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Rule of Morality versus Rule of Law? A Multi-Method Comparative Study into the Values that Characterize a Good Civil Servant in China and the Netherlands

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Summary

"Towards the architectures of macromolecules, modeling of multi-dimensional polymer chain distributions"

Control of end use properties of branched polymers such as low-density Polyethylene (ldPE) produced at industrial scale is difficult at the molecular level since experimental techniques fail to detect the most decisive microstructural properties. Therefore, mathematical models are important in predicting the interesting microstructural properties of polymers. Besides chain length, properties such as number of branch points, number of combination points, number of radical sites, number of terminal double bonds, etc., also provide valuable microstructural information, and hence are of great interest for industrial applications. Thus, the main goal of this thesis was to provide reliable multi-dimensional models of ldPE accounting for chain length, degree of branching and combination points as dimensions.

Obviously, to obtain reliable models of polymerization mechanisms and to interpret results appropriately, the outcomes of all model assumptions are followed closely. Key assumptions are related to the random scission reaction (breaking can take place in any random position of the chain), being modeled as linear or 'topological' scission, and to allowing/disallowing gelation.

An extensive explanation of the decisive reactions, modeling assumptions and the potential modeling schemes is given in Chapter 1. All the provided models in this thesis are more or less resembling the free radical polymerization condition of ldPE, while the implementations of the models have been done in MATLAB©. In Chapter 2, the developed population balance model forms a sound basis for further investigations of molecular weight and degree of branching distribution of ldPE. The 1-dimensional chain length-model, accounts for degree of branching by branching moments or pseudo distributions of branch points. The common free radical polymerization reactions including chain scission have been considered in the model. The scission reaction is modeled by either the linear or the topological scission model. . The latter takes (in comparison to linear chains) the varying scission length distributions into account by applying an empirical Monte Carlo based function of fragment lengths resulting from random scission of branched topologies. Regarding the numerical treatment of the distributions, the Galerkin-finite element method has been applied, which is based on the same principles as PREDICI®. The fundamental numerical problem arising from topological scission has been solved by developing a special method to deal with grid refinement problems. Thus, the model provides more accurate results, allowing a precise comparison to earlier results of Molecular Weight Distribution (MWD) by Size Exclusion Chromatography- Multi Angle Laser Light Scattering (SEC-MALLS) data, and to Monte Carlo simulations.

In Chapter 3, the model from Chapter 2 has been developed further to investigate the effect of multiradicals (multiple radical sites on a chain) and gelation on the molecular weight distribution of ldPE. The number of radical sites dimension is treated by pseudo-distributions. The model shows that in the absence of combination, gel does not form, but that accounting for multiradicals leads to a better prediction of the long molecular weight distribution tail. Results of the multiradical model with topological scission are well in line with Monte Carlo simulations,

which implicitly but properly accounts for multiradicals. For the case of combination without scission, the multiradical model gave a perfect agreement with Monte Carlo simulations as regards prediction of the gel fraction and chain length distribution of sol molecules. The classical monoradical (maximum of one radical site per chain) model failed to describe the gel regime. A remarkable outcome of this model is that the classic model under the conditions of strong branching and combination termination gives rise to extremely broad and bimodal distributions, which according to the multiradical model is an absolute artifact, although mathematically correct. This effect is entirely due to the assumptions stating that gel is absent and transfer to polymer is exclusively occurring to dead chains. The multiradical model does not have to apply these erroneous assumptions. A non-gel assuming variant of this model allowed us to properly detect the gelpoint and the associated distribution. The scission model adopted, linear or topological scission, was also of extreme importance for the gel regime prediction. Regarding the performance of the proposed models, we could conclude that for full random scission the (deterministic) multiradical model assuming topological scission was the closest to the exact solution from Monte Carlo simulations.

