 DOI: 10.1002/masy.201200068

Coupling Deterministic and Stochastic Simulation to Model the Polymeric Microstructure of LDPE

Eric Neuhaus,[1] *Markus Busch,**[1] *Andrei Gonioukh,*[2] *Thomas Herrmann,*[3] *Dieter Lilge,*[3] *Gerd Mannebach,*[3] *Iakovos Vittorias*[3]

Summary: Simulation based process development of new LDPE grades often requires a deep insight into the exact microstructure of individual macromolecules. Therefore, we developed an approach, which combines the advantages of the deterministic (low computational time and high accuracy) and stochastic simulation (individual macromolecules with distinct microstructure). The approach can be used for the modeling of continuously driven autoclave and tubular reactors. First results visualize the random conformation of a distinct macromolecule as well as the resulting contraction factor.

Keywords: hybrid simulation; LDPE; Monte-Carlo simulation; stochastic simulation

Introduction

As the polymerization of ethylene is carried out at high-pressures up to 3000 bar and temperatures up to 300 °C experiments for the exploration of new process variants are very time and cost intensive. Thus simulation based product development is a major goal in LDPE research. As rheological models (e.g. from McLeish et al.[1]) require individual polymeric microstructures, an appropriate model has to describe the individual molecular architecture besides material, heat and pressure balances. In this connection a deterministic approach allows a fast and accurate simulation of temperature and pressure profiles, concentrations of low-molecular species as well as moments and molecular-weight distributions (MWD) of polymeric species. As the deterministic approach permits only the computation of averaged microstructural properties (e.g. averaged long-chain branch density) stochastic approaches (Monte-Carlo) are used as an alternative or add-on, because they offer a deeper insight into the polymeric microstructure of each macromolecule. The major disadvantage of full Monte-Carlo modeling with sufficient accuracy is the high computational demand.[2]

The first approach generating individually branched macromolecules was developed by Tobita et al.,[3] who established the concept of primary polymers. A primary polymer is a linear chain "which would exist if all branch points connected to it were severed".[3] In the stochastic algorithm the primary polymers are connected with each other to generate branched architectures. As the molecular-weight distribution (MWD) of primary polymers must be known a priori (e.g. Flory distribution)[4] and steady state conditions are required this concept is limited to continuous stirred tank reactors (CSTR). Furthermore, Tobita uses a three-dimensional random walker to visualize a random conformation of a branched macromolecule and determine its radius of gyration.[5]

Iedema et al.[4] also use the concept of primary polymers for their conditional Monte-Carlo sampling. Compared to Tobita's approach, conditional Monte-Carlo sampling allows the generation of macromolecules with

[1] Technische Universität Darmstadt, Ernst-Berl-Institut, Petersenstr. 20, 64287 Darmstadt, Germany
E-mail: busch@chemie.tu-darmstadt.de
[2] Basell Polyolefine GmbH, Brühler Str. 60, F346, 50389 Wesseling, Germany
[3] Basell Polyolefine GmbH, Industriepark Hoechst, C657, 65926 Frankfurt a. M., Germany

specified length and branching density. As large highly-branched macromolecules are of special interest this feature allows a "fast statistical evaluation [...] of just these most interesting large molecules".[4] Furthermore, Iedema extended the concept of primary polymers to batch reactors with the limitation, that the "scission and branching history is identical for all primary polymers present in the reactor".[6] Therefore, this concept is inapplicable for multi-zone tubular reactors.

Kiparissides et al. developed a full Monte-Carlo approach using externally introduced temperature and pressure profiles for the modeling of LDPE tubular reactors.[7] They assume a volume element with a certain number of molecules from low-molecular species and observe the polymerization in this ensemble during its way through the reactor. As the resulting macromolecules leave the reactor altogether they have the same residence time. Therefore, this approach is inapplicable for a CSTR.[8] Furthermore, the stochastic algorithm has to capture also molecules from low-molecular species. This leads to a high computational demand.

The first work on direct coupling of deterministic and stochastic simulation was published by Schütte and Wulkow, who introduced the concept of a hybrid approach.[2] They model an ensemble of macromolecules for each polymeric species which is used to determine a property distribution in addition to the chain length.

Besides the generation of an interface for rheological simulation the knowledge of the exact architecture of an individual macromolecule allows its graphical visualization and the computation of its contraction factor g. The latter is the ratio of the mean square radius of gyration of a branched macromolecule and a linear molecule with same chain length.

