Modeling Rheological Properties of HDPE Based on Polymerization Kinetics

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A three-step modeling approach to obtain rheological properties from the kinetics of the metallocene-catalyzed homopolymerization of ethene is developed. With that, linear as well as slightly branched high-density polyethylene is investigated. Therefore, a deterministic kinetic model of the metallocene-catalyzed polymerization of ethene is set up and coupled with a Monte Carlo algorithm to obtain molecular weight distributions and polymeric microstructures. The topological information is used as input for the rheology model to compute linear and non-linear rheological properties.

1 Introduction

Polyethylene (PE) is of great importance within the chemical industry with its large share of the overall global plastic material demand. The division of PE in different types is done using its density that is given by variations of microstructure. In particular, the degree and length of branching of the backbone influences polymer properties like the density or melting behavior. The branching of the polymer backbone is determined by the synthesis method, chosen process, and process parameters. High-density polyethylene (HDPE) is produced using a catalytic system, mainly heterogeneous Ziegler-Natta or homogeneous metallocene catalysts, at temperatures up to 300 °C and pressures up to 200 bar. This leads to the characteristic structure of linear chains with almost no branching. Depending on the chosen catalyst low amounts of long-chain branching can be detected. Especially ansa-metallocenes are able to introduce macromolecules with terminal double bonds in the polymer chain and, thus, long-chain branches (LCB) can be formed. [1, 2]

These are able to affect the physical properties of the polymer strongly [3]. The physical properties and particularly the rheological melt properties are essential for further processing of polyolefins including HDPE. Knowledge of the melt flow behavior supports the design and parameter selection for processes like extrusion and injection molding. Another common example is the film blowing process where the linear and non-linear rheological properties of polymer melts are important for operation parameters and product properties.

Theoretical approaches in addition to experiments are advantageous due to possible reduction of experimental expense. Modeling as a tool is valuable to predict experimental outcomes and to investigate different parameters

independently and dependently of each other in processes. Of particular interest in polymer modeling are approaches that cover several steps in the production process and are able to predict the product properties from the reactor input. Therefore, a three-step modeling approach is applied for the metallocene-catalyzed polymerization of ethene. This approach combines a computational efficient deterministic kinetic model with a detailed stochastic model to obtain the produced polymer characteristics including their microstructure. Further that hybrid approach is coupled with a model to compute the rheological properties out of polymeric microstructures. The introduced modeling approach is transferable to other polymerization processes. Similar approaches, both two- and three-step models, were already successful applied for different polymerization processes with different degree of accuracy and amount of obtained information. [4]

The demonstrated approach in this work is able to compute linear and non-linear rheological properties of HDPE out of process parameters including temperature, pressure, and composition for a continuous operated solution-polymerization miniplant using an ansa-meallocene. Thereby, information about the molecular weight distribution (MWD), average polymer properties and the polymeric microstructure are obtained. Further, this modeling approach enables the investigation of the influences of low amounts of LCBs in HDPE particularly in regard to their rheological properties.

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2 Three-Step Modeling Approach

The three-step modeling approach consists of a deterministic model, a stochastic model, and a rheology model. In Fig. 1 the three-step modeling approach is shown including the required input and obtained output data. The deterministic as well as the rheology models are usable and beneficial by themselves. Using only the deterministic model the metallocene-catalyzed polymerization process can be simulated in regard to MWD, average polymer properties, and temperature profile. In contrast the used stochastic model is only applicable in combination with the deterministic model, due to the required event frequencies out of the deterministic model and was developed as a hybrid approach. [5]

The deterministic model is set up using the software Predici [6, 7], which allows calculating complex polymerization networks efficiently. Therefore, the resulting system of differential equations is solved numerically using a linear implicit Euler method and includes an adaptive time increment control. The MWDs of polymer species are obtained using the h-p-Galerkin method. The model includes heat balance, momentum balance, and mass balance and the kinetic network of the metallocene-catalyzed polymerization based on the mechanism of coordinative polymerization. [8]

The reviewed system consists of a continuous lab-scale stirred tank reactor operated at temperature around 120 °C and pressure at around 130 bar with a homogenous solution including the monomer ethene, the precursor rac-dimethylsilylbis(indenyl)hafnium dimethyl, the activator tetrakis(pentafluorophenyl) borate, the scavenger trioctyl-aluminium, and the solvent toluene. The kinetic network is shown in Tab. 1. It is set up according to Soares et al. [9, 10] in regard to reactions and their kinetic parameters.

