

# Modelling of Tubular High-Pressure Polyethylene Reactors



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## Abstract

The goal of simulation-aided product design of polymers is to optimize the processability of the polymers produced by varying reaction conditions. As the processability of polymers is predominantly influenced by the polymeric microstructure, a model of an industrial high-pressure polyethylene reactor must describe the molecular weight distribution as well as degrees of long- and short-chain branching. Furthermore, it is highly desirable to obtain chain-length differentiated microstructural properties. Based on the software Predici, a model has been developed that computes temperature and pressure

profiles for transient (PDE module) and steady-state (ODE module) operating conditions and obtains detailed information about the polymer microstructure. Due to the complexity associated with solving coupled equations for heat and material balance and differential equations needed to determine the chain-length differentiated quantities, it is reasonable to use a two-stage toolkit. In the first step, temperature and pressure profiles are computed by the ODE module which are then used for the calculation of chain-length differentiated observables such as the number of long-chain branches per chain.

## Conversion dependent transfer to polymer

- Kinetic data from laboratory experiments show decreasing rate of transfer to polymer with conversion
- For transfer to polymer reactions to occur, two macromolecules need to diffuse so that the radical center can abstract a hydrogen atom from a polymer chain
- » Is it possible to use the correlation describing the effect of diffusion on the rate coefficient of termination for the transfer to polymer reaction?

$$\frac{k_{tp}}{k_{tp}^0} = \frac{k_t}{k_t^0} = \frac{0.832}{\eta_r} + 8.04 \cdot 10^{-6} (1-X) \cdot \frac{k_p^0}{1 + \frac{k_p^0}{1.13 \cdot 10^{10}} \eta_r}$$

conversion dependence of termination rate coefficient from Buback et al.

Due to limited experimental data, no reliable activation energy could be obtained. Diffusion limitation was assumed to affect only the pre-exponential factor. Adapting to a single tubular grade results in good agreement with experimental branching densities of a variety of tubular grades and an autoclave grade.

