



Advanced analysis of polymer emulsions: Particle size and particle size distribution by field-flow fractionation and dynamic light scattering



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ABSTRACT

Field flow fractionation (FFF) is an advanced fractionation technique for the analyses of very sensitive particles. In this study, different FFF techniques were used for the fractionation and analysis of polymer emulsions/latexes. As model systems, a pure acrylic emulsion and emulsions containing titanium dioxide were prepared and analyzed. An acrylic emulsion polymerization was conducted, continuously sampled from the reactor and subsequently analyzed to determine the particle size, radius of gyration in specific, of the latex particles throughout the polymerization reaction. Asymmetrical flow field-flow fractionation (AF4) and sedimentation field-flow fractionation (SdFFF), coupled to a multidetector system, multi-angle laser light scattering (MALLS), ultraviolet (UV) and refractive index (RI), respectively, were used to investigate the evolution of particle sizes and particle size distributions (PSDs) as the polymerization progressed. The obtained particle sizes were compared against batch-mode dynamic light scattering (DLS). Results indicated differences between AF4 and DLS results due to DLS taking hydration layers into account, whereas both AF4 and SdFFF were coupled to MALLS detection, hence not taking the hydration layer into account for size determination. SdFFF has additional separation capabilities with a much higher resolution compared to AF4. The calculated radii values were 5 nm larger for SdFFF measurements for each analyzed sample against the corresponding AF4 values. Additionally a low particle size shoulder was observed for SdFFF indicating bimodality in the reactor very early during the polymerization reaction. Furthermore, different emulsions were mixed with inorganic species used as additives in cosmetics and coatings such as TiO₂. These complex mixtures of species were analyzed to investigate the retention and particle interaction behavior under different AF4 experimental conditions, such as the mobile phase. The AF4 system was coupled online to inductively coupled plasma mass spectrometry (ICP-MS) for elemental speciation and identification of the inorganic additive. SdFFF had a larger separation power to distinguish different particle size populations whereas AF4 had the capability of separating the organic particles and inorganic TiO₂ particles, with high resolution.

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1. Introduction

Polymer emulsions are typically complex formulations that consist of various components including the polymer part, emulsifiers, pigments (e.g. TiO₂) and other additives. The chemical heterogeneity of an emulsion can vary significantly and the final composition, particle size and particle size distribution (PSD) is

of high importance for various applications [1]. Emulsions with very small particle sizes can result in very high viscosities, while very large particle sizes could lead to unstable emulsion particles [2,3]. The particle size determined by batch dynamic light scattering (DLS) gives an average size value based on one detector angle (e.g. 173° or 90°) and is a fast and simple way of determining the hydrodynamic radius of colloidal species [4–6]. Nucleation and particle growth mechanisms during free radical emulsion polymerization are often deducted based on DLS measurements [7]. For more in-depth and reliable particle size information, a fractionation method with suitable detectors for the determination of different

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size parameters is key towards a better understanding of complex organic nanoparticle systems.

Field-flow fractionation (FFF) invented by Giddings in 1966 is a separation technique based on chromatographic-like principles which separates particles and molecules by an external force which is applied orthogonally to the sample flow streamline [8]. The most common FFF techniques used for particle size analysis are asymmetrical flow field-flow fractionation (AF4) and sedimentation field-flow fractionation (SdFFF). AF4 features a second axial flow (cross-flow), applied perpendicular to the longitudinal sample flow. Separation takes place inside a ribbon-like, trapezoidal channel with particles being separated according to their diffusion coefficients, which is related to hydrodynamic radius (R_H), and subsequently the radius of gyration (R_g) [9,10]. In SdFFF a centrifugal field ensures sample separation according to hydrodynamic radius and density of the particles [11]. The centrifugal force, which is applied perpendicular to the axial flow in SdFFF, can be varied to achieve particle separation.

Recently, applications of FFF in drug delivery [4,12–19], cosmetic [20], environmental [21–25], and food industry [26–31] have increased significantly. FFF of latex particles has been studied by various research groups. Polystyrene latexes have been studied by DLS and asymmetrical flow field flow fractionation coupled to multi-angle laser light scattering detection (AF4-MALLS) to evaluate band broadening effects in nanoparticle analysis [7]. Polystyrene particles synthesized by unseeded emulsion polymerization have been studied by AF4 and compared to DLS to investigate the presence of primary particles during the synthesis procedure [5,6]. Similarly, Bartsch et al. investigated the particle size development in seeded styrene polymerization by AF4-MALLS in comparison to the disc centrifugation method [32]. Schauer investigated pigments, fillers as well as emulsions used in coatings by symmetric and asymmetrical flow FFF based on a single detector (UV) system in comparison with offline DLS [33]. The effect of pH and ionic strength on the swelling behavior in core-shell latex particles was studied by Frankema et al. to investigate changes in particle size upon changing these variables using AF4-MALLS and ultraviolet (UV) detection, or AF4-MALLS-UV [9]. Thermal FFF has also been used in ABS and polystyrene latex particles. Mes et al. studied the effect of surfactants on the calculated particle size [34].