Reaction Mechanism

The model for the free-radical polymerization of ethylene includes the reaction steps depicted in Scheme 1. The kinetic rate constants are taken from Busch.[9] Furthermore, a conversion dependent transfer to polymer reaction rate constant is implemented which was developed by Herrmann and Busch[10] (Eq. 1). Using this approach a consistent description of industrial tubular and autoclave reactors becomes viable. The different transfer to polymer requires a slight adaption of the absolute frequency of the β-scission. The resulting reaction rate constant allows a good agreement between simulated and experimental results and equals the expression published by Goto.[11] The latter was converted to the kinetic scheme used here by Busch[12] (Eq. 2). As short-chain branching is

Initiation:
$$\mathrm{I} \xrightarrow{k_{\mathrm{initiator}}} 2 f_{\mathrm{initiator}} \cdot \mathrm{R}_1$$

Propagation:
$$\mathrm{R}_i + \mathrm{E} \xrightarrow{k_{\mathrm{propagation}}} \mathrm{R}_{i+1}$$

Transfer to monomer:
$$\mathrm{R}_i + \mathrm{E} \xrightarrow{k_{\mathrm{transfer\_ethylene}}} \mathrm{P}_i + \mathrm{R}_1$$

Transfer to polymer:
$$\mathrm{R}_i + \mathrm{P}_j \xrightarrow{j \cdot k_{\mathrm{transfer\_ethylene}}} \mathrm{P}_i + \mathrm{R}_{j,\mathrm{sec}}$$

Propagation of secondary radicals:
$$\mathrm{R}_{i,\mathrm{sec}} + \mathrm{E} \xrightarrow{k_{\mathrm{propagation}}} \mathrm{R}_{i+1} + LCB$$

β-scission:
$$\mathrm{R}_{i,\mathrm{sec}} \xrightarrow{k_{\beta}} \mathrm{R}_{i-k} + \mathrm{P}_k$$

Disproportionation:
$$\mathrm{R}_i + \mathrm{R}_j \xrightarrow{k_{\mathrm{disproportionation}}} \mathrm{P}_i + \mathrm{P}_j$$

Recombination:
$$\mathrm{R}_i + \mathrm{R}_j \xrightarrow{k_{\mathrm{recombination}}} \mathrm{P}_{i+j}$$

Scheme 1.
Reaction steps implemented in the model for free-radical polymerization of ethylene.

of minor interest in this work it was neglected here.

$$k_{\text{transfer\_polymer}} = 1.377 \cdot 10^8 \cdot e^{\left(-\frac{49154\frac{\text{J}}{\text{mol}} - 0.34\frac{\text{J}}{\text{mol}\cdot\text{bar}}p}{R\cdot T}\right)} \cdot \frac{k_{\text{termination}}}{k_{\text{termination},0}} \quad (1)$$

$$k_{\text{beta}} = 1.953 \cdot 10^7 \cdot e^{\left(-\frac{42562\frac{\text{J}}{\text{mol}} - 3.08\frac{\text{J}}{\text{mol}\cdot\text{bar}}p}{R\cdot T}\right)} \quad (2)$$

Hybrid Concept

Our hybrid concept is based on the idea to use the stochastic simulation as an add-on for the deterministic one. The latter is used to compute an integral probability distribution function for the formation of radicals with the chain length one and the effective reaction rates of the reactions implemented in the deterministic model. The effective reaction rate equals the reaction rate constant in the case of a monomolecular reaction. In the case of a bimolecular reaction it is determined by the product of reaction rate constant and concentration of a low-molecular reactant or moment of a polymeric species. If a tubular reactor is modeled, the effective reaction rates depend on the axial position. Furthermore, the position dependent axial flow rate must be determined. If an autoclave reactor is simulated, we assume a steady state CSTR with fixed effective reaction rates. After the deterministic simulation the whole data set is exported to the Monte-Carlo algorithm, where the modeling of individual macromolecules and their exact topology is executed one after each other. Thus our approach has to handle at maximum two individual macromolecules at the same time in the case of recombination or β-scission. Concerning propagation, backbiting, transfer to low-molecular species, intermolecular transfer to polymer and disproportionation only the topology of the currently observed macromolecule changes.

For the computation of g a random conformation of the macromolecule at θ-condition is generated by a three-dimensional random walker.[5] The algorithm starts with a monomer at a chain end, which is placed in the origin of an Cartesian coordinate system. Then two random numbers determine an azimuth angle and a polar angle. Together with the fixed bond length b both angles allow the determination of the Cartesian coordinates of the second monomer. This procedure is repeated until all monomers are positioned in the coordinate system. Afterwards the radius of gyration R_g^2 (Eq. 3) is determined by summing over all monomer monomer distances.[13] Finally equations 4 and 5 allow the computation of g.[13]

$$R_g{}^2 = \frac{1}{s^2}\sum_{i=1}^{s}\sum_{j=i+1}^{s}\left(\vec{R}_i - \vec{R}_j\right)^2 \quad (3)$$

$$\left\langle R_g{}^2\right\rangle_{s,\text{linear}} = \frac{b^2 s}{6} \quad (4)$$

$$\langle g\rangle = \frac{\left\langle R_g{}^2\right\rangle_{s,\text{branched}}}{\left\langle R_g{}^2\right\rangle_{s,\text{linear}}} \quad (5)$$

As pure deterministic models only generate chain-length differentiated averaged long-chain branching densities a structure averaging model is required to determine g (e. g. Zimm-Stockmayer-Theory[14]). Thus a deterministic model cannot distinguish between macromolecules with same length and branching density but different branching architecture or segment lengths. The concept depicted here captures these differences which are important concerning rheological predictions of the polymer melt.

