A Report Submitted to the Faculty Research Grant Committee

Purchase and Installation of a Zeta Potentiometer at Arkansas Tech University

(Grant Research Title: A Zeta Potentiometer for the Electrophoretic Deposition of Hydroxyapatite)

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ABSTRACT

A Malvern model Zetasizer Nano Z zeta potentiometer was recently purchased, installed, and tested at Arkansas Tech University (McEver Building, Instrument Lab). The total cost of the "demo" instrument was $30,230, which included the instrument, installation, training and a one-year warranty (new instrument cost is $43,000 plus tax). One important function of the zeta potentiometer is to measure the stability of colloids in solution (suspended particles) as a function of temperature and surface charge (a function of solution pH). This information is required for effective electrochemical deposition of these colloids as films onto metal substrates. This process is called electrophoretic deposition (EPD). Our group at ATU is interested in the EPD of hydroxyapatite (synthetic bone, synthesized in our laboratory) onto titanium substrates (mimicking titanium implants). Eventually, with appropriate funding, this instrument will be upgraded (by adding components) to a state-of-the-art model Zetasizer Nano ZS for the simultaneous and automated determination of zeta potential (using an auto titrator), particle size distribution analysis, and molecular weight.

INTRODUCTION AND BACKGROUND

Human bone is an inorganic/organic composite material made up of collagen, a calcium phosphate mineral, and small amounts of sodium, magnesium, fluorine and other trace elements. The crystal structure of the calcium phosphate in natural bone and teeth resembles that of a substance called hydroxyapatite (HAP). [1,2,3,4,5] This makes HAP an attractive material for biomedical applications such as a surgical implant material in orthopedics and dentistry due to its excellent biocompatibility and osteoconduction properties.[6,7]

But because HAP is a metal oxide ceramic material, it is brittle and lacks the mechanical properties necessary for total bone replacement. Instead, metallic implants have been used for many years to repair and replace bone. More recently, studies have been directed at improving metallic implant fixation using physical and chemical methods. To improve chemical adhesion and biocompatibility, HAP has been used to promote bone growth and fixation towards implant surfaces and was found to encourage faster recovery times for the recipient.[8] However, HAP coatings are currently deposited by high-temperature plasma spraying techniques that result in unpredictable films consisting of undefined phases (chemical composition unknown), and undesirable thick films (causing micro-cracking). In contrast, electrophoretic deposition (EPD) has been shown to provide high-quality and reproducible coatings on metallic substrates, in particular, HAP coatings on medical-grade titanium, TiAl6V4.[9] Although relatively inexpensive, EPD requires **zeta potential measurements** to determine the charge on the colloidal particles and relative

stability of the particles (so as to prevent unwanted clumping or aggregating) prior to deposition onto the metallic substrate.

PURCHASE, ACQUISITION AND INSTALLATION OF THE ZETA POTENTIOMETER

We are pleased to report that full funding for the total cost of the zeta potentiometer was appropriated from several sources and the "demo" model was ordered for a total price of $30,230 including installation, on-sight training, and a one-year warranty (compare: the cost of a brand new instrument is $43,000 plus tax). The instrument arrived at Tech over the summer, and was installed on September 18, 2008. In this report we present a very "brief" description of how the zeta potentiometer works, some theory behind the zeta potential, the data that can be acquired, and how we can use this data to form the desired films by the electrophoretic deposition (EPD) process.

WHAT IS THE ZETA POTENTIAL AND WHY IS IT IMPORTANT?

Our research group at ATU is currently investigating electrophoretic deposition (EPD) as an inexpensive, fast and superior method of depositing films onto metallic substrates. In contrast to conventional electrochemical plating methods, where "molecules" are deposited onto electrodes, EPD involves the migration and deposition of "colloids" or suspended "nano-particles" onto electrodes (metallic substrates) as stable films. For EPD to work, however, the suspended particles must be properly characterized in terms of particle size (this

will be measured at UALR until this capability is added to our instrument) and surface charge (related to the zeta potential and electro-mobility). The pH of the solution (initial phase: 98% ethanol; pH adjusted with HCl or NaOH) and/or conductivity will be adjusted to optimize the charge of the suspended nano-particles so that migration to the appropriate electrode will occur most efficiently.

