figure 4, gel effect and conversion limitation, as well as their correct prediction by the model are clearly visible.

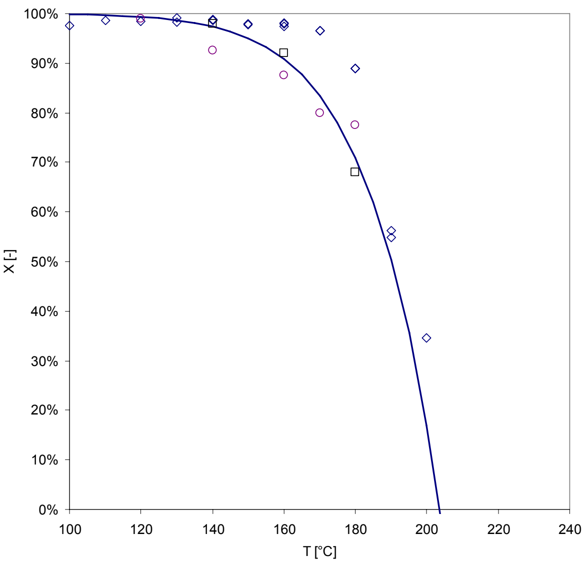

Figure 3: Conversion limitation at high polymerization temperatures (points: experiment, solid line: model)

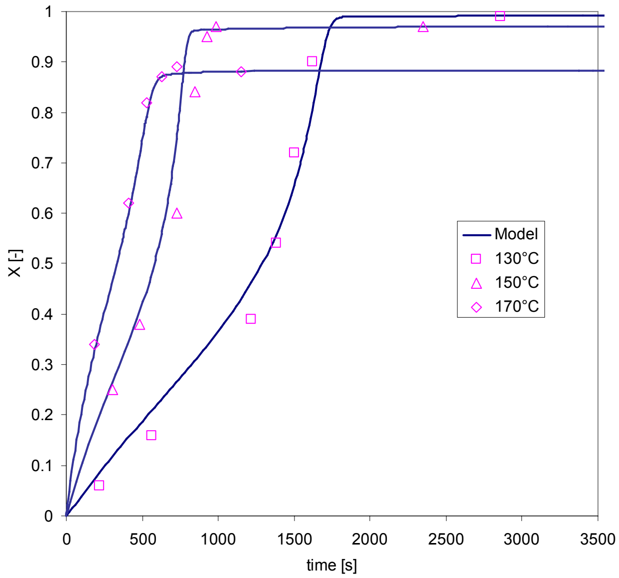

Figure 4: Conversion evolution for batch experiments in bulk, $[I]_0$=1000ppm DTBP (points: experiment, solid lines: model)

For model verification, a continuous pilot plant with a maximum capacity of 10kg/h is used to obtain experimental data. The reactor is built from double-jacketed DN20 tubes equipped with Sulzer Chemtech (Winterthur, Switzerland) SMX/SMXL static mixing elements and consists of two parts: a loop with high recycle ratio (CSTR mode) and a tubular part with plug flow conditions. Thereafter, a flash valve is installed, by means of which the polymer melt is flashed into a vertical two-phase heat-exchanger that ends into a vacuum devolatilization chamber. From here, the degassed polymer melt is evacuated from the reactor by a gear pump. The plant setup is presented schematically in Figure 6.

In order to achieve an inline conversion measurement, the reactor contains two ultrasound probes calibrated for the reaction system. A separate paper dealing with inline conversion measurement of acrylate polymerizations by ultrasound will follow. Additional information is already available in [4]. For verification of the ultrasound measurement, conversion data is also available by offline Headspace-GC from the two sampling valves. From the same samples, molecular weight data is obtained by offline triple detection size exclusion chromatography. The final polymer is granulated for further analysis and processing, e.g. injection moulding.

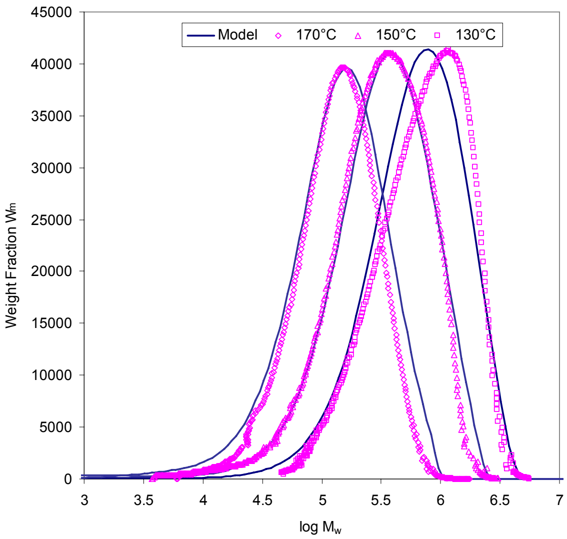

Figure 5: Molecular weight distribution for batch experiments, $[I]_0$=1000ppm DTBP (points: experiment, solid lines: model)