The network consists of initiation, propagation, deactivation, β-hydride elimination, transfer to monomer, and transfer to cocatalyst, whereby all transfer steps to aluminum species are summed in one reaction step. The reaction rate coefficient from β-hydride elimination and from transfer to cocatalyst are estimated collectively from experiments in literature [9]. The activation of catalyst is neglected due to the adaptation of the amount of activated species by a proportional-integral-derivative (PID) controller regarding the conversion of ethene. LCBs in
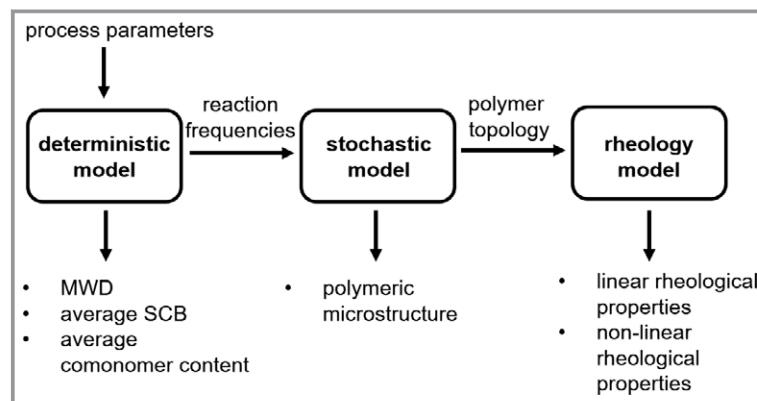

Figure 1. Schematic overview of the three-step modeling approach consisting of a deterministic, stochastic and rheology model. Process parameters are required for the deterministic model, the result of which is MWD, temperature, pressure, and concentration profiles as well as average polymer properties. During the simulation event frequencies are exported and used for the stochastic model to calculate the polymeric microstructure, which is required for rheological simulations to obtain linear and non-linear rheological properties.

HDPE result from macromolecules with terminal double bonds introduced in the polymer by the catalyst. In order to investigate the impact of different LCB amount on polymer properties, the reaction rate coefficient of the propagation of terminal double bonds is adjusted due to unknown reaction rates according to the desired LCB amount. The reaction rate of the propagation of terminal double bonds varies between 0 and $10\,\mathrm{L\,mol^{-1}s^{-1}}$, which is two orders of magnitude lower than the propagation step of monomers. In the equations of Tab. 1, M is a monomer molecule, C^* active catalyst, C deactivated catalyst, P_s^* living polymer with chain-length s, P_s dead polymer with chain-length s, $P_s^=$ macromonomer with chain-length s, and Al are aluminum species.

Table 1. Implemented kinetic network for a metallocene-catalyzed homopolymerization including initiation, propagation, deactivation, β-hydride transfer, transfer to monomer, transfer to cocatalyst, and the propagation of terminal double bonds.

Reaction step	Chemical equation	Reaction rate coefficients [9]
initiation	$C^* + M \xrightarrow{k_p} P_1^*$	$1.143 \cdot 10^3\,\mathrm{L\,mol^{-1}s^{-1}}$
propagation	$P_s^* + M \xrightarrow{k_p} P_{s+1}^*$	$1.143 \cdot 10^3\,\mathrm{L\,mol^{-1}s^{-1}}$
deactivation	$P_s^* \xrightarrow{k_d} P_s + C$	$3.169 \cdot 10^{-3}\,\mathrm{s^{-1}}$
	$C^* \xrightarrow{k_d} C$	
β-hydride elimination	$P_s^* \xrightarrow{k_{\beta H}} P_s^= + C^*$	$5.2 \cdot 10^{-2}\,\mathrm{s^{-1}} - k_{Al}\,[Al]$
transfer to monomer	$P_s^* + M \xrightarrow{k_M} P_s^= + P_1^*$	$0.2\,\mathrm{L\,mol^{-1}s^{-1}}$
transfer to cocatalyst	$P_s^* + Al \xrightarrow{k_{Al}} P_s + C^*$	$(5.2 \cdot 10^{-2}\,\mathrm{s^{-1}} - k_{\beta H})\,[Al]^{-1}$
propagation of terminal double bond	$P_s^* + P_r^= \xrightarrow{k_{p,tDB}} P_{s+r}^*$	–

