IN-LINE MONITORING OF POLYMER NANOPARTICLE GROWTH DURING SYNTHESIS IN CONCENTRATED SYSTEMS BY PHOTON DENSITY WAVE SPECTROSCOPY

Roland Hass, University of Potsdam, Physical Chemistry – innoFSPEC, Am Muehlenberg 3, Germany
rhass@uni-potsdam.de
Oliver Reich, University of Potsdam, Physical Chemistry – innoFSPEC, Am Muehlenberg 3, Germany

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Photon Density Wave (PDW) spectroscopy [1-4] determines the absolute optical properties of highly turbid liquid dispersions without a need for prior method calibration. As parameters, the absorption coefficient m_a and the reduced scattering coefficient m_s' are obtained. Based on Mie theory and theories for dependent light scattering, the reduced scattering coefficient is linked to the particle size of the suspended particles, allowing for dilution-free particle sizing in size regimes of approx. 50 nm to 500 µm. Currently, PDW spectroscopy provides a time resolution of approx. 2 min^{-1} and can be operated with fiber-optical process probes [5], thus it allows for in-line particle size measurements during polymerization processes.

Here, PDW spectroscopy was applied to investigate the growth of polymer nanoparticles in-line during their synthesis. Examples cover polymerization of styrene at 20 wt%, semi-batch polymerization of vinyl acetate up to solid fractions of 50 wt%, and starved feed copolymerization of acrylate-based monomers [6] up to 40 wt%. For example, in the case of the synthesis of polyvinyl acetate, it could be observed in-line that the growth of the polymer nanoparticles only commenced after a significant amount of monomer had been fed into the reactor (approx. 20 wt%), thus indicating that during the first hour after polymerization start mainly particle nucleation occurred. The results obtained with respect to particle size agreed well with off-line dynamic and static light scattering reference experiments, which required sampling and sample dilution.

By the use of multiple laser wavelengths for PDW spectroscopy, an estimation of the particle size distribution during synthesis can be obtained as well [2]. In the case of polyvinyl acetate, the findings indicate an increasing particle size distribution width during its synthesis. Based on the estimation of the particle size distribution, particle numbers and particle growth rates can be calculated, thus providing access for an increased process understanding and finally an approach for real-time process control during synthesis of polymer nanoparticles in concentrated dispersions.

[1] Bressel L., Hass R., Reich O., Particle sizing in highly turbid dispersions by photon density wave spectroscopy, J. Quant. Spectrosc. Radiat. Transf. 126:122-129 (2013).
[2] Hass R., Münzberg M., Bressel L., Reich O., Industrial applications of Photon Density Wave spectroscopy for in-line particle sizing, Appl. Opt. 52:1423-1431 (2013).
[3] Fishkin J.B., Fantini S., van de Ven M.J., Gratton E., Gigahertz photon density waves in a turbid medium: Theory and experiments, Phys. Rev. E 53:2307-2319 (1996).
[4] Richter S.M., Shinde R.R., Balgi G.V., Sevick-Muraca E.M., Particle sizing using frequency domain photon migration, Part. Part. Syst. Charact. 15:9-15. (1998).
[5] Hass R., Munzke D., Vargas Ruiz S., Tippmann J., Reich O., Optical monitoring of chemical processes in turbid biogenic liquid dispersions by photon density wave spectroscopy, Anal. Bioanal. Chem. 407:2791-2802 (2015).
[6] Hass R., Reich O., Photon Density Wave spectroscopy for dilution-free sizing of highly concentrated nanoparticles during starved-feed polymerization, ChemPhysChem 12:2572-2575 (2011).