In Chapter 4, we provide a model of the molecular weight distribution under circumstances of ldPE for a tubular reactor with realistic non-isothermal (industrial) conditions and for a series of Continuous Stirred Tank Reactors (CSTRs). The existence of multiradicals and the occurrence of gelation were allowed. The presented deterministic model is based on the Galerkin method and employed the moments of the radical sites distribution using pseudo distributions to model the second dimension next to the chain length for several CSTRs in series and a batch reactor. For reference, Monte Carlo simulations have been carried out for the same reactor configurations. Assuming topological scission to account for the highly branched characteristic of the system, good agreement was found between the multiradical model and Monte Carlo simulations. As conditions of ldPE polymerization lead to broad molecular weight distributions being close to gel point, allowing for gel turned out to be crucial. Not allowing for gel resulted into extremely broad bimodal distributions, which with the present set of models were identified as an artifact. The experimentally observed bimodal distribution was indeed obtained for a single tank reactor, but the bimodality decreased as the number of the reactors in series increased and it finally disappeared in batch reactor. The resulting distributions from deterministic models always showed perfect agreement with Monte Carlo simulations for the case of no scission and satisfactory agreement for mild scission.

A set of models to calculate the contraction factor of the radius of gyration (compactness), which to maximum extent account for the kinetics of a radical polymerization closely resembling ldPE, is presented in Chapter 5. The models provide an alternative to the Zimm and Stockmayer's (1949) analytical expression of contraction factor for molecules with terminal branching. The new models take more realistic kinetics- branching due to chain transfer to polymer and termination by combination reactions- into account and are based on the results of a 3-dimensional population balance model of chain length, number of branch points and number of combination points. The results, being representative for branched molecules such as ldPE, show significantly stronger contraction than those predicted by the model of Zimm and Stockmayer. In the case of termination by disproportionation only, the calculated molecular sizes were smaller by a factor of almost two. It was shown that the interpretation of contraction factor as measured by SEC-MALLS to find the branchedness of ldPE leads to a considerably lower estimate of branching with the new model than by using the standard Zimm and Stockmayer model.

A full 2-dimensional model of ldPE chain length/branching distribution is provided in Chapter 6. This chapter is limited to model the linear problem of termination by disproportionation only, without recombination. Full 2-dimensional population balance equations were solved by the Galerkin method to obtain the distributions, accounting for 2-dimensional topological scission. It was concluded that besides the fragment length distribution as discussed before, explicit assumptions have to be made concerning the redistribution of the branch points on scission fragments. In earlier studies with pseudo distribution models, it was observed that the hypergeometric function is the best model for estimating the branching on scission fragments, since it allows for allocating the branch points on fragments in proportion to the fragment lengths. However, employing the hypergeometric function to this end is not a straightforward task with the presented solution strategy in the Galerkin scheme, since it leads to an even more serious grid refinement problem than implementing the fragment length distribution (Chapter 2). Thus, the full 2-dimensional model was based on the simpler assumption of branching redistribution, where the number of branch points on the fragment is independent of fragment length. The results of the 2-dimensional model without scission are in line with the results of 1-dimensional models that are addressed in the previous chapters, under conditions where the effect of multiradicals may assumed to be negligible.

The provided 2-dimensional distributions are also in perfect agreement with Monte Carlo simulations, if the resolution of the grid nodes on chain length dimension is high enough. It is remarkable that the required resolution of grid points in chain length dimension turned out to be higher in the 2-dimensional model in comparison to the 1-dimensional models. In the results with scission, the effect of applying the simplifying assumption of redistributing branch points on scission fragments is visible in the plot of branching distribution, which shows a maximum. It differs to the results of pseudo-distribution models with hypergeometric distribution and Monte Carlo simulation showing constant values for higher chain lengths. In the case of linear scission the bimodal MWD was exactly reproduced by the 2-dimensional model, but in the case of topological scission, disagreements with MWD from 1-dimensional models have been observed when a parameter-free variant was applied for fragment length distribution.

The focus of Chapter 7 was especially on the role of combination termination in the context of 2- and 3-dimensional population balance models, implying that a mathematically non-linear problem had to be addressed in those modeling schemes. Termination by combination is assumed to be present in most ldPE-modeling studies. Full 3-dimensional population balance equations were solved by the 2-dimensional Galerkin implementation presented in Chapter 6 to estimate trivariate chain length/branching/number of combination points distribution. Accordingly, the third dimension- the combination points- was treated using the pseudo-distributions framework. In the case without scission, good agreements with Monte Carlo simulations as well as with results from lower-dimensional models were observed with sufficiently enough grid resolution. In the case with scission, some deviations were seen as in Chapter 6 due to the way of implementing number of branch points redistribution on scission fragments.