Short communication

The structure of fibers produced by colloid-electrospinning depends on the aggregation state of particles in the electrospinning feed

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Shuai Jiang [a], Wei He [a], Katharina Landfester [a], Daniel Crespy [a, b, *], Steven E. Mylon [c, **]

[a] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
[b] Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand
[c] Lafayette College, Department of Chemistry, Easton, PA 18042, USA

ABSTRACT

Colloid-electrospinning is a technique widely used to immobilize nanoparticles in nanofibers. Such hierarchical structures are advantageous because they benefit from the properties of both nanoparticles and nanofibers. Controlling the aggregation state of nanoparticles in nanofibers is essential for the properties of the resulting materials. We investigate here the relationship between the aggregation state of nanoparticles in dispersion before spinning and in electrospun nanofibers. The aggregation state of nanoparticles in nanofibers was found to depend on the aggregation state of the nanoparticles in dispersion.

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1. Introduction

The electrospinning of nanoparticles is a method to immobilize nanoparticles in non-woven nanofibers [1,2]. In contrast to nanoparticle dispersions, non-woven nanofibers fabricated by colloid-electrospinning can be visually handled and separated from a reaction medium. This property is particularly useful because the non-woven nanofiber is then a scaffold, which can be used for catalysis after embedding catalytically active nanoparticles [3,4], for affinity separation by incorporating molecularly imprinted nanoparticles [5], or for surface-enhanced Raman scattering via loading metal nanoparticles [6]. Control of nanoparticle aggregation state within the fiber matrix is important in order to avoid phenomena such as Förster resonance energy transfer between quantum dots in fibers [7] or reactions between different nanocapsules containing reactive molecules [8]. When the concentration of nanoparticles in fibers is increased, the nanoparticles become densely packed [9,10]. In this case, aggregates of particles

in fibers are also often observed, especially if the fiber's diameter is smaller than the particles' size [11,12]. In one case, it was reported that electrospinning, and more exactly the elongational flow of the dispersion, enhanced the dispersion of silica particles in poly(vinyl butyral) and polyvinylpyrrolidone fibers [13].

The localization and distribution of nanoparticles is commonly measured in the nanofibers by electron microscopy [6,7,9–11]. However, the aggregation state of the nanoparticle dispersions in the presence of the polymer required as polymer matrix, normally goes unreported. Here we present an investigation of the aggregation state of nanoparticles before and after electrospinning.

Nanoparticle aggregation occurs when attractive interaction forces, commonly van der Waals forces, outcompete other repulsive interaction forces such as electrostatic forces and steric interactions [14]. Nanoparticle aggregation state can be measured in a semi-quantitative sense using dynamic light scattering (DLS) to determine an apparent hydrodynamic radius, R_H, and compare that against the measured hydrodynamic radius of a dilute mono-disperse sample of non-aggregated particles [15]. The DLS techniques commonly measure an intensity-weighted distribution that determines the contribution of scattered light intensity of each particle in dispersion. Within the paradigm of the Rayleigh approximation, the intensity contribution for particles will be proportional to R_H^6. Thus small changes in R_H can be observed by

employing DLS. DLS does however possess some limitations which must be overcome. For example, solutions must not be so viscous to inhibit a reasonable degree of particle diffusion which is the source of scattered light intensity fluctuations necessary for the photon correlation. Additionally, solution concentrations must be sufficiently diluted so as to avoid multiple photon scattering. These experimental challenges have limited the determination of aggregation state for particles in electrospinning feed solutions because these solutions are typically highly concentrated in both particles and polymers resulting in high viscosities. Here we employ sensitive DLS techniques to determine the aggregation state of nanoparticles in electrospinning feeds, and we compare the aggregation state of both silica and polystyrene electrospinning feed solutions with their aggregation in the fibers resulted from electrospinning (see Scheme 1). The details of the experimental protocols can be found in the supplementary information.

2. Experimental section

2.1. Materials

Styrene (Sigma Aldrich, $\geq$ 99.5%), hexadecane (Sigma Aldrich, $\geq$ 99%), 2,2′-azoisobutyronitrile (AIBN, Wako Chemicals), and sodium dodecyl sulfate (SDS, Alfa Aesar, 99%) were used as received. Polyvinyl alcohol (PVA) with M_w of 25,000 g mol^{-1} and 125,000 g mol^{-1} (both 88 mol% hydrolyzed) were purchased from Polysciences Inc. Silica nanoparticles (SiNPs) dispersion was purchased from Sigma Aldrich. Polystyrene nanoparticles (PSNPs) with diameter of 200 nm were synthesized by miniemulsion polymerization [16]. Briefly, styrene, hexadecane, and AIBN were mixed while sodium dodecyl sulfate that was dissolved in water. The two liquids were mixed, stirred, and sonicated to yield miniemulsions that were subsequently polymerized by heating them.