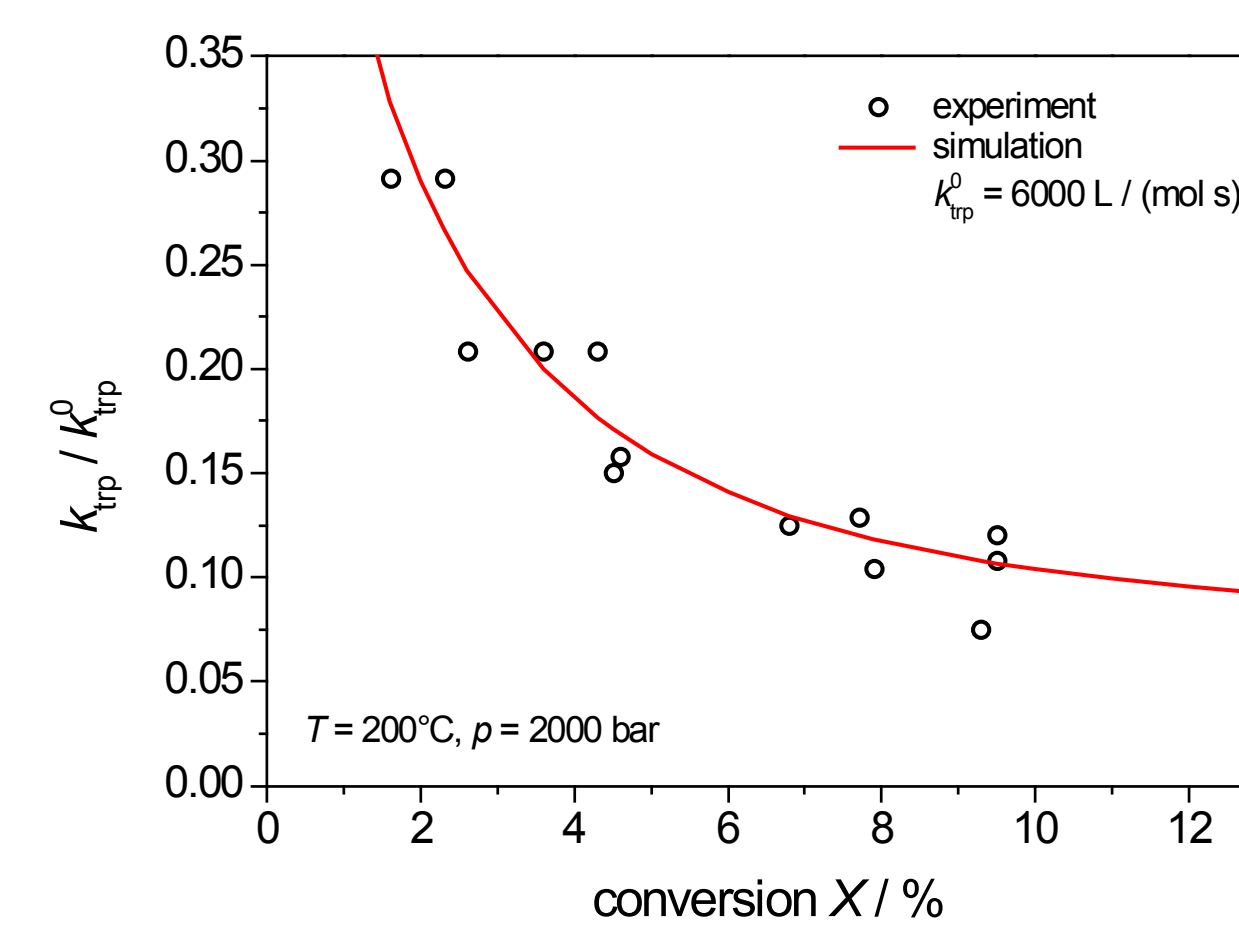


Figure 1: Comparison of normalized rate coefficients for the transfer to polymer reaction obtained from laboratory experiments and the correlation taken from Buback et al.

