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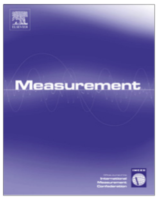

Enabling the measurement of particle sizes in stirred colloidal suspensions by embedding dynamic light scattering into an automated probe head

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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.

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 section reports the particles sizes measured using the probe head for both experimental setups along with the off-line reference measurements taken during particle synthesis.

2. Material and methods

2.1. Particle Metrix/Microtrac Nanotrac 250

The commercial device, which is equipped with the novel probe head is a Nanotrac 250 (Particle Metrix/Microtrac Europe GmbH, Germany). The measurement principle is shown in Fig. 1. This device is factory-equipped with an immersion probe, which allows an easy access to the sample due to the probe's small form factor. The light emitted by a laser (780 nm) is guided to the optical probe by a fiber and is focused into the sample close to the protective sapphire window, allowing measurements in highly concentrated suspensions of up to 40 wt% solids. The 180° backscattered light is collected and guided through a fiber to a detector. The laser light reflected by the protective window is also guided to the detector. The scattered light of the particles and the reflected light from the protective window are overlaid on the detector and cause interferences. The time-resolved intensity fluctuations correlate with the motion of the particles from which the particle size distribution is calculated by suitable mathematical models [22]. This device covers a particle size range from 0.8 nm to 6.5 µm. The above described heterodyne method improves the signal to noise ratio especially for small particles (<100 nm), low particle concentrations and enables accurate particle sizing over a large concentration area [22,23]. The software delivered from the manufacturer (Microtrac FLEX 11.0.0.1) controls the device and calculates the particle sizes.

2.2. Probe head

To perform measurements in stirred fluids with the Particle Metrix/Microtrac Nanotrac 250, a custom designed probe head pictured in Fig. 2 was developed. The probe head was tailored to be attached directly to the commercial probe, which is then immersed together with the probe head into the reaction fluid. The task of this probe head is to separate a small amount of volume from the bulk fluid, which can then be measured using the commercial probe. This is further called compartmentalization. Additionally, the probe head has to actively exchange the sample volume between two measurements. The requirement for this probe head were compactness, so it can be applied in common laboratory reactors and it had to be robust enough to be used in industrial stirred reaction vessels. The separated sample volume should be as small as possible, it should be exchanged sufficiently fast between each measurement, and most importantly it has to be protected from external motion and stray light.

The probe heads outer diameter is 35 mm and its length is 82 mm. The probe head consists of three parts for the enclosure (A, B, C) made from stainless steel. A miniature stepper motor (0620C006B K1855, Dr. Fritz Faulhaber GmbH & Co.KG, Germany) (E) with a diameter of 6 mm is secured by a stainless steel holder (D). The rotor made from polytetrafluorethylen (PTFE) (F) is attached to the stepper motor. There are several sealings in the probe head to keep moisture away from the stepper motor.

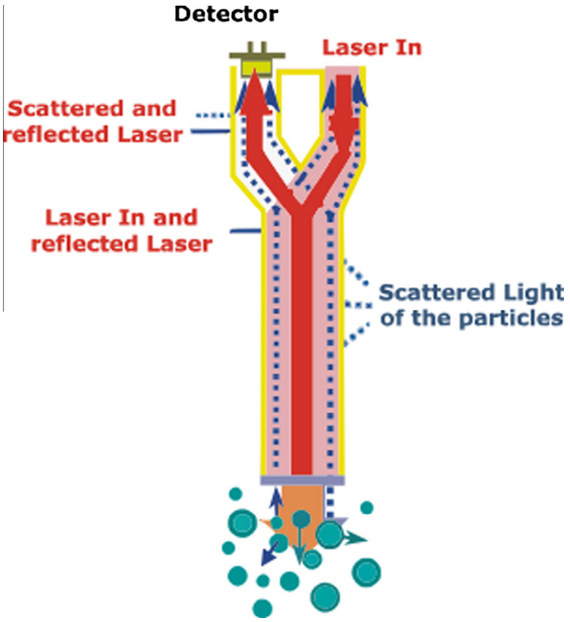

Fig. 1. Overview of the heterodyne FOQELS measurement principle. (Reprinted with permission from Particle-Metrix, Germany.)

