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Short communication

Surfactant-free synthesis of extremely small stimuli-responsive colloidal gels using a confined impinging jet reactor

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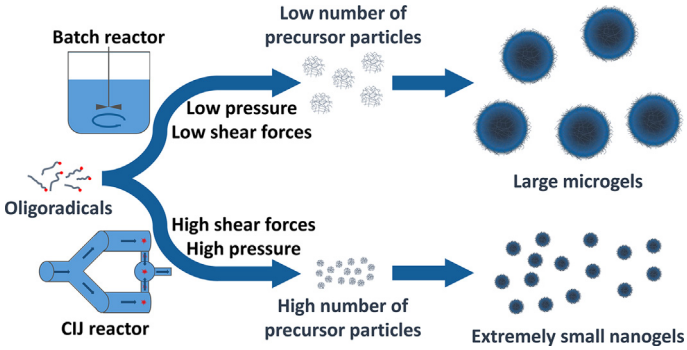
HIGHLIGHTS

- Sub 50 nm microgels were synthesized in a confined impinging jet reactor.
- Microgels were synthesized by a surfactant-free precipitation polymerization.
- Monodisperse and temperature-responsive microgels were obtained.
- Microgel size decreases with increasing pressure due to high shear forces.

GRAPHICAL ABSTRACT



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ABSTRACT

Extremely small monodisperse stimuli-responsive poly(*N*-vinylcaprolactam) (PVCL) colloidal gels with a radius of 45 nm were synthesized for the first time by surfactant-free precipitation polymerization in a high-pressure confined impinging jet reactor. We demonstrate that high pressures, combined with high mechanical shear forces inside the reaction chamber, resulted in size reduction and improved stabilization of microgel precursors leading to extremely small and uniform colloidal gels.

1. Introduction

Microgels are defined as a three-dimensional colloidal network of physically or chemically cross-linked polymers [1]. They exhibit stimuli-responsive behavior [2], responding to external stimuli like temperature [3], pH [4], ionic strength [5], light [6] and electrochemistry [7].

The size of microgels is an important parameter that determines their behavior in solution like diffusion, colloidal stability as well as performance in complex systems like stabilization of emulsions [8] or permeability control in membranes [9,10].

In recent years microgels gained in interest in the area of biomedical applications, as drug delivery systems [11], biointerface coatings [12] and wound healing [13]. Especially in the field of drug delivery systems particles with sizes of less than 100 nm are interesting as they are able to be internalized by cells [14] or even pass the blood-brain barrier, if smaller than 50 nm [15].

So far, microgels with a size of less than 50 nm have only been produced using surfactants in a aqueous precipitation polymerization [16] or microemulsions [17]. Alternatively, small microgels were

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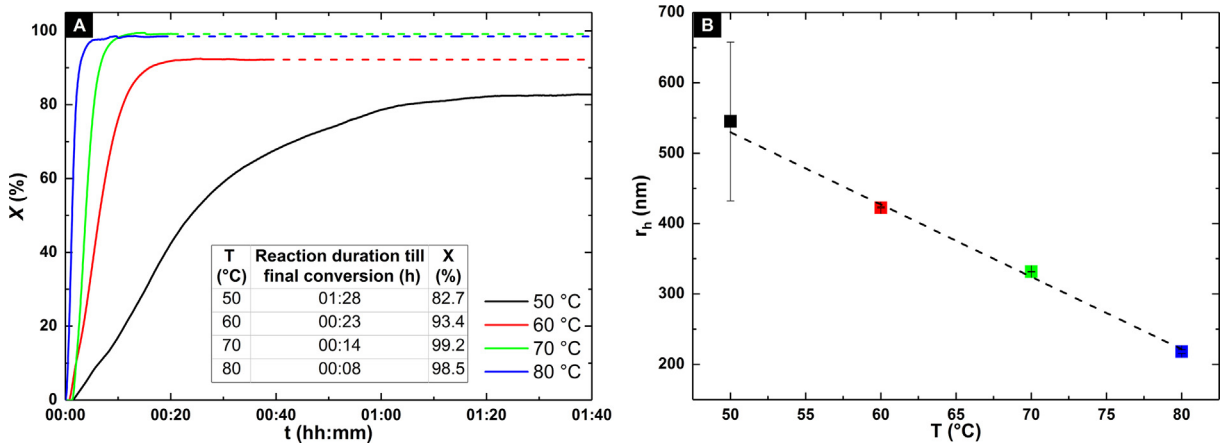


