



Enabling the measurement of particle sizes in stirred colloidal suspensions by embedding dynamic light scattering into an automated probe head



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ABSTRACT

A novel probe head design is introduced, which enables in-line monitoring of particle sizes in undiluted stirred fluids using dynamic light scattering. The novel probe head separates a small sample volume of 0.65 ml from the bulk liquid by means of an impeller. In this sample volume, particle sizing is performed using a commercially available fiber-optical backscatter probe. While conventional light scattering measurements in stirred media fail due to the superposition of Brownian motion and forced convection, undistorted measurements are possible with the proposed probe head. One measurement takes approximately 30 s used for liquid exchange by rotation of the impeller and for collection of scattered light. The probe head is applied for in-line monitoring of the particle growth during microgel synthesis by precipitation polymerization in a one liter laboratory reactor. The in-line measurements are compared to off-line measurements and show a good agreement.

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1. Introduction

Measuring particle sizes and size distributions in colloidal suspensions is of great importance in many technical processes. These processes are necessary for the production of polymers, pharmaceutical active ingredients

and additives for the food-, cosmetic- and paint-industry [1]. For a better process monitoring of these technical processes, online measurements of the particle size without time-consuming sampling are needed.

Dynamic light scattering (DLS) is one of the standard methods for measuring particle sizes in fluids and has been established for many years [2]. This method is based on the examination of random particle movement due to constant Brownian motion. The collision of particles with surrounding liquid molecules results in a diffusional process with small particles moving faster than large particles. To monitor this diffusion, the sample is illuminated with a monochromatic laser beam. Depending on the position of the particles relative to each other, light scattered by the particles undergoes constructive or destructive interference. The resulting intensity fluctuations are detected

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time-resolved by a photomultiplier positioned at a certain angle to the incident light. The decay of the autocorrelation of the measured intensity is correlated to the translational diffusion coefficient, which in turn is used to calculate the hydrodynamic radius of the particles using the Stokes–Einstein equation. For accurate determination of the diffusion coefficient, multiple light scattering has to be avoided. In concentrated suspensions, which are typical in industrial polymer production, the incident light is scattered multiple times before it is detected, which directly influences the intensity autocorrelation. To circumvent this issue, there are different enhancements of DLS, such as two color-cross correlation [3,4] or 3D cross correlation [5]. Another demand for industrially applicable particle sizing is the possibility of direct in-line measurements. While able to measure in concentrated suspensions, both cross-correlation DLS methods involve complex optical setups and are not suitable for in-line measurements. In contrast, fiber-optic-quasi-elastic light scattering (FOQELS) [6] or fiber optic dynamic light scattering (FODLS) [7] methods use an immersion probe with a simple and robust optical setup and are therefore ideally suited for in-line applications. Both techniques are fiber-coupled and collect the backscattered light for particle size determination. With small penetration depths, concentrated dispersions with high solid content up to 40 wt% [6] can be measured [8]. Nevertheless, in-line DLS measurements are challenging, since laboratory as well as industrial reactors typically are stirred. Accurate particle sizing using DLS necessitates a resting fluid in the measured sample. In actively-mixed fluids the diffusion is overlaid by a turbulent convection, which prohibits diffusion measurements. Hence, it is not possible to apply DLS in fluids that exhibit forced convection either due to stirring or even due to sufficiently large pressure- or temperature gradients.

Apart from DLS, there are several other methods to determine the particle size in fluids [9], such as angular resolved static light scattering (SLS) of particles. This method is capable of sizing of particles with diameters of at least a size several tens of nanometers. To avoid multiple scattering, SLS measurements are usually performed in highly-diluted samples. Therefore, SLS is not applicable for in-line monitoring of samples with high solids content. Also commonly used for size determination of industrial polymers or macromolecules is size exclusion chromatography (SEC), a method that involves sample drawing and uses small flow rates [10] and hence is not suitable for in-line monitoring.

In practice, the aforementioned methods are used either off-line by taking samples from the production line to the laboratory or by installing fully automated on-line trains in bypasses or loops [11]. Sampling and further sample preparation by dilution or separation are time-consuming and induce a delay of up to several minutes between sampling and size information. In contrast, in-line measurements can provide real-time data or only have a delay of a few seconds, depending on the applied method, facilitating possible improvements on process- and quality control. Hence, a particle sizing method capable of measuring in-line in undiluted and stirred suspensions and enabling a close to real-time monitoring of technical processes is desired.

By measuring the bulk turbidity of a sample, one can calculate the particle size for monodisperse particles with known optical constants [12]. Since these optical constants can vary during polymerization processes, turbidity measurements are not sufficient for reliable particle size measurements. Optical imaging methods have also been applied in combination with in-line probes in stirred vessels [13]. These methods are based on capturing images using a CCD camera, and as such restricted by the optical diffraction limit and cannot detect nanometer sized particles. A promising approach for in-line particle sizing of stirred turbid colloidal suspensions is Photon Density Wave (PDW) spectroscopy [14]. Using a special in-line probe, intensity-modulated light is detected at multiple distances between excitation and collection fiber. Since the method relies on strong multiple scattering, it can only be applied for dispersions exhibiting at least a certain level of turbidity [15] and hence cannot be used to monitor the initial stage of particle growth in processes that still exhibit single scattering.

This paper introduces a novel probe head to enable in-line FOQELS measurements in stirred colloidal suspensions. To achieve this, the novel probe head and the probe of a commercial DLS device were mounted together and then immersed directly into the reactor.

A possible application of such an in-line particle sizing method is monitoring of microgel particle growth in precipitation polymerization process. Microgels are soft colloidal particles formed by cross-linked polymer chains [16]. The particle growth during precipitation polymerization depends on the reaction conditions like concentration of main reagents (monomer(s), crosslinker, surfactant and initiator) as well as reaction temperature. Higher polymerization temperatures and initiator concentrations result in a faster particle growth. A typical microgel synthesis takes between 5 and 20 min from initiation to final conversion [17]. For highly diluted syntheses at low temperatures, the growth of microgel particles inside a cuvette was successfully monitored using static light scattering [18]. Kara et al. conducted microgel syntheses inside quartz cells at room temperature [19,20] and for temperatures up to 50 °C [21]. Placing the cell inside a UV–VIS spectrometer, they observed a decrease in transmitted intensity during the gelation process. This decrease was attributed to an increase in light scattered by the particles. The scattered light intensity was correlated to the particle volume using Rayleigh's equation, which is only valid for particles smaller than 0.1 of the laser wavelength [19]. To monitor microgel particle growth at lab production scale in undiluted and stirred systems without being restricted to particles smaller than 40–70 nm [19], this method is not suitable.

The remaining article is structured as follows. In the experimental section the design of the probe head is presented together with commercially available DLS devices used for the in-line measurements as well as off-line validation measurements. Furthermore the experimental setups involving the probe head are described, which consist of stirred and unstirred measurements of a colloidal suspension using particles of a fixed size as well as the application of the probe head for in-line monitoring of the particle growth during microgel syntheses. The result

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