The stochastic model is based on a Monte-Carlo (MC) algorithm [5, 11, 12] and is newly adapted for the metallocene-catalyzed solution polymerization. The information of the deterministic model, which is used as input, is exported in form of event frequencies R_i for each possible reaction i. For ideal continuous stirred tank reactors these event frequencies are assumed to be constant under steady-state conditions. A single molecule approach is used meaning one molecule is followed through the reactor and based on the respective probabilities P_i for the reaction steps the respective reaction occurs. The probabilities for the reactions are calculated dividing the respective reaction frequency by the sum of the reaction frequencies of every possible reaction step.

$$P_i = \frac{R_i}{\sum_i R_i} \qquad (1)$$

In this manner, several million molecules are simulated and the topological information of every molecule is stored in form of polymer segments that include the position of branching occurring through propagation of the terminal double bond.

To calculate linear and non-linear rheological properties of slightly branched HDPE the branch-on-branch (BoB) algorithm from Read et al. [13, 14] is used. The rheological properties are calculated with an iterative computational approach following the relaxation of the polymers. To use this software the topological results from MC simulations are required to be reduced from several million to several thousand molecules and to be changed in notation. This is done by reducing the polymers independently from their molecular weight and its amount inside the polymer sample to similar numbers. The original distribution is maintained by the weight fraction of each polymer. This guarantees to include enough high molecular structures to obtain a representative sample of polymer topologies.

3 Results and Discussion

The newly developed modeling approach for a metallocene-catalyzed polymerization is evaluated regarding the quality of communication of the three models with each other as well as the predictive capabilities. The correspondence and validation of the model communication is done by comparing the resulting MWD and LCB amount of the three models. The simulation without propagation of terminal double bonds shows high agreement of the number average molar mass M_n and the weight average molar mass M_w for all models. The dispersity of the polymer is, as expected for a metallocene-catalyzed polymerization, around 2. The results of the simulation with propagation of terminal double bonds show slightly higher deviations regarding M_n and M_w with a maximum deviation of 5 % when comparing the deterministic and stochastic model. Further, the dispersity increases slightly when increasing the propagation of terminal double bonds. The deviation can be reduced by increasing the ensemble size in the MC simulation, which indicates a statistical deviation. The interface between the rheology and stochastic model shows no deviation between these molecular weights. The results represent a successful implementation of the hybrid MC model for a metallocene-catalyzed polymerization in a stirred tank reactor. Further, the required interface between the MC and rheology models show firstly a good distribution of selected molecules performing the reduction of the ensemble and secondly the MWDs show satisfying agreement. The simulated MWDs by all three models are shown in Fig. 2 for the simulation of a) a linear HDPE and for b) a slightly branched HDPE.