What is meant by the "surface charge" of the suspended nano-particles? The net charge at the particle surface affects the distribution of ions in the surrounding interfacial region resulting in an increased concentration of counter ions – thus an **electrical double layer** exists around each particle as depicted in Figure 1. The liquid layer surrounding the particle consists of a strongly bonded inner layer (Stern layer) and a loosely bonded outer layer (diffuse region). Within the diffuse layer is a hydrodynamic shear plane, and the charge at this shear plane is called the **zeta potential**. We are interested in optimizing the zeta potential because this affects the particle stability (to prevent flocculation) and its electro-mobility. If all the particles have a large negative or positive zeta potential they will tend to repel each other and there is no tendency for the particles to come together. In general, particles with zeta potentials more positive than +30 mV or more negative than -30 mV are normally considered stable.

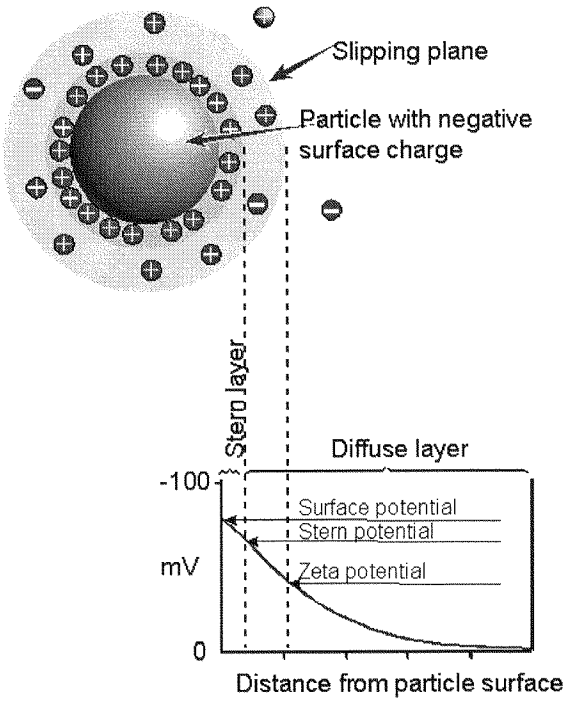

Figure 1 The electrical double layer of a suspended nano-particle.

The most important parameter affecting the zeta potential is the solution pH. In fact, it makes no sense to quote a zeta potential without also quoting a corresponding pH value. The graph shown in Figure 2 shows how pH could affect the zeta potential. In basic solution (high pH) the suspension of particles acquires a negative charge, whereas in acidic solution (low pH) the particles acquire a positive charge. A certain point is reached where the particle has zero charge (neutralized) – this is the **isoelectric point**. From this graph it is likely that most efficient mobility of these particles (in this case) will occur below a pH of 4 or above a pH of 8. Of course, the electro-mobility depends on other factors as well including particle size (measured at UALR), strength of the electric field (voltage gradient), and dielectric constant and viscosity of the solution.

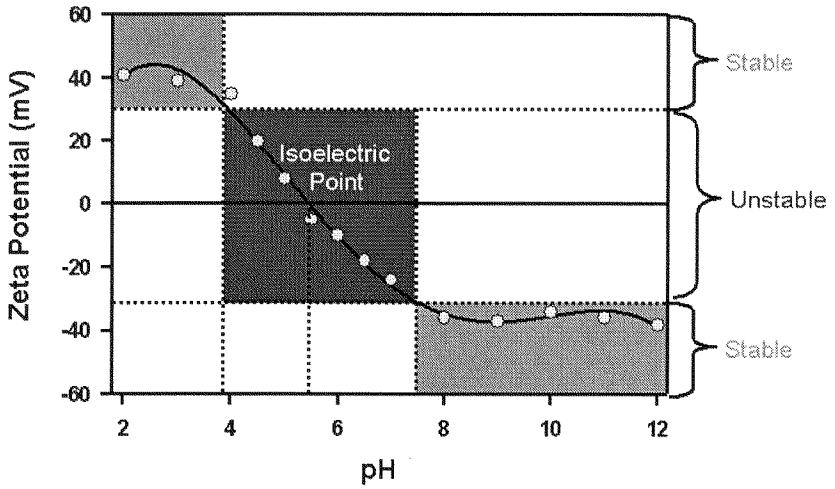

Figure 2 Plot of pH versus zeta potential for a colloidal suspension.