Results

The simulation of one macromolecule allows its visualization and the computation of its contraction factor g (Figure 1). Furthermore, we know its exact history. In the following example we randomly picked out a macromolecule which developed in a technical autoclave LDPE reactor: The simulation started with the propagation of 145 monomers followed by

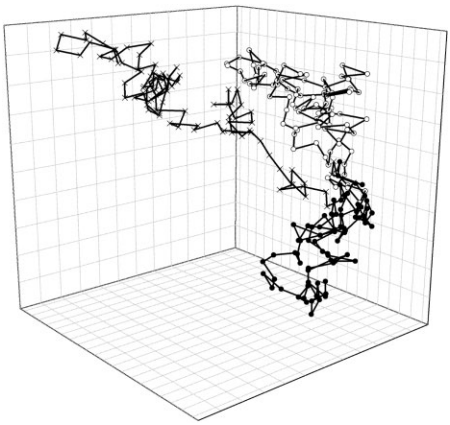

Figure 1.
Visualization of a random conformation of a macromolecule from a technical LDPE autoclave with a chain length of 264 monomers and one long-chain branch. This conformation leads to a contraction factor of $g = 0.7323$. Averaging over 1000 conformations yields an averaged contraction factor of $\langle g \rangle = 0.777 \pm 0.006$.

the recombination with another linear radical of chain length 23. Reactivation by intermolecular transfer to polymer causes the abstraction of a hydrogen atom at monomer 78. Afterwards a long-chain branch with length 77 grows at this position followed by termination by disproportionation or transfer to monomer, chain transfer agent or polymer. After another reactivation of the macromolecule β-scission occurs leading to fragmentation between monomers 50 and 51 of the long-chain branch (looking from the branching point to the end point). The branched fragment gets the radical functionality, adds another 46 monomers and terminates. After its individual residence time is reached, it leaves the reactor with an overall chain length of 264 monomers. The deterministic simulation of the technical autoclave reactor requires a simulation time of 10 minutes until steady state conditions are reached. The stochastic simulation of the described macromolecule and its topology is done within 0.0036 seconds. Assuming θ-conditions and averaging over 1000 conformations yields a contraction factor $\langle g \rangle = 0.777 \pm 0.006$ for this individual macromolecule.

Conclusion

Our hybrid concept allows the simulation of individual macromolecules and their complete polymeric microstructure. As we compute the chemical surrounding in a deterministic simulation, we do not have to handle discrete molecules from low-molecular species in the stochastic part of the approach. This conception leads to a remarkable reduction of the required computational time. It allows both, microstructural detailed and fast modeling. Furthermore, the accuracy of the stochastic part of our hybrid simulation is independent of the size of the macromolecular ensemble. Thus it is possible to simulate only one macromolecule or a whole ensemble of several million macromolecules with the same accuracy. Due to that the parallelization of the approach is easy to handle. Finally, the developed approach can be used for all reactor types, because it requires no a priori knowledge of the MWD's shape or type and assigns an individual residence time to every macromolecule. Thus it offers a higher universality than the established approaches from Tobita et al.,[3,5] Iedema et al.[4,6] and Kiparissides et al.,[7,8] which can be used either for autoclaves or tubular reactors. In a following publication we will have a look on the results received from the simulation of a whole ensemble of macromolecules both in tubular and autoclave reactors and compare them with experimental results.

[1] D. J. Read, T. C. B. McLeish, *Macromolecules* **2001**, *34*, 1928–1945.
[2] C. Schütte, M. Wulkow, *Macromolecular Reaction Engineering* **2010**, *4*, 562–577.
[3] H. Tobita, *Journal of Polymer Science Part B* **1993**, *31*, 3163–3171.
[4] P. D. Iedema, H. C. J. Hoefsloot, *Macromolecules* **2006**, *39*, 3081–3088.
[5] H. Tobita, *J. Polym. Sci. B* **2001**, *39*, 391–403.
[6] P. D. Iedema, *Macromol. Theory. Simul.* **2012**, *21*, 166–186.

[7] D. Meimaroglou, P. Pladis, A. Baltsas, C. Kiparissides, *Chemical Engineering Science* **2011**, *66*, 1685–1696.
[8] D. Meimaroglou, C. Kiparissides, *Macromolecules* **2010**, *43*, 5820–5832.
[9] M. Busch, *Macromol. Theory. Simul.* **2001**, *10*, 408–429.
[10] T. Herrmann, Dissertation, TU Darmstadt, **2011**.
[11] S. Goto, K. Yamamoto, S. Furui, M. Sugimoto, *J. Appl. Polym. Sci.* **1981**, *36*, 21–40.
[12] M. Busch, *Macromol. Theory Simul.* **2001**, *10*, 262–274.
[13] M. Rubinstein, R. H. Colby, *Polymer Physics*, Oxford University Press, Oxford **2003**.
[14] B. H. Zimm, W. H. Stockmayer, *J. Chem. Phys.* **1949**, *17*, 1301–1314.