To investigate the influence of LCB the amount of LCB per molecule is varied using the deterministic model. Further, the LCB amount is kept constant for varying molecular weight. The characteristics of the simulated polymers are listed in Tab. 2 including M_n, M_w and LCB amount. Using these polymers linear and non-linear rheological results are
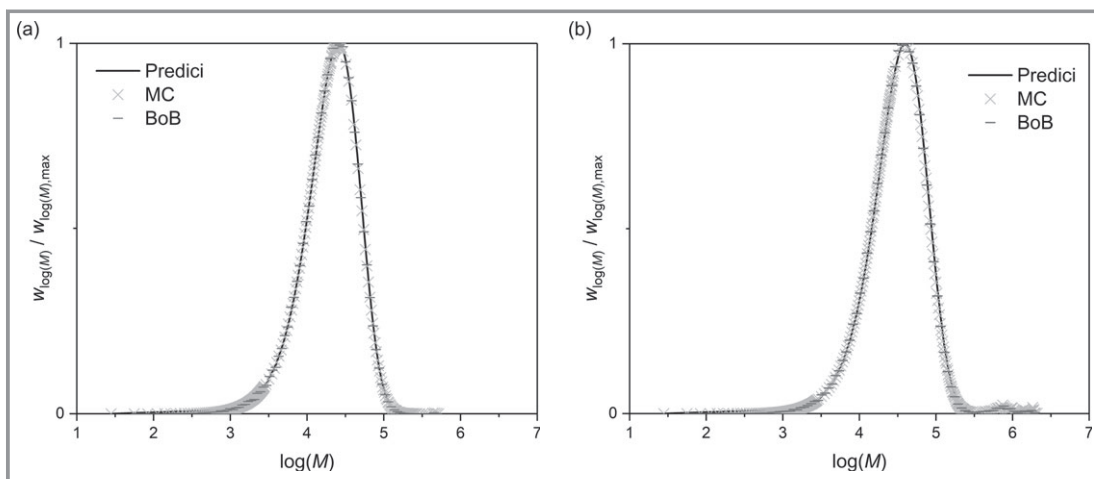

Figure 2. Simulated MWD of the deterministic, stochastic and rheology model plotted for a simulation run a) without propagation of terminal double bond and b) with propagation of terminal double bond. The MWDs of the models are in good agreement with each other.

Table 2. Characteristics of the simulated polymer samples including M_n, M_w, and LCB amount.

Polymer sample	M_n $[10^4\,\mathrm{g\,mol^{-1}}]$	M_w $[10^4\,\mathrm{g\,mol^{-1}}]$	LCB [molecule]
1	1.26	2.50	0
2	1.26	2.56	0.1
3	1.27	2.62	0.2
4	1.27	2.67	0.3
5	2.01	4.62	0.3
6	3.21	6.75	0.3

modeled by the BoB model. The linear rheological results of all samples are compared using the loss modulus G'' and storage modulus G' in Fig. 3. The loss modulus indicates the viscous amount and the storage modulus indicates the elastic amount within the polymer melt. The results in Fig. 3 illustrate the low influence of the LCB amount on the loss and storage modulus. In contrast the molecular weight of the polymer shows a relatively high influence on the moduli and on the cross-over point (COP).

The non-linear rheological results for two different frequencies are shown in Fig. 4. In comparison to the linear properties, the LCB amount has a high influence on the non-linear properties including the strain and shear viscosity. For increasing LCB amount the phenomenon of extension hardening and shear thinning appears slightly. This complies with measurements from literature [1] and is due to the effect of branches in the polymer structure. LCBs are present in the polymer when it is able to form more than two entanglements. The branches change the polymers relaxation behavior by preventing reptation and with rapid deformation rates the chains are stretching without relaxation by reptation, leading to extension hardening. Thus,

these results strengthen the predictive character of this modeling approach.

4 Conclusion

A newly developed three-step modeling approach for the metallocene-catalyzed polymerization and its successful setup was presented. Therefore, the deterministic model is set up using the kinetic network and coupled with the stochastic model. The obtained topological information was then used for rheological calculations with the BoB model. Using the MWDs the successful setup of the models and interfaces is validated.

For slightly branched HDPE, which is possible using ansa-metallocene as catalyst, trends of linear and non-linear rheological properties were theoretically investigated. The results are in agreement with literature and theory demonstrating the possibility of this approach to investigate a polymerization process and product including their properties for further applications.

