

Introducing a Semi-Batch Approach to Start Emulsion Polymerization by Ultrasound

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Objective

Emulsion polymerization (EP) initiated by ultrasound offers the potential to produce water based polymer dispersions of high purity and a strong molecular homogeneity without any chemical initiator. The essential radicals to start the polymerization reaction are generated by cavitation. The stirring of the medium is as unnecessary as high emulgator concentrations. Till now the high energy input as well as the less polymer yield of ca. 85% (because of pyrolytic side reactions) build up a strong barrier denying the performance of the process in a technical scale [1].

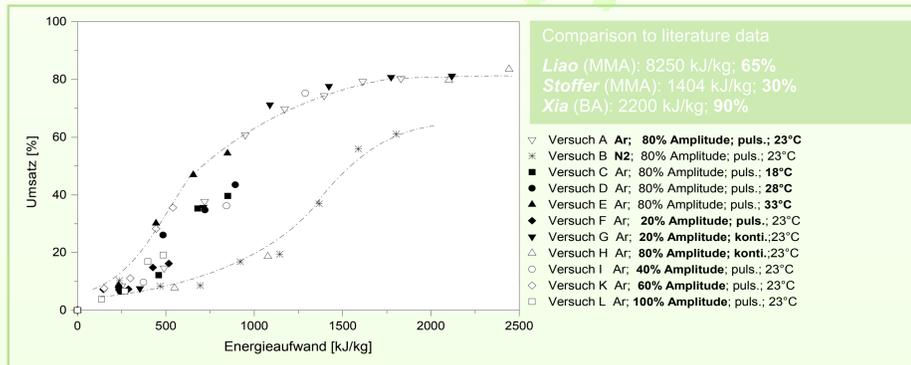


Fig. 1: MMA polymerization in batch modus: reaction yield [%] versus energy input [kJ/kg]

Approach

The main idea of rebuilding the EP process is the use of a sonotrode integrated in an external flow cell and coupled with a stirred reaction vessel (Fig 2). The sonification is carried out with a 11 mm Ø sonotrode in a closed 20 ml cell at a pressure of 2 bar. As model systems methyl methacrylate and butylacrylate (10% solids content in a 1% SDS solution) as well as mixtures of both monomers were used. The radicals generated in the flow cell are transferred to the reactor by a short pressure drop impulse.

The advantages of separating the sonification and the reaction are:

- a considerable reduction of energy,
- the avoidance of pyrolytic side reactions and polymer degradation.

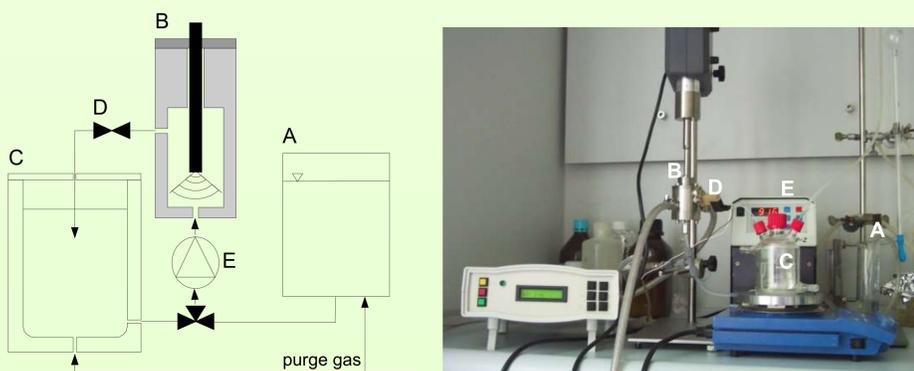
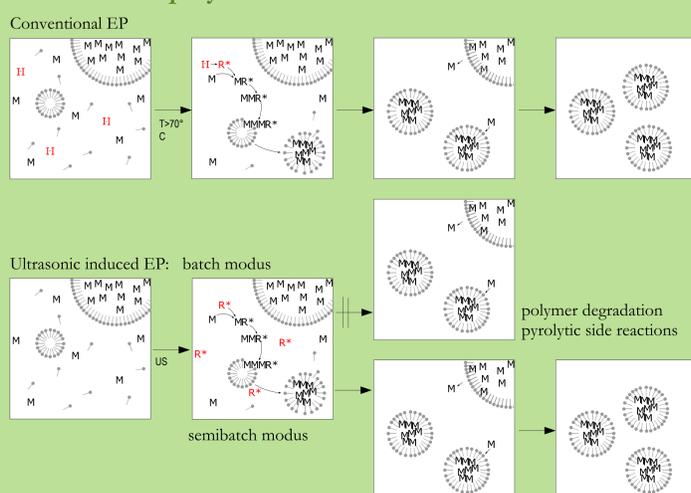


Fig. 2: Semi batch approach (A monomer supply, B ultrasonic flow cell, C reaction vessel, D solenoid valve, E pump)

The new approach requires a detailed knowledge of the radical formation and lifetime and the reaction mechanism.

