



Ultrasonic in-line monitoring of styrene miniemulsion polymerization

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HIGHLIGHTS

- ▶ Ultrasound attenuation is used to monitor miniemulsion polymerization of styrene.
- ▶ In the early stage thermoelastic effect dominates the attenuation.
- ▶ From the change in thermoelastic contrast we calculated the conversion.
- ▶ In the later stage of polymerization attenuation shows a maximum.
- ▶ The maximum originates from the glass transition in the polymer particles.

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ABSTRACT

Ultrasonic transmission is a simple, non-destructive method to characterize turbid systems like e.g. emulsions or polymer dispersion. Here we use this technique for in-line monitoring of the miniemulsion polymerization of styrene. Either the ultrasound attenuation or the velocity signal provides a fingerprint characterizing the reaction process. During the reaction process the sound velocity increases by about 150 m/s and the attenuation coefficient α changes by more than 75%. In the early stage of polymerization the thermoelastic effect dominates α and accordingly α decreases when more and more polymer chains are generated. In this regime the fractional conversion of monomer to polymer X is obtained from a calibration of the α values using gravimetrically determined X data. In the later stage of the process polymer relaxation dominates and α goes through a sharp maximum when the reaction temperature matches the dynamic glass transition temperature $T_{g,dyn}$ of the polymer/monomer mixture within the droplets. Then X can be directly calculated from $T_{g,dyn}$ without calibration only using physical material parameters for the given monomer/polymer system, and the corresponding data are in excellent agreement with gravimetrically determined values.

This method may be applied to the emulsion polymerization of other monomers, but also for monitoring solution polymerization processes as long as the reaction temperature T_R is below $T_{g,dyn}$. In case of emulsion polymerization the initial decay of α may also be used for process control for systems, which exhibit a change in thermoelastic contrast during polymerization, even if $T_R > T_{g,dyn}$, but needs additional calibration.

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1. Introduction

Emulsion polymerization is a process of great industrial importance for manufacturing of latex paints, adhesives, coatings, paper and textile binders, and synthetic rubber. The need for constant product properties, the reduction of time-to-market, the continuous optimizing of reactor yield, and operation time, as well as the improvement of the safety and the ecological issues lead to high demand for more advanced methods to control the production process. Typical parameters of interest during polymerizations are conversion and reaction rate, molecular weight, chain length

distribution, copolymer composition, as well as particle size distribution and concentration.

Calorimetric measurements have a long tradition to measure the conversion and reaction rate on-line [1]. Optical techniques such as near-infrared (NIR), mid-infrared (MIR), Raman, UV/Vis, or fluorescence spectroscopy, which can be used for simultaneous monitoring of monomer conversion, particle size, comonomer concentration during copolymerizations, are promising but are still on the research level [1,2]. Other on-line methods used on the industrial scale are based on densimetry, surface tension, or chromatographic methods involve sophisticated flow through cells, placed in-line the latex stream [2]. This is critical because the polymer emulsions are sensitive to shear and tend to form polymer films and can clog the measurement device. Another problem is that

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