Symbols used

G	[Pa]	modulus
k	$[\mathrm{L\,mol^{-1}s^{-1}},\ \mathrm{s^{-1}}]$	reaction rate constant
M_n	$[\mathrm{g\,mol^{-1}}]$	number average molar mass
M_w	$[\mathrm{g\,mol^{-1}}]$	weight average molar mass
P_i	[–]	probability of reaction i
R_i	$[\mathrm{s^{-1}}]$	frequency of reaction i
t	[s]	time
η	[Pa s]	viscosity
ω	$[\mathrm{s^{-1}}]$	frequency
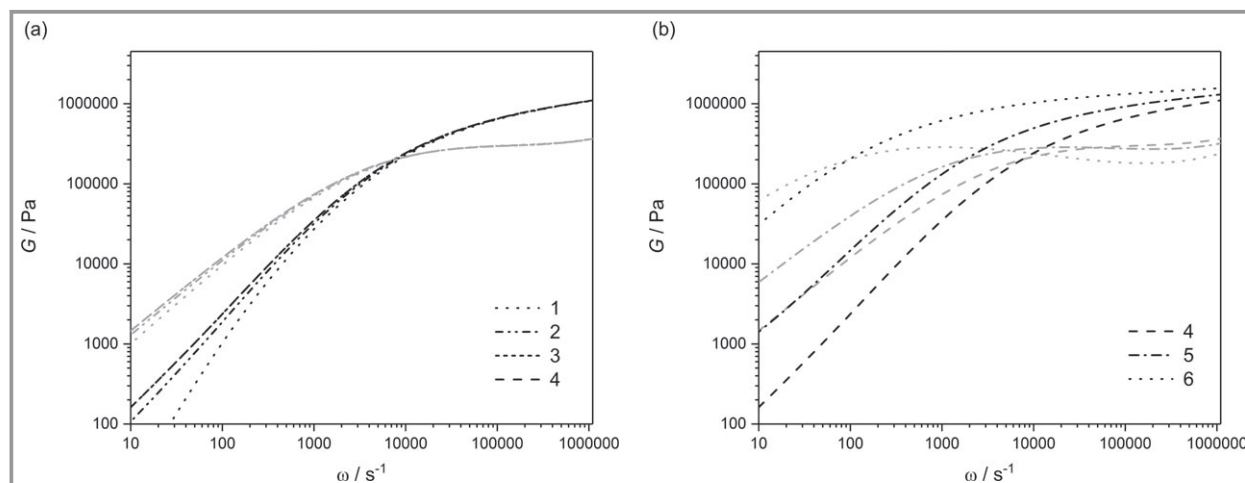
Figure 3. Storage modulus (black) and loss modulus (gray) plotted for a) different amount of LCB by almost constant molecular weight and b) same amount of LCB by different molecular weight.
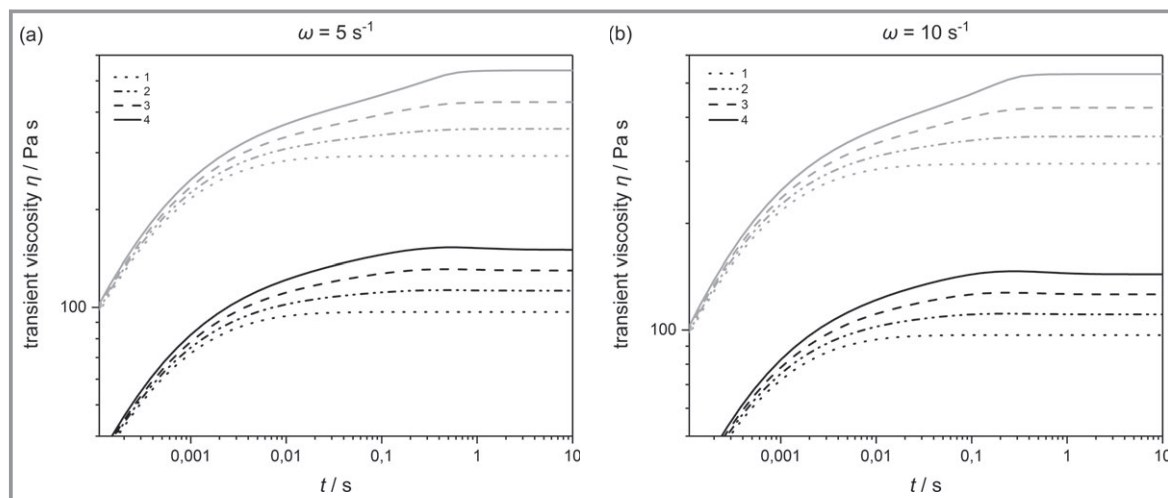
Figure 4. Non-linear rheological properties including the extensional viscosity (gray) and the shear viscosity (black) plotted for polymer sample 1 to 4 for a) a frequency of $\omega = 5\,s^{-1}$ and b) a frequency of $\omega = 10\,s^{-1}$.