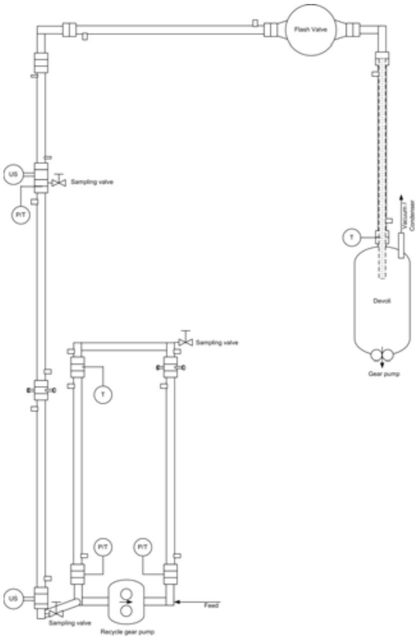

Figure 6: Schematic depiction of the Sulzer Pilot Plant as used in this work

First runs with the pilot plant show good agreement between model and experiment. Figure 7 exhibits exemplary results obtained for a polymerization at 170°C with pilot plant and the model. As regards the time necessary to reach the stationary state as well as maximum conversion and molecular weight, the model correctly mirrors measured data. A small delay in time is noticeable for the measured conversions in the instationary period, which is due to the fact that on one hand the sampling valve is not immediately at the loop exit, and on the other hand the feed flow passes several valves and a pump between the feed tank and the loop inlet. The conversion reached in the loop is rather low at this temperature (X~35%), which can be explained by a rather strong depolymerization. Therefore, rather high initiator concentrations are needed to push the conversion towards higher values.

As can be seen in figure 8, even the molecular weight distribution is astonishingly well predicted by the model, which is a crucial point in simulating polymerization reactions since it is the distribution that influences product properties at a large extent rather than average molecular weights.

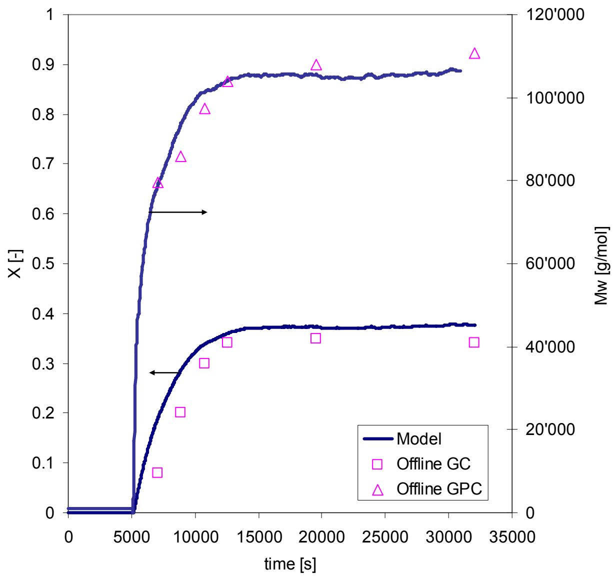

Figure 7: Conversion and molecular weight evolution in the loop reactor at 170°C, model and experimental data

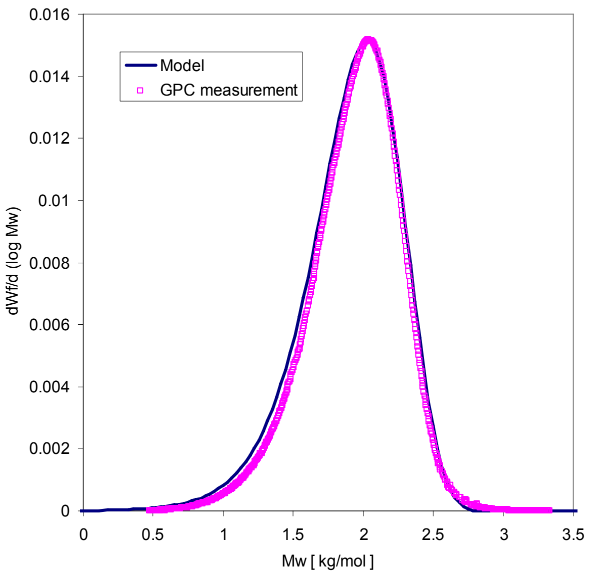

Figure 8: Molecular weight distribution Mw at loop exit in stationary state, modelled and GPC distribution

The goal of these high-temperature experiments is to gradually increase the reaction temperature above 120°C, which will reveal the changes in product properties (molecular weight, thermostability) as well as important reaction parameters such as initiator and chain transfer agent concentrations that are necessary to achieve desired conversions and molecular weight distributions.

References

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[3] Chiu, W.Y., G.M. Carratt, and D.S. Soong, Macromolecules, 1983, 16, 348-357
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