

INFLUENCE OF REACTION CONDITIONS ON THE SOLUTION POLYMERIZATION OF VINYL ACETATE

Sandra Pietrasch, TU Darmstadt
sandra.pietrasch@pre.tu-darmstadt.de
Markus Busch, TU Darmstadt
Kristina Zentel, TU Darmstadt

Key Words: poly(vinyl acetate), free-radical polymerization, kinetic modeling, chain-transfer agent, retarder

Poly(vinyl acetate) (PVAc) is a widely used polymer, partly due to its great variety of possible applications such as paints, adhesives or coatings. It is produced in high quantities - more than one and half million metric tons were produced in 2020 - so a quick adjustment of product properties is especially desirable to minimise costs, time delays and waste material resulting from test series. The use of computer simulations can aid greatly and predicting product properties based on reaction parameters such as temperature or solvent.

Only few modern publications address this topic in the context of PVAc synthesis,^[1] so this work deals with the implementation of a kinetic model for free-radical polymerization of PVAc in a wide range of reaction conditions.

The impact of three of the most important reaction parameters on the solution polymerization of vinyl acetate are examined experimentally and from the modelling point of view: temperature ($T = 50, 70, 90\text{ }^{\circ}\text{C}$), solvent (toluene, methanol, ethyl acetate) and monomer weight fraction ($w(\text{VAc}) = 20, 40, 50, 60\text{ wt}\%$) are varied systematically and the polymerization is characterized regarding conversion and molecular weight distribution. The products are analysed additionally via NMR spectroscopy to gain insights into their microstructure. Simultaneously, a kinetic model of the reaction network is constructed within the commercial software *PREDICI* and its results are compared with the experimental ones to validate the model and further improve its quality. In this context, the retarding effect of toluene is observed during the experiments and an attempt is made to implement this in the model.

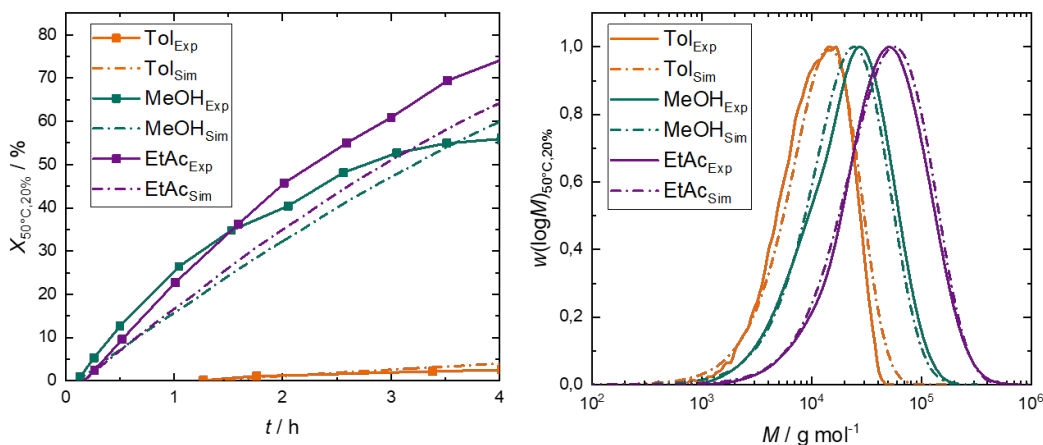


Figure 1 – Influence of various solvents on the polymerization of vinyl acetate: (left) conversion profile, (right) molar mass distributions.

Overall, a good to very good agreement between simulation and experiment is found and the observed trends are reflected well by the kinetic model, as can be seen exemplary in Fig. 1. The variation of the solvent shows the effect of the solvent radical on conversion and molecular weight. Especially the simulated molar weight distributions are in very good agreement with the experimental results and demonstrate the model quality.

Finally, a kinetic model for the solution polymerization of vinyl acetate is developed and successfully applied to a broad range of reaction conditions. Implemented in the model is a good understanding of the polymerization kinetics, which can be used for simulation-based product design. In the next step, further model extensions can be performed, which consider more fundamental details and/or broaden the range of applicable reaction conditions.

[1] Feuerpfeil, Andreas, et al. "Modeling Semi-Batch Vinyl Acetate Polymerization Processes." *Industrial & Engineering Chemistry Research* 60.50 (2021): 18256-18267.