Abbreviations

Al	aluminum species
BoB	branch-on-branch
C	deactivated catalyst
C*	active catalyst
HDPE	high-density polyethylene
LCB	long-chain branch
M	monomer
MC	Monte-Carlo
MWD	molecular weight distribution
PE	polyethylene
$P_s{}^*$	living polymer with chain-length s
P_s	dead polymer with chain-length s
$P_s{}^=$	dead polymer with terminal double bond with chain-length s

References

[1] F. J. Stadler, C. Piel, K. Klimke, J. Kaschta, M. Parkinson, M. Wilhelm, W. Kaminsky, H. Münstedt, *Macromolecules* **2006**, *39 (4)*, 1474–1482. DOI: https://doi.org/10.1021/ma0514018

[2] V. Karimkhani, F. Afshar-Taromi, S. Pourmahdian, F. J. Stadler, *Polym. Chem.* **2013**, *4 (13)*, 3774–3790. DOI: https://doi.org/10.1039/C3PY00319A

[3] P. M. Wood-Adams, J. M. Dealy, A. W. deGroot, O. D. Redwine, *Macromolecules* **2000**, *33 (20)*, 7489–7499. DOI: https://doi.org/10.1021/ma991533z

[4] K. Pflug, *Linking Reaction Conditions with Polymer Properties for the LDPE Process*, PhD, TU Darmstadt **2018**.

[5] E. Neuhaus, T. Herrmann, I. Vittorias, D. Lilge, G. Mannebach, A. Gonioukh, M. Busch, *Macromol. Theory Simul.* **2014**, *23 (7)*, 415–428. DOI: https://doi.org/10.1002/mats.201400014

[6] M. Wulkow, *Predici*, Computing in Technology GmbH, Rastede **2011**.

[7] K.-D. Hungenberg, M. Wulkow, *Modeling and Simulation in Polymer Reaction Engineering*, 1st ed., Wiley-VCH, Weinheim **2018**.

[8] M. Bochmann, *J. Organomet. Chem.* **2004**, *689 (24)*, 3982–3998. DOI: https://doi.org/10.1016/j.organchem.2004.07.006

[9] S. Mehdiabadi, J. B. P. Soares, D. Bilbao, J. L. Brinen, *Macromol. React. Eng.* **2011**, *5 (9–10)*, 418–430. DOI: https://doi.org/10.1002/mren.201100015

[10] S. Mehdiabadi, J. B. P. Soares, D. Bilbao, J. L. Brinen, *Macromolecules* **2013**, *46 (4)*, 1312–1324. DOI: https://doi.org/10.1021/ma302513u

[11] H. Tobita, *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31 (10)*, 3163. DOI: https://doi.org/10.1002/polb1993.090311011

[12] D. Eckes, *Modellierung der industriellen LDPE-Synthese für die Tail-End Reaktortechnologie*, PhD Thesis, TU Darmstadt **2017**.

[13] D. J. Read, D. Auhl, C. Das, J. den Doelder, M. Kapnistos, I. Vittorias, T. C. B. McLeish, *Science* **2011**, *333 (6051)*, 1871–1874. DOI: https://doi.org/10.1126/science.1207060

[14] D. J. Read, *J. Polym. Sci., Part B: Polym. Phys.* **2015**, *53 (2)*, 123–141. DOI: https://doi.org/10.1002/polb.23551