In the context of radical polymerizations the intermolecular transfer to polymer commonly denotes a reaction, in which the radical functionality of a growing chain is passed on to a dead polymer. This requires the abstraction of a methylene hydrogen atom and thus leads to the formation of a secondary macroradical. If a sequence of propagation steps follows such a transfer reaction, a so called long chain branch (LCB) will be created. [1] Together with the short chain branches (SCB), which only contain a few monomer units, the LCBs determine the overall topology of the polymer. The latter plays an important role in many respects, e.g. for radii of gyration as a microscopic quantity or rheological properties of the material in a macroscopic sense. [2,3] Hence it is desirable for polymer engineers to gain control over the mechanism that generates LCBs. This would be a progress towards the long-term goal of influencing the polymeric properties just by sophisticated design of the production process.

However, controlling the formation of LCBs first requires knowledge of the rate for chain transfer to polymer. Either it must be assessed as an absolute value at defined conditions or as a ratio with respect to any of the well-characterized elementary reactions in the polymerization such as the propagation. Moreover a supposed non-trivial dependency on different reaction parameters should be considered for the rate coefficient. Not only temperature and pressure but also viscosity of the reaction mixture, final degree of conversion, degree of polymerization or initial monomer concentration could have an impact on the rate of intermolecular transfer to polymer. [4]

Some of the aforementioned correlations for the chain transfer to polymer have already been successfully tested in special systems. Ahmad and coworkers for example have examined the variation of LCB density with the initial monomer concentration for the radical solution polymerization of n-butyl acrylate. [5] Nevertheless, there is no comparable study concerned with the polymerization of ethylene yet. This lack may be due to the extraordinary process parameters under which the branched, low-density type of polyethylene is typically being produced.

The polymerization of ethylene is done in mass, involves high pressures of up to 300 MPa and high temperatures in the range of 450-550 K. This prevents a straightforward analysis of reactions such as the chain transfer to polymer which is part of a complex reaction network. In fact kinetic studies under high pressure require material-consuming and also otherwise costly experiments. For this reason a careful preparation, which allows to perform only a minimum of experiments for the investigation of the chain transfer to polymer, is attractive.

One possibility to designate the most appropriate approach is to simulate experiments of different design and analyze their outcome with respect to the variation of detectable properties. Therefore we use an established model that takes into account the complete reaction network of the polymerization, the physical properties of the reaction mixture, the reactor geometry and the residence time. It employs differential equations which are solved numerically. We can evaluate the quality of different sensors for the reaction rate in focus and differentiate between more and less favorable experimental parameters.

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