The custom probe head (A, B, C) surrounds the optical DLS-probe (G) of the DLS device and provides a small enclosed sample chamber (~0.65 ml) for the DLS-measurements. The exchange of the sample fluid is carried out by the miniature stepper motor. The miniature stepper motor stops the rotor in a defined position after exchanging the sample so the optical path for the DLS-probe is free and the measurement chamber is properly capsulated. Because of the small sample chamber size the fluid stalls very fast and does not disturb the measurement due to any overlaid motion. The stepper motor is controlled by a motion controller (MCBL3002, Dr. Fritz Faulhaber GmbH & Co.KG, Germany) and software to program the motion profile (Motion Manager 5.0.0, Dr. Fritz Faulhaber GmbH & Co.KG, Germany).

2.3. Malvern Zetasizer Nano ZS

A Zetasizer Nano ZS (Malvern Instruments Ltd, England) was used as an off-line reference device. This device uses classical single-scattering DLS methods to calculate particle sizes in a range from 0.3 nm to 10 µm with a 633 nm laser and detects the backscattered light at 173°. The device features a temperature-controlled holder for a cuvette. The sample in the cuvette needs to be diluted to avoid multiple scattering.

2.4. Experiments in open beaker

Before the probe head is applied for in-line measurements during microgel synthesis, the suitability of the

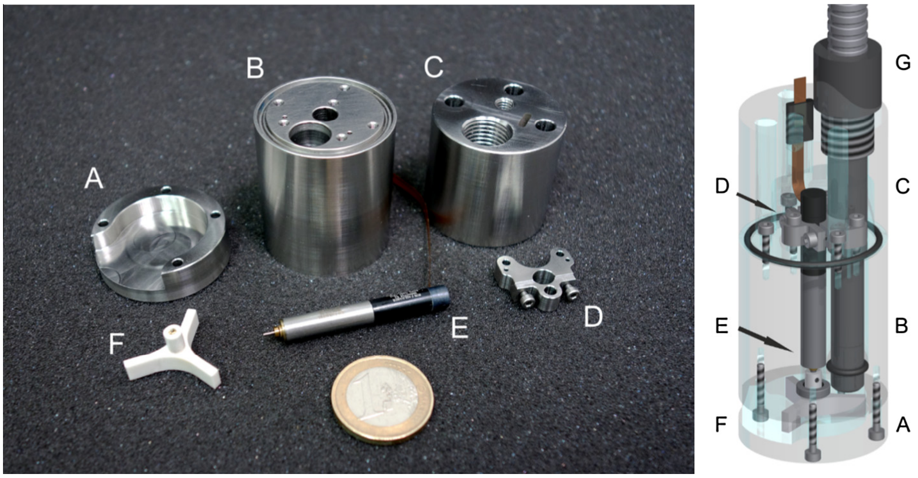

Fig. 2. Left: Components of disassembled probe head for DLS measurements in stirred solutions. 1€-coin is shown for size reference. Right: CAD image of assembled probe head with DLS measurement probe.

compartmentalization is tested on previously synthesized microgel particles. Therefore, the probe head was immersed into a beaker filled with the colloidal microgel suspension and a magnetic stir bar was added. The beaker was placed on top of a magnetic stirrer. Measurements were conducted with and without stirring. For comparison, the same measurements were repeated without the probe head. The integration time of the scattered light for each DLS measurement was 30 s with six repeated measurements per setup.

2.5. Experiments in a one liter reactor

In order to show that the new probe head can be used for an in-line monitoring of particle growth during a polymerization reaction, a one liter double-walled reactor with temperature controlled oil heating mantle was equipped with the new device.