The coupling of AF4 to element-sensitive detectors such as inductively coupled plasma mass spectrometry (ICP-MS) has been under utilized compared to other hyphenated techniques. Nanoparticles, especially gold nanoparticles have been studied by hydrodynamic chromatography and AF4, with both techniques coupled to online ICP-MS (AF4-ICP-MS) to determine particle size and quantification of nanoparticles in submicron dispersions [35,36]. A recent review article on FFF-ICP-MS by Pornwilard and Siripinyanon briefly covered the main FFF-ICP-MS applications [37], attributed to the first offline coupling of FFF and ICP-MS in 1991 by Beckett [38] and Taylor et al. [39] in 1992. More recently Bednar, Gray and Mitrano studied online coupling of FFF with single particle ICP-MS [24,36,40], respectively. TiO_2 separation with multi-detection by SdFFF and AF4 has been studied by a few research groups [20,41,42].

In this study, online AF4-MALLS-UV as well as an online refractive index detector (AF4-MALLS-UV-RI), online sedimentation FFF with MALLS and UV detection (SdFFF-MALLS-UV), and DLS were utilized for detailed characterization of styrene-acrylic and pure acrylic emulsions used primarily in coatings, which were synthesized by free radical polymerization. During the emulsion polymerization, samples were taken from the reaction vessel at pre-defined time intervals. The obtained particle sizes and PSDs of both emulsion systems were subsequently compared using AF4 and SdFFF with multiple detectors, and batch DLS. The DLS

measurements were conducted in different laboratories under identical experimental conditions.

Furthermore, model blends of a polymer emulsion and TiO_2 particles were analyzed online using AF4-MALLS-UV-RI detection as well as an ICP-MS detector coupled as AF4-MALLS-UV-RI-ICP-MS in order to separate, specify and identify the organic and inorganic species dispersed in solution. Styrene-acrylic and pure acrylic emulsions were studied independently and spiked with TiO_2 before analysis.

2. Experimental

2.1. Theory of separation techniques

AF4 and SdFFF both have a parabolic flow velocity profiles inside its respective channels.

As per first FFF principles for a constant force field the force acting on the particles or macromolecules are given by Eqs. (1) and (2) for AF4 and SdFFF, respectively [8,41,43–45].

$$F_{AF4} = f|U| = \frac{kT|U|}{D} = 3\pi\eta|U|d \quad (1)$$

Where d is the diameter of molecule or particle, D is the diffusion coefficient and U represents the field induced velocity.

$$F_{SdFFF} = m'G = V_p|\Delta\rho|G = \frac{\pi}{6d^3}|\Delta\rho|G \quad (2)$$

where m' is the effective mass of the particle, V_p is the particle volume, $\Delta\rho$ the difference in density between particles and mobile phase and G is the gravitational force. Similarly, the hydrodynamic diameter can be determined, deduced from Eqs. (1) and (2), respectively. In AF4 the diameter is calculated by:

$$d_H = \frac{2kTV^0}{\pi\eta w^2 V_c t^0 t_r} \quad (3)$$

where k denotes Boltzmann constant, T is the absolute temperature in Kelvin, V^0 is the void volume of the channel, η is the mobile phase viscosity, w is the thickness of the channel, V_c is the subsequent cross-flow rate and the void time is denoted by t^0 . For SdFFF:

$$d_H = \left(\frac{6kT}{\pi G w \Delta\rho t^0 t_r} \right)^{\frac{1}{3}} \quad (4)$$

where G is the acceleration speed of the rotating channel. The added parameter, density during separation has an added benefit, adding a higher resolution power in comparison to AF4. Both FFF techniques can be complementary or superior to DLS depending on the nature of the analyzed material. DLS is known to be a fast tool to screen nanoparticles. DLS lacks separation power since average particle size of particles in dispersion are analyzed, therefore sizes may be erroneously calculated due to overestimation as a result of small amounts of large aggregated particles. This phenomenon is overcome by the fractionation and resolution power of AF4 and SdFFF. In this study, the emulsion particles are subjected to a larger field force in SdFFF which is proportional to $1/d^3$, which imparts very large resolution depending on the strength of the gravitational force. In AF4 the force acting on the particles are proportional to d and $1/V_c$ as variables for resolution improvement.

2.2. Materials and sample preparation

The pure acrylic latex (sample 1) featuring a low glass transition temperature (T_g) was synthesized with *n*-butyl acrylate (*n*-BA), methyl methacrylate (MMA) and methacrylic acid (MAA) while the styrene-acrylic (sample 2) latex was produced using styrene (Sty), *n*-BA, MMA and MAA as monomers, respectively.

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