2.2. Light scattering measurements of nanoparticles dispersed in polymer solution

To assess aggregation state we employed DLS to measure the hydrodynamic radius of particles in dispersion. For the DLS measurements of the solutions with SiNPs, we employed a single-detector light scattering unit (ALV-CGS-3, Langen, Germany). Reasonable autocorrelation functions were observed with a 60 s collection time. Depending on solution conditions, scattering angles were varied from 90° to 140°. Data fitting employed ALV's non-linear fitting routines which are capable of fitting systems with 1–3 different scattering components. We assessed the goodness of fit by calculating χ^2 and only fit to a larger number of components when we observed a significant decrease in χ^2 as a result. For the system of SiNPs in high concentrations of PVA, fitting to a single component was never adequate, and therefore we chose to fit to a two or three component system which is reasonable considering that scattering could result from the polymer itself, single particles, and/or aggregates. Hydrodynamic radii were calculated using the Stokes-Einstein equation and the viscosity of each solution was determined using a Canon-Fenske viscometer. Because of the challenges measuring the viscosity of these solutions, the reported R_H values mostly are within 10% of their actual values.

For systems of high concentrations of PSNPs we employed a Malvern Zetasizer utilizing its non-invasive backscattering (NIBS) technique which is capable of measuring particle sizes in highly concentrated solutions. R_H was determined using Malvern's software with proper consideration of individual dispersion viscosity.

2.3. Nanofibers containing nanoparticles

PVA powders with M_w of 125,000 g mol^{-1} were dissolved in demineralized water at 80 °C with vigorous stirring for 6 h to obtain 10 wt% PVA aqueous solution. For the PVA with M_w of 25,000 g mol^{-1}, the concentration of PVA solution was set to be 20 wt%. The electrospinning solutions were then prepared by mixing the PVA solution with dispersions of silica or polystyrene nanoparticles. The final concentration of nanoparticles in the electrospinning solution is 1.7 g L^{-1} or 54.4 g L^{-1}.

Electrospinning was carried out at room temperature and ~25% relative humidity using a model fabricated by IME Technologies. The size dimensions of spinneret (flat-head needles) are 0.5 mm (inner diameter)*42 mm (length). The feeding rate and applied voltages were adjusted depending on M_w of the PVA. In the case of nanofibers prepared from a dispersion composed of NPs in 10 wt% PVA with $M_w = 125,000$ g mol^{-1}, an applied voltage of 15 kV, a working distance between the spinneret and the collector (aluminum foil) of 10 cm, and a feeding rate of 0.2 mL h^{-1} were used. In the case of nanofibers prepared from a dispersion composed of 20 wt% PVA with $M_w = 25,000$ g mol^{-1}, an applied voltage of 17 kV, a working distance of 10 cm, and a feeding rate of 0.15 mL h^{-1} were used. The diameters of electrospun nanofibers
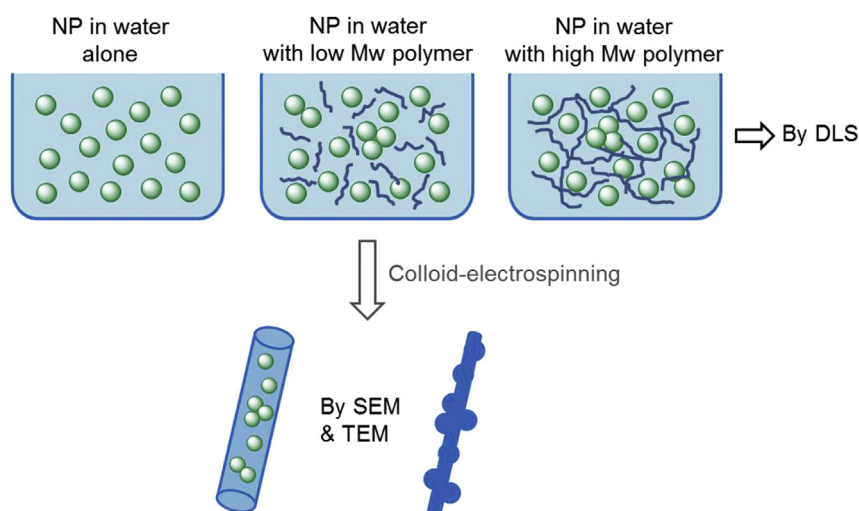
Scheme 1. Schematic illustration of aggregation states of nanoparticles (NPs) in polymer solutions and in electrospun nanofibers.