As exemplary application for in-line monitoring of particle growth a microgel synthesis was selected. Two different polymerization reactions were analyzed, namely the particle formation of poly-N-vinylcaprolactam (PVCL) and of poly-N-isopropylacrylamide (PNIPAM). The following chemicals were used for the synthesis of the microgels. As monomers N-isopropylacrylamide (NIPAM) (Sigma–Aldrich) and N-vinylcaprolactam (VCL) (Sigma Aldrich) were employed. N,N′-Methylenebisacrylamide (BIS) (Sigma Aldrich), Cetyltrimethylammoniumbromid (CTAB) (Merck) and 2,2′-Azobis(2-methylpropionamidine) dihydrochloride (AMPA) (Sigma Aldrich) were used as crosslinker, surfactant and initiator, respectively. NIPAM and VCL were purified by recrystallization in hexane with subsequent high-vacuum distillation at 80 °C. All other chemicals were used as received. Deionized water was used as solvent. The synthesized microgels have a polymer content of about 1.5 wt%. The exact amount of each chemical used in the two discussed experiments can be found in Table 1. Each microgel synthesis was performed following the procedure described in Pich et al. [16]. After the deionized water was heated to the required temperature, the components monomer, cross-linker and surfactant were added. During the entire process, the reactor was under constant nitrogen atmosphere. After 30 min, the initiator was added to start the polymerization. From this point, the light scattering measurements were started. The integration time of the Nanotrac was set to 10 s. Once a DLS measurement is finished, the sample is exchanged by movement of the impeller, which stops in the pre-defined position (see Section 2.2) before triggering a new DLS measurement. The whole measuring cycle including data processing takes about 30 s.

In addition to the in-line measurements, 5 ml samples were taken at certain intervals during polymerization using a syringe with a long needle. For the first ten minutes after initiation, these samples were taken each minute. Between minute 10 and 30, the samples were taken every five minutes. From then on, the samples were taken every ten minutes. The samples were directly cooled down in numbered sample vials placed in liquid nitrogen and an inhibitor (Hydrochinon, Merck) was added to prevent further polymerization and particle growth. To confirm the particle sizes measured with the novel probe head, these samples were measured off-line in a Malvern Zetasizer Nano ZS in a fused silica cuvette. Before, the samples were diluted to avoid multiple scattering and filtered through a 1.2 μm PET filter to remove dust. An additional surfactant (CTAB) was added to prevent particle aggregation due to the instability of the particles at the early stage of reaction. The surfactant concentration was below the critical micelle concentration, to prevent any influence on the DLS measurements. The cuvette temperature of the Zetasizer Nano ZS was set to 50 °C and the integration time was automatically set to get a good signal-to-noise ratio. Every measurement was repeated three times and the resulting arithmetic average size was used for comparison to the in-line measurements.

Table 1
Mass of reactants (g) used in the two experiments.

Component	1 l PVCL	1 l PNIPAM
Water	1050.000	1050.000
VCL	15.505	N/A
NIPAM	N/A	12.600
BIS	0.420	0.420
AMPA	0.350	0.350
CTAB	0.154	0.126

3. Results and discussion

3.1. Test of compartmentalization

For the test of compartmentalization the open beaker setup was used. Four different conditions were examined. First, the bare optical probe of the DLS device was used in stirred and unstirred microgel suspension. The magnetic stirrer was set to 1000 rpm for the stirred measurements. Afterwards, the optical probe of the DLS device was equipped with the new probe head and the measurements in stirred and unstirred microgel were repeated.

Fig. 3 shows the results of these measurements. Zone 1 shows the particle size determined from repeated measurements with the bare probe in the unstirred suspension for a size reference. Zone 2 displays the sizes resulting from measurements taken during active stirring. Due to the convection, the particle sizes are erroneously identified to be remarkably smaller. The calculated sizes differ between 70 nm and 350 nm and a reliable value cannot be evaluated. Zone 3 contains particle sizes from measurements using the custom probe head, albeit without stirring. The deviation between the detected sizes is slightly smaller than the deviation without the custom probe head (zone 1). This smaller distribution of measured particle sizes could be caused by the compartmentalization of the sample, which effectively keeps away ambient light from the detector and restricts even small liquid movements. The particle sizes of measurements with the new probe head under stirred conditions are depicted in zone 4. The particle sizes determined under agitated condition match the values determined in unstirred condition, which ultimately proofs the operational capability of the developed probe head.

