

Determination of the local viscosity inside polymerising emulsion particles via polarized fluorescence spectroscopy.

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In heterogeneous reaction mixtures like an emulsion, it is important to determine thermodynamical and dynamical properties not only for the whole system, but also scaled down to the sizes of the heterogeneous structures. Among others fluorescence techniques belong to the methods allowing the study of a great variety of phenomena occurring in such systems. Advantages of fluorescence are the high sensitivity, the possibility of probe delegation and the easy accessibility of the ns-time scale for dynamical investigations. By the appropriate choice of the fluorescence probe, fluorescence can be used for example to give an insight into kinetical aspects of an emulsion polymerisation.

My thesis addresses the application of the fluorescence depolarisation technique to solve relevant problems in polymerisation system, notably the investigation of the local viscosity inside a polymerising particle. The viscosity of the whole system changes marginally during the polymerisation while the local viscosity inside the polymerisation particle changes drastically. The local viscosity was derived from the fluorescence anisotropy r , which is linked to the rotational mobility of the fluorescence probe.

For the experiments of the present work, perylene was used as hydrophobic fluorescence probe. This probe is soluble only in the oil phase of the investigated Styrene/Water micro-emulsion. This system was chosen, because it is transparent at the beginning of the polymerisation and shows a relatively low turbidity after the reaction. Turbidity is a major problem for the investigation of emulsion polymerisation with polarized light: in a turbid medium unwanted multiple scattering of the excitation and fluorescence photons occurs, leading to a reduction of the anisotropy and thus too low values of the viscosity.

To obtain the desired correct micro-viscosity inside the particle a correction method, which accounts for the influence of multiple scattering on the fluorescence anisotropy, was applied. To achieve this goal, the polarized intensities of purely scattered light at the fluorescence excitation and emission wavelength were recorded together with the fluorescence intensities.

The corrected anisotropy and thus the micro-viscosity show a relatively fast (~10 min) increase to a constant value. However, the also determined degree of conversion (measured online via dilatometry) increases typically for another 20 min before the polymerisation is completed. A comparison of the conversion and the particle size leads to the observation that the size of the particle changes very little during the process.

The results of the thesis clearly demonstrate that the fluorescence depolarisation technique is a good tool for the investigation of the local properties of a polymerising emulsion system. Moreover, combined with dilatometry, it also gives the opportunity to investigate kinetic parameters of the process.