DESCRIBING TRANSFER-TO-POLYMER CORRECTLY OR THE TASK OF ANALYZING LONG-CHAIN BRANCHES QUANTITATIVELY

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ABSTRACT

Nowadays, Low-Density Polyethylene (LDPE) is a largely used commodity polymer with a worldwide production of 40 million tons in 2014.[1] Despite high investment and production costs it is desirable due its long-chain branches (LCBs). They result from the transfer of a radical functionality to a macromolecule and result in unique flow and processing properties.

Modeling the free radical polymerization of ethene correctly - especially with respect to the transfer-to-polymer step - is a highly complex but crucial task. While mean values can be attained by performing deterministic simulations, stochastic simulations - such as Monte Carlo - can reveal chain-length dependent properties as well as macromolecular topologies.[2] Simulating the rheological behavior using these molecular topologies can be the missing link to application.[3] (At the same time it can deepen the understanding of the effect of long-chain branching on flow properties.)

But tackling this problem requires first of all the performance of well-defined experiments as well as a careful analytic investigation of the resulting samples. For the analysis of LCBs several methods are known and have been discussed in literature[4]: The most prominent ones are ^{13}C-NMR measurements, light scattering experiments and rheological studies. However, due to the unique non-uniformity and inertia of LDPE transferring these methods is not that easy. Moreover, the named methods reveal different information connected to the existing long-chain branches. However, a correct interpretation of the data as well as the extraction of universal key figures, such as LCB/1000C, is problematic as the data is usually interpreted using model assumptions.

In order to improve the understanding of the kinetic transfer-to-polymer step as well its impact on the molecular structure a detailed investigation of the analytical possibilities and obstacles has been performed. Results obtained analyzing the samples in various ways will be compared and observed differences explained. Additionally, the analytic results will be compared to simulation results. In some respects, good agreement has already been achieved, whereas especially when comparing absolute LCB/1000C numbers discrepancies are still present. Nonetheless, the combination of careful analytic investigation combined with simulations results seems promising to enhance the understanding of LCB-formation and impact on product properties.

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References:

[1] Plastics Europe – The Facts 2015, Brussels, **2015**.
[2] E. Neuhaus, *PhD thesis*, Darmstadt, **2013**.
[3] D. J. Read, J. *Polym. Sci. Part B: Polym. Phys.* **2014**, *53*, 1099.
[4] L. I. Kulin, N. L. Meijerink, P. Strack, *Pure & Appl. Chem*. **1988**, *60*, 1403.