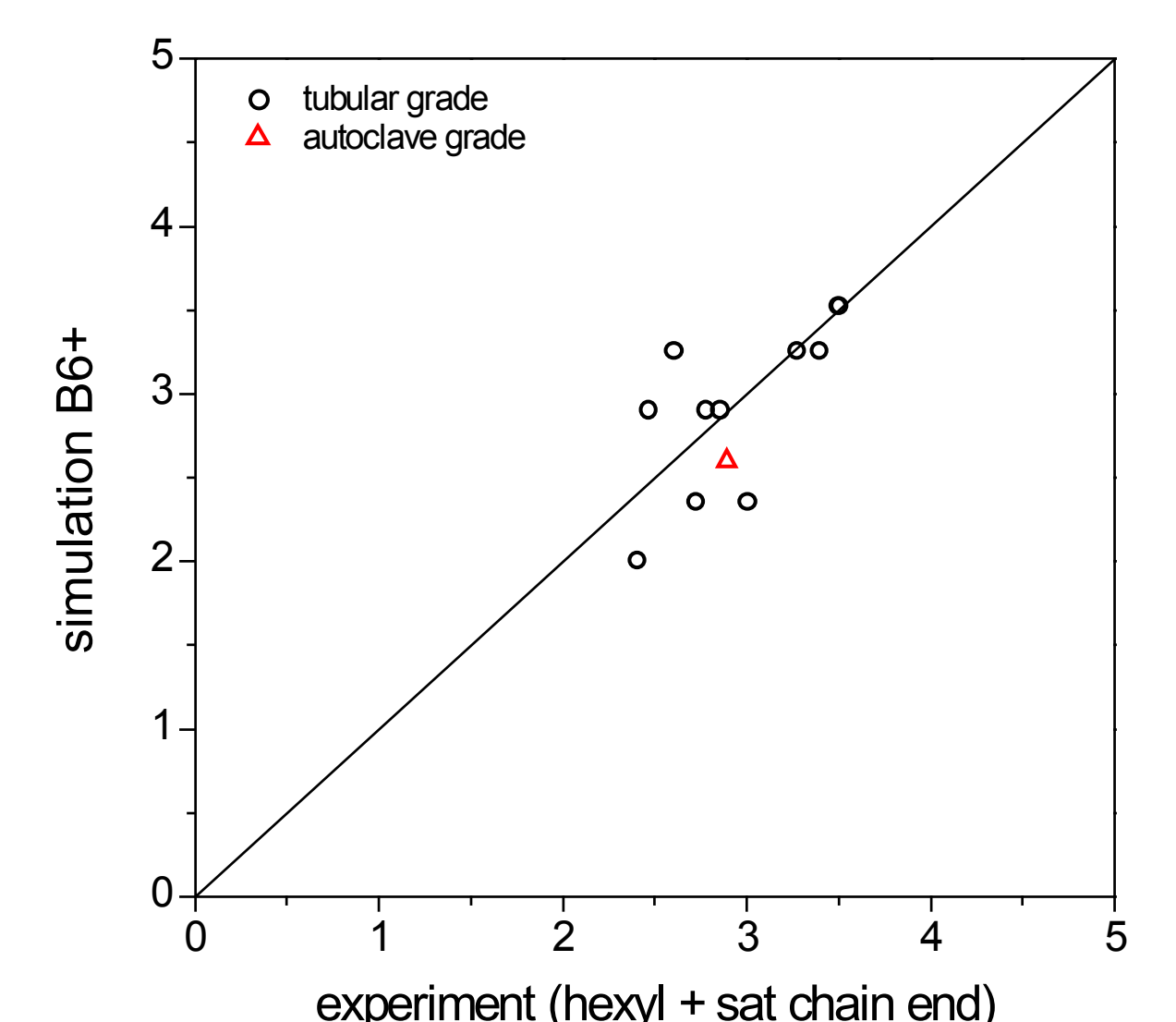


Figure 2: Comparison of molecular weight averaged branching densities obtained from <sup>13</sup>C-NMR measurements and simulations.