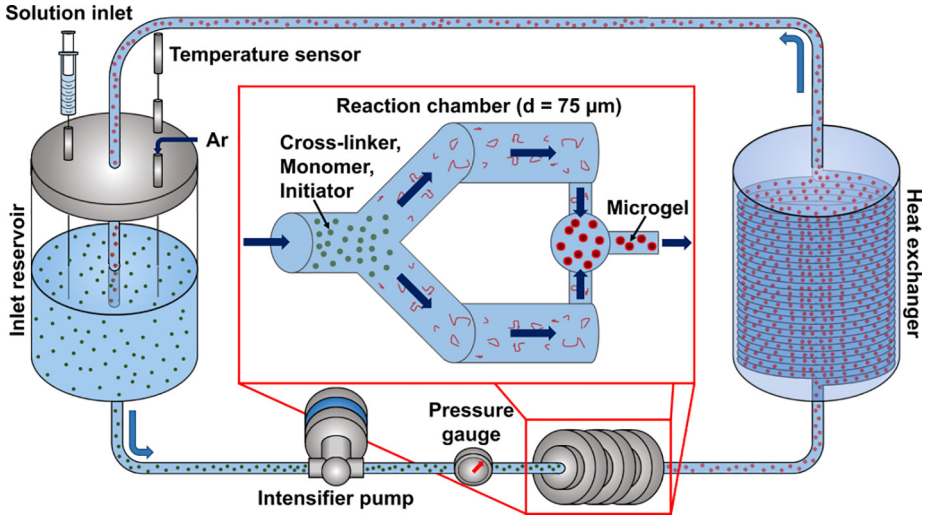
Fig. 1. (A) Monomer conversions during precipitation polymerization of PVCL microgels synthesized in a batch reactor at four different temperatures. Dashed lines represent extrapolated monomer conversions achieved at 60, 70 and 80 °C, allowing for a better comparison with the synthesis performed at 50 °C. The table shows the final conversion and time, at which the final monomer conversion is reached, for each synthesis temperature. (B) Influence of reaction temperature on particle size of PVCL microgels produced in batch (measured at 20 °C).

synthesized by sonication of partially hydrophobic prepolymers in water [18]. Another interesting pathway to small microgels is the application of enzymes, acting simultaneously as biological catalysts for the initiation of the polymerization process and stabilizing agents for the formed colloids [19]. While the use of surfactants proves to be challenging due to their difficult removal from the microgel [20] and their cytotoxicity [21]. The synthesis of prepolymers requires several steps and complicated purification/transfer into the aqueous phase. Though enzymatic polymerizations can be performed without toxic solvents, the required enzymes are still quite expensive.

In this work, we demonstrated that very small microgels with a size of less than 50 nm could be synthesized using aqueous one-step precipitation polymerization of *N*-vinylcaprolactam (VCL) under surfactant free conditions. VCL has been used as a model water-soluble monomer for the synthesis of temperature-responsive microgels. Since typical batch precipitation polymerization in stirred reactors normally results in microgel sizes larger than 100 nm, a new method using a Microfluidizer® PureNano™ MRT-CR5 from Microfluidics with a high-pressure confined impinging jet reactor (CIJR) was developed. Until now, CIJRs have been used for the fabrication of nano-emulsions [22], nanocellulose [23], nanoparticles [24] and quantum dots [25]. Most of those syntheses rely on a top-down approach where macroscopic materials are broken down into smaller parts. In the present work, we used a bottom-up approach, where the high pressures and shear forces result in a restricted growth of precursors, resulting in extremely small microgel particles with a radius of less than 50 nm. As to the authors' knowledge, this represents the first-time synthesis of extremely small microgels in a high-pressure confined impinging jet reactor (CIJR).

2. Results and discussion

Before starting the experiments in the impinging jet reactor, the optimal reaction temperature for the synthesis of PVCL microgels had to be determined. Standard PVCL microgel synthesis conditions, consisting of a 1.5 wt% VCL solution in water with 2.5 mol% cross-linker *N*,*N*′-methylenebis(acrylamide) (BIS) (in regard to VCL) and 1.2 mol% initiator 2,2′-azobis(2-methylpropioamidine) dihydrochloride (AMPA), were used. The conventional batch precipitation polymerization of VCL was monitored on-line at 50, 60, 70 and 80 °C in a RC1su reaction calorimeter from Mettler-Toledo. During the microgel synthesis, the progress of the reaction can be monitored using the heat generated by the cleavage of double bonds from monomer molecules. From this calorigrams, one can obtain the heat output during the polymerization (Supporting Information (SI): Fig. S2). Knowing the heat of polymerization ($\Delta H_{(VCL)}$) of VCL (76.0 ± 0.9 kJ/mol) [26], the monomer conversion over time can be calculated by integration of the calorigrams (Fig. 1A). From this, one can see that the time until the final conversion is reached decreases with increasing reaction temperature.



Scheme 1. Experimental setup of Microfluidizer ® high-pressure impinging jet reactor (CIJR) for precipitation polymerization of PVCL microgels.