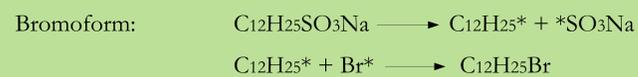
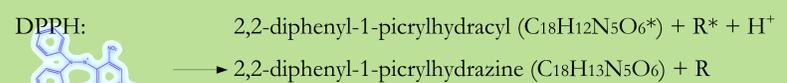
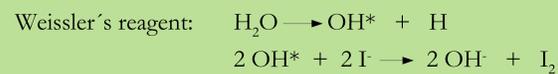
Reaction mechanism: comparison between conventional and ultrasonic induced emulsion polymerization



Results

To study the formation, source and lifetime of the produced radical species various radical trapping experiments were performed, using DPPH, bromoform or the Weissler reagent as radical trapping agents. Changing the pH value of Weissler's reagent gives the possibility to discriminate free OH radicals from H₂O₂ in order to determine the lifetime of free OH radicals.

Radical trapping reactions



The origin of the free radicals formed by cavitation is discussed controversially. While some authors esteem the emulgator molecules as the most important radical source, others describe the decomposition of water and monomer as the main sources. In our study we investigated the radical formation in pure water, water plus emulgator and emulsion (water/emulgator/monomer). In all cases we found nearly the same amount of trapped radicals, suggesting that the decomposition of water predominantly contributes to the formation of free radicals.

The amount of the ultrasonically formed radicals in the flow cell is much higher than that in batch reactors because of the intensified cavitation at increased pressure. In addition the sonification of only a part of the reaction medium reduces the energy input significantly.

Working with an external ultrasonic cell requires the transfer of reactive radicals into the reaction vessel. The transmission time has to be shorter than the lifetime of the radicals. If pure water is sonificated, the OH radicals recombine forming hydrogen peroxide, before they reach the reaction vessel. In presence of monomer molecules OH radicals are scavenged to give secondary free radical species, that initiate polymerization.

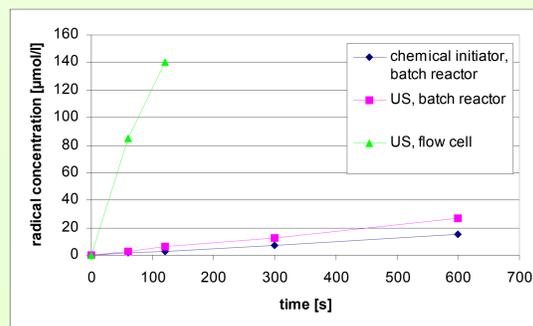


Fig. 3: Ultrasonic versus thermic radical formation

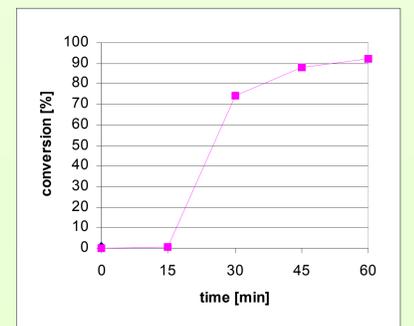


Fig. 4: Polymerization of butylacrylate

Conclusions

- External sonification supplies enough radicals to start the polymerization reaction.
- Radicals mainly originate from the decomposition of water.
- The ultrasonic degradation of polymer chains can be prevented.
- The crucial point is the transfer of the reactive species to the reactor. Further experiments are now employed to shorten the time between radical formation and polymerization reaction.

[1]Hampel, C., Gai, S., Lieske, A., Hahn, M., Krüger, K., Chem. Ing. Tech. 77(2005) 6, 54-61

Acknowledgement:

We gratefully acknowledge the financial support of AIF PRO INNO II FK 0035305UL5