## Simulation vs Experiment

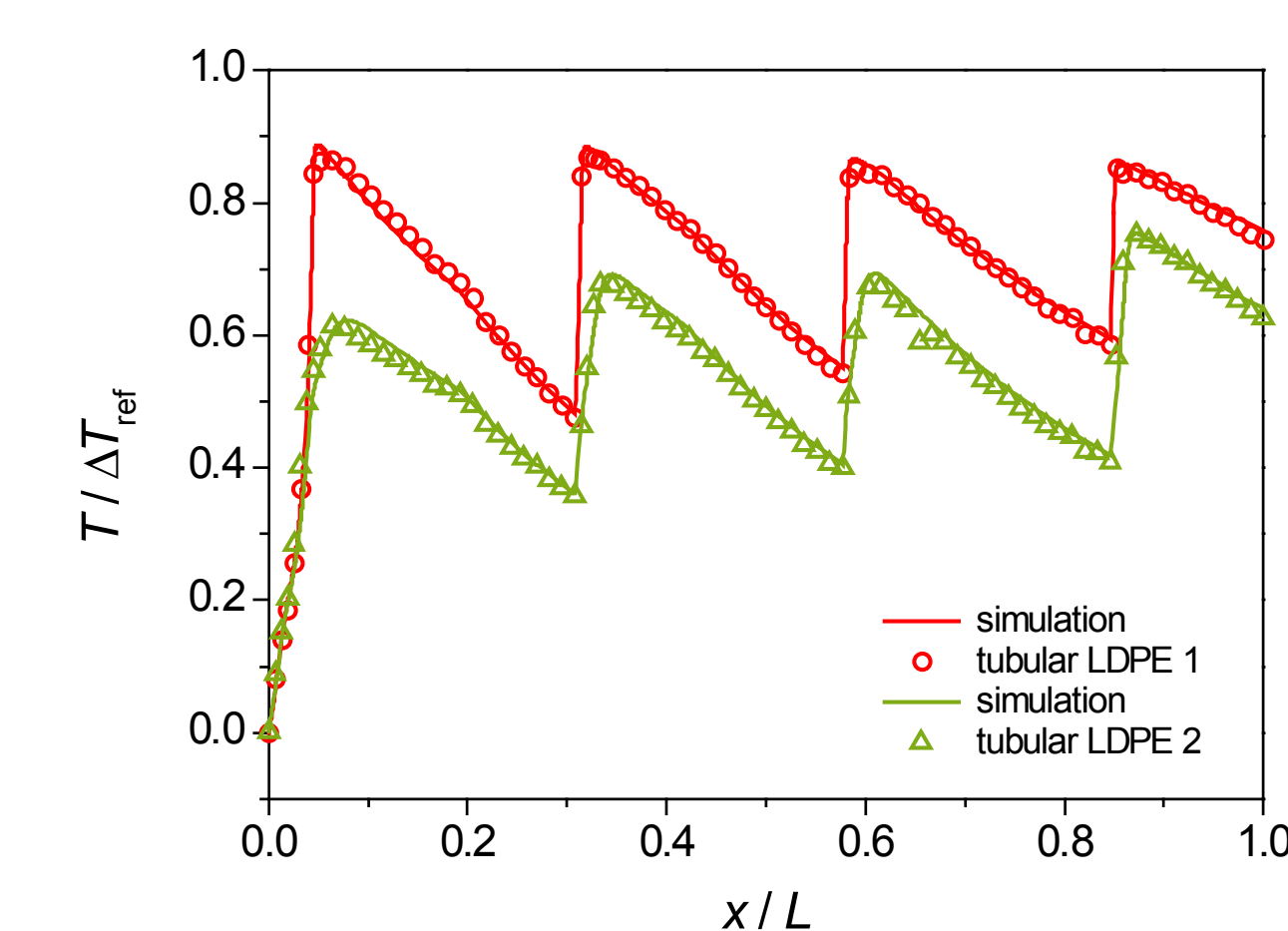


Figure 3: Comparison of simulated and measured temperature profile of a technical industrial tubular reactor for two LDPE grades.