Table 2 shows the calculated values of the average and standard deviation for each zone. The standard deviation for the measurements with the attached custom probe head are improved by a factor of 2.4–3.2 over the measurements with the bare probe of the DLS-device. The deviations of the averages from zone 3 and zone 4 are within the deviation of zone 1.

The results of the measurements of the colloidal microgel suspension show that the design of the custom probe head is suitable to isolate and measure a small volume from the system, thereby preventing any interference of the encapsulated sample with the stirred bulk fluid. The accuracy of the custom probe under stirred conditions is at least as good as the bare probe in unstirred conditions. This renders reliable DLS measurements even in vigorously stirred environments possible.

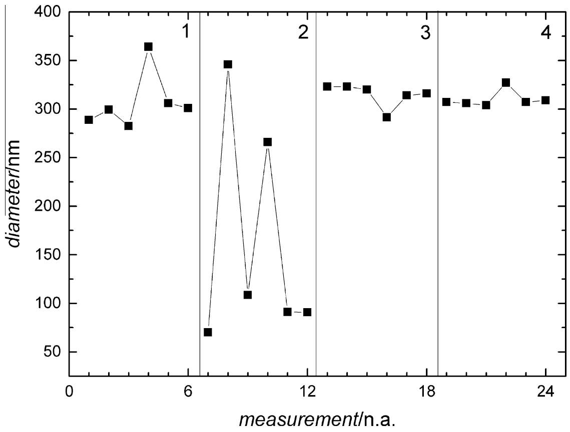

Fig. 3. Performance tests of the new probe head with PVCL microgel. Comparison of the measurements with bare and custom probe in stirred and unstirred sample. 1: Unstirred liquid, bare optical DLS probe; 2: Stirred liquid, bare optical DLS probe; 3: Unstirred liquid, custom probe head; 4: Stirred liquid; custom probe head.

Table 2
Average and deviation of the comparison measurements from Fig. 5.

Zone	Average size (nm)	Standard deviation (nm)
1	307	29
2	N/A	115
3	330	12
4	316	9

3.2. Monitoring of polymerization

Following the test of compartmentalization in the open beaker, the probe head was applied to monitor microgel syntheses in the temperature-controlled one liter reactor under nitrogen atmosphere. Fig. 4 displays the particle size monitoring during polymerization of PVCL at a reaction temperature of 60 °C. This temperature was chosen since it is the lowest temperature that reliably starts the polymerization of PVCL using AMPA as initiator and hence permits most measurements during the particle growth phase. Each dot in the figure represents one particle size measurement, of which the red[4] triangles were visually identified as outliers and excluded for computation of the floating mean, which is determined piecewise over three successive values. The two outliers might be caused by small air bubbles that reached the measurement chamber.

The first measurements after the addition of the initiator at time zero show a particle size of 2–3 nm due to background scattering. From minute five onwards, the growth of the particles can be seen very well. Approximately twelve minutes after initiation, the particle sizes reach a plateau at ~81 nm ± 3 nm SD diameter. The time between the first noticeable change in particle size and the onset of the plateau is about 8 min.

The second system monitored using the probe head was a polymerization of PNIPAM at a reaction temperature of

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[4] For interpretation of color in Figs. 4 and 5, the reader is referred to the web version of this article.

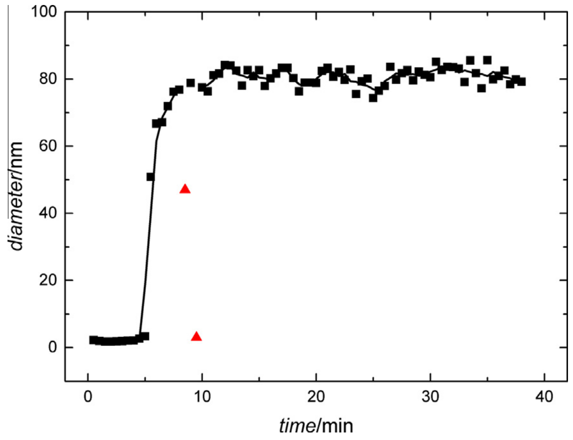

Fig. 4. Monitoring of particle size during polymerization of PVCL at 60 °C in 1 L laboratory reactor. Triangles show visually identified outliers.