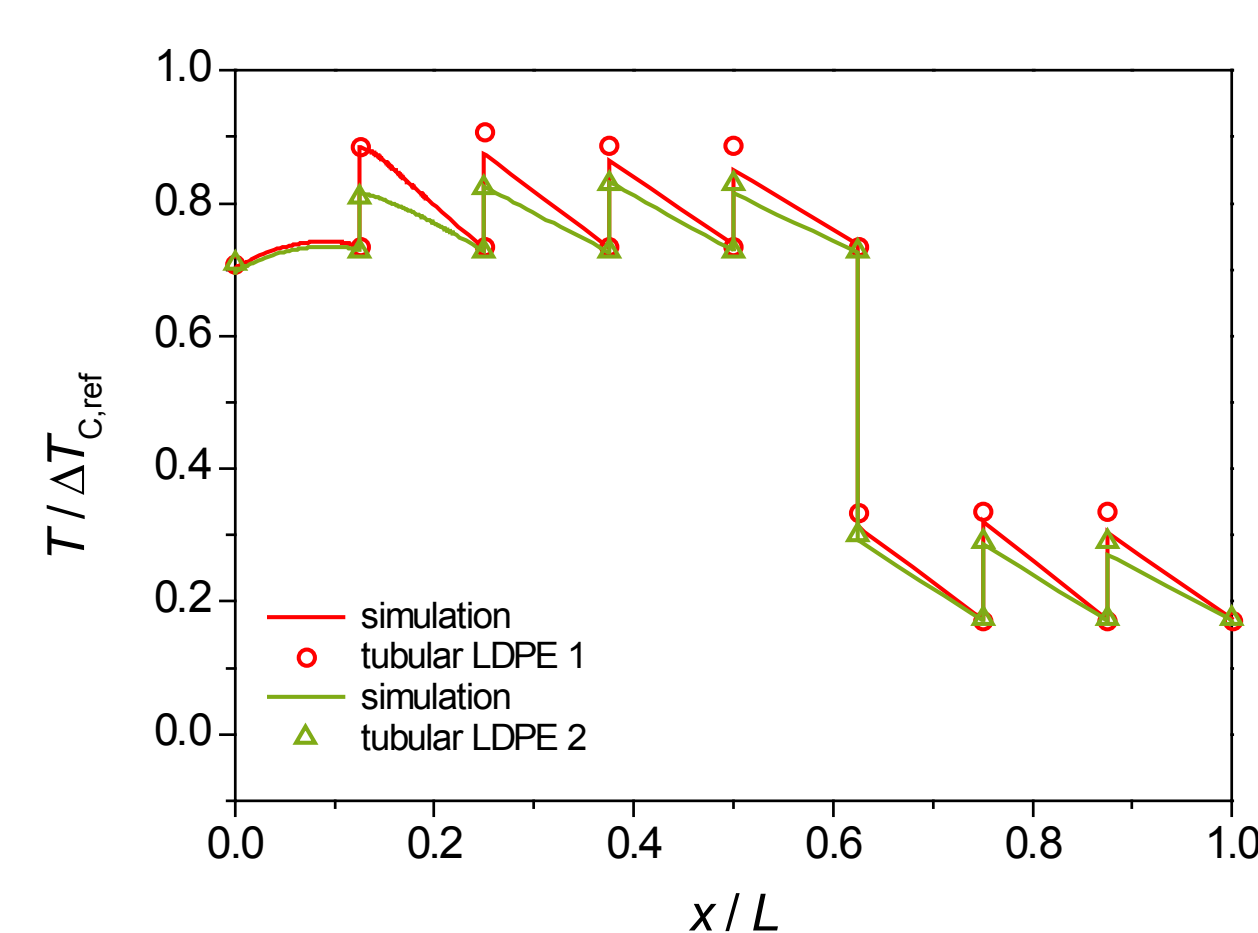


Figure 4: Comparison of simulated and measured cooling water temperatures in a reaction zone of an industrial tubular reactor for two LDPE grades.

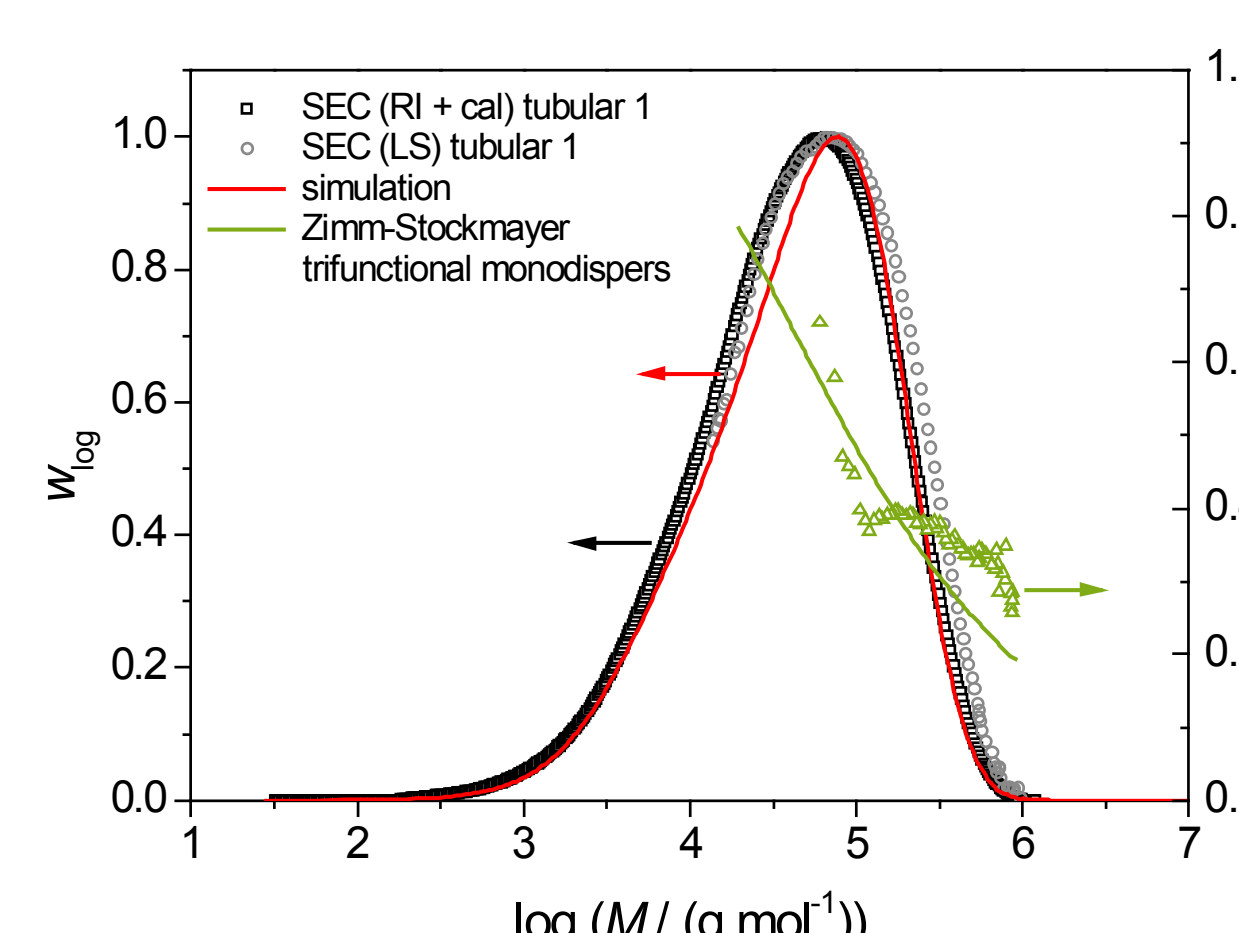


Figure 5: Comparison of simulated and measured molar mass distributions for different tubular grades (scaled to maximum). The squares represent data determined by SEC with RI detection using standard calibration. The circles represent light-scattering data.