65 °C. The corresponding in-line recorded particle sizes are displayed in Fig. 5.

To assess the validity of the particle sizes determined using the novel probe head, samples were taken during a microgel synthesis, directly quenched to stop further reaction and subsequently analyzed off-line. In Fig. 5, the particle sizes measured using the in-line probe head are depicted using black squares and the particle sizes measured off-line using blue dots. Again, red triangles represent visually selected outliers. The slopes of both measurements are in good agreement with each other. While the in-line measured sizes remain at their initial level until minute ten, the off-line measurements are able to depict small particle growth from minute six. Starting with the significant jump to 55 nm at minute 10, the in-line measurements display a constant particle growth, which is in accordance with the off-line measurements. The differences between both measurement techniques present at early reaction times decrease as the reaction progresses. The particle sizes from both techniques reach a plateau of 111 ± 4 nm SD for the in-line and 114 nm for the off-line measurements, respectively. A reason for the decreasing differences between in-line and off-line data could be the integration time of the Particle Metrix/Microtrac Nanotrac 250. Since the particles continue to grow during the acquisition time, the scattering pattern changes as well. The DLS evaluation method then determines a particle size that best approximates the measured signal, which might be distorted due to the shifting scattering pattern. The slower the reaction becomes, the smaller are the differences between both methods. The handling time from taking the sample and stopping the reaction with fluid nitrogen also takes a certain amount of time in which the particles keep growing.

After the syntheses, a minor contamination from chemical residue is visible on the surface of the probe head and on the protective window of the optical DLS probe. Examination of the DLS measurements shows no remarkable influence of these contaminations on the detected particle sizes. The residue rather causes a static reduction of the mean scattering intensity and thus might increase the measurement time necessary to retain the targeted measurement uncertainty. Nevertheless, the accuracy reached using the custom probe head in stirred surroundings is in a region that is at least as good as measurements performed with a bare DLS probe in unstirred fluids.

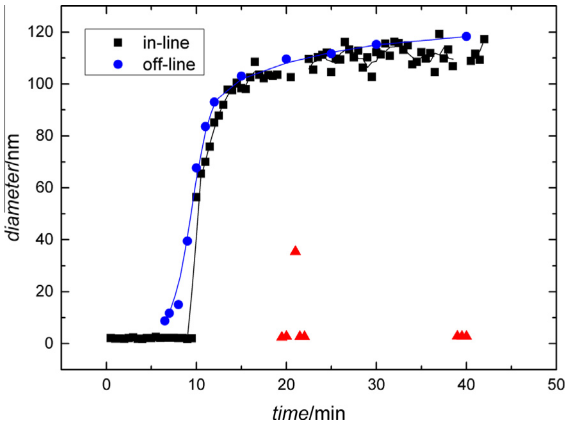

Fig. 5. Monitoring of particle size taken in-line (squares) during polymerization of PNIPAM at 65 °C in 1 L laboratory reactor together with off-line DLS reference measurements (circles). Triangles show visually identified outliers.

4. Conclusions

A novel probe design has been introduced to enable in-line monitoring of particle sizes inside a stirred fluid based on dynamic light scattering without the need for sampling and dilution. It was shown that the fluid compartmentalization in the probe head is sufficient to exclude any influences of the stirred bulk liquid. Further experiments showed that the growth of microgel particles could be suitably followed during stirred polymerization. A comparison between the direct in-line measurements and off-line determined particle sizes using a state-of-the-art device showed that both measurement techniques are in good agreement with each other. The application of the probe design in industrial environments that currently rely on tedious off-line analysis of drawn samples could vastly facilitate product quality control. In batch productions it could lead to faster reaction times, since the end of particle growth can automatically be detected. It renders possible the discovery of unexpected product conditions and triggering of counteractive measures that might be untraced for considerably longer times with conventional monitoring techniques.

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