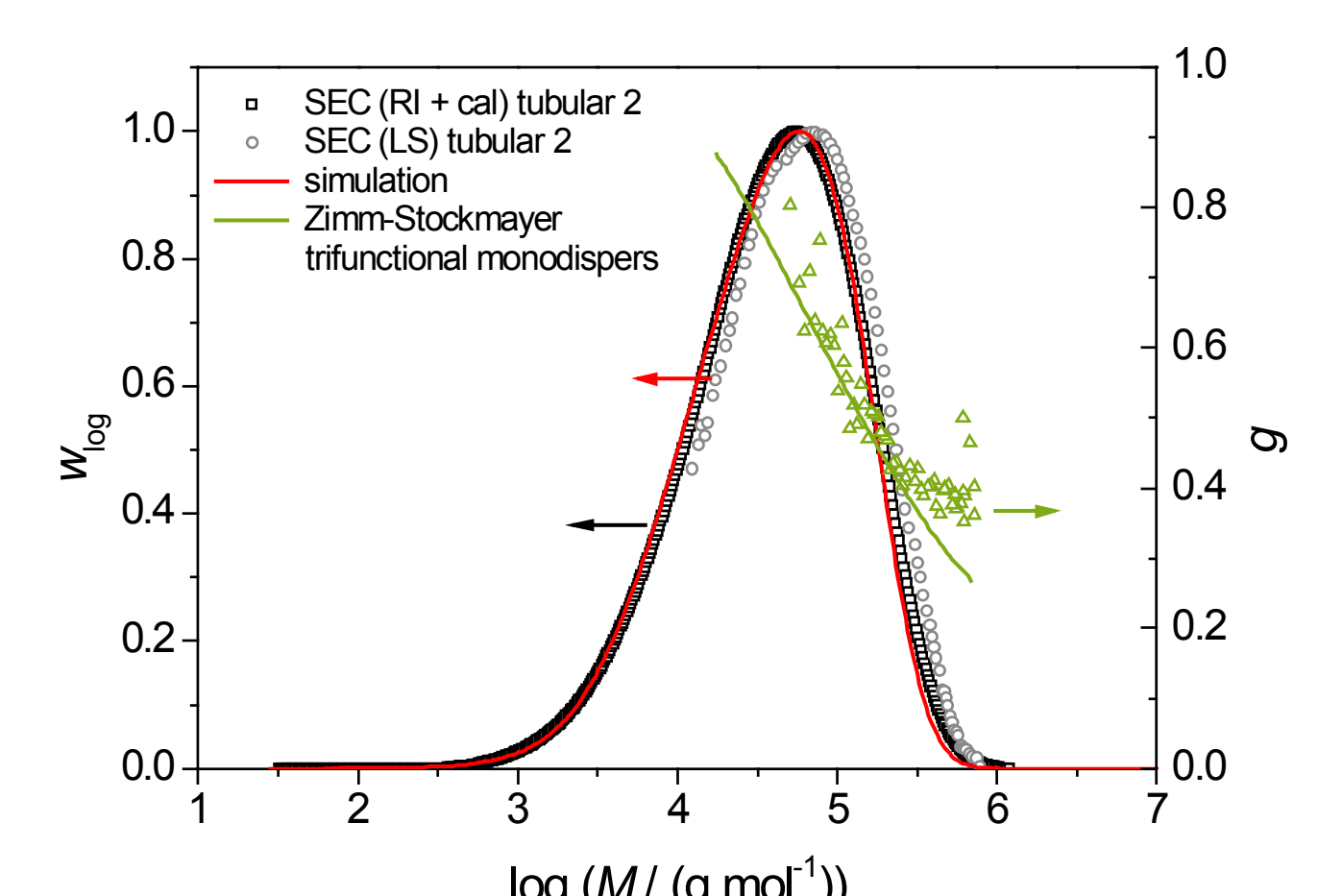


Figure 6: Comparison of simulated and measured molar mass distributions for an autoclave product (scaled to maximum). Squares represent experimental data from SEC with RI detection using standard calibration. The circles represent data from light-scattering. For the simulation, the same rate coefficients were used as those for the tubular grades. The flow rate of chain transfer agent accumulating in the cycle gas is not known. It is therefore adapted to match the maximum of the SEC curves.

- Fouling layer, which is set constant in each reaction zone, increases monotonously from section to section with axial reactor coordinate
- As the flow rate of chain transfer agent is unknown due to accumulation in cycle gas, it is determined by adapting to the maximum of the molecular weight distribution
- » Good agreement for temperature profiles and molecular weight distributions
- » Successful transfer to autoclave reactor with different chain transfer agent on different production site

## Effect of band broadening

Band broadening shifts molecular weight distributions toward smaller molar masses. As the flow rate of chain transfer agents in the cycle gas is unknown, it is adapted to match the experimentally determined MWD. Therefore CTA feeds are overestimated by 10-20%. As long as the effect of band broadening is comparable for the analysis of laboratory experiments and industrial scale samples, kinetic data can be successfully transferred.

Figure 7: (left) Effect of  $\epsilon$  on the molecular weight distribution scaled to first moment obtained from the RI detector signal with calibration. "True MWD" refers to the simulation results for tubular LDPE 2 (c.f. figure 5). (right) Effect of  $\epsilon$  on the molecular weight distribution scaled to first moment and g-factor obtained from the light-scattering detector signal. With increasing  $\epsilon$  the hydrodynamic volume of long polymer chains is reduced. Therefore they co-elute with chains of lower molecular weight. As an average molecular mass is determined, this leads to a narrower molecular weight distribution.