THE OLD WAY OF MEASURING THE ZETA POTENTIAL (RELATED TO THE ELECTROPHORETIC MOBILITY)

Early methods of measuring the electrophoretic mobility involved the process of directly observing individual particles using ultra-microscope techniques and manually tracking their progress over a measured distance as shown in Figure 3.

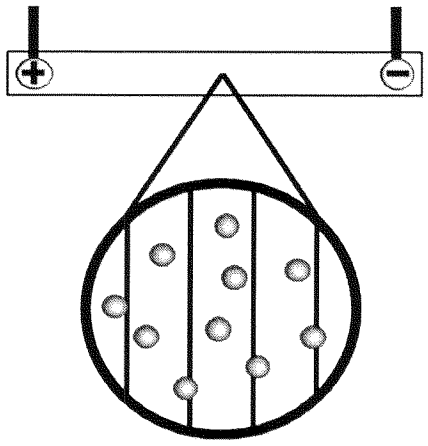

Figure 3 Measuring electrophoretic mobility by timing the movement of particles in a capillary cell using a microscope.

This procedure, although still being used by many groups world wide, suffers from several disadvantages, not least that of the strenuous effort required to make a measurement, particularly with small or poorly scattering particles.

ELECTROPHORETIC MOBILITY (ZETA POTENTIAL) USING THE LASER DOPPLER ELECTROPHORESIS (MALVERN ZETASIZER)

Laser Doppler electrophoresis is a technique used to measure the movement of charged particles in an electric field, which utilizes the well-known Doppler effect.

Light scattered from a moving particle experiences a frequency shift as shown in Figure 4.

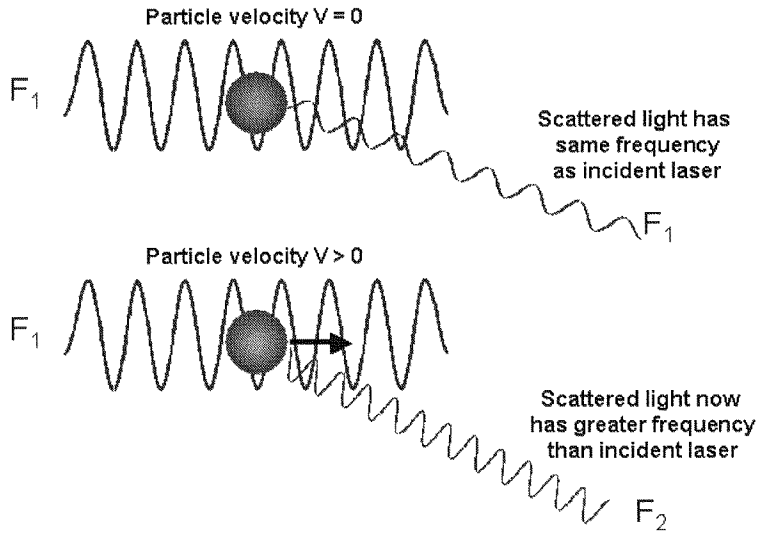

Figure 4 The frequency of the scattered light will be the same for stationary particles (F_1) but will be different (F_2) for moving particles (Doppler Effect).

Since the frequency of light is so high (10^{14} Hz), the shift in frequency can only be measured by an optical mixing or **interferometric** technique. A laser beam (HeNe laser, 632.8 nm) is split into two mutually coherent beams following similar path lengths. One of these beams must pass through the particle dispersion (this is called the scattering beam). The other beam (called the reference beam) can either pass through the sample or can be routed around the cell. The scattered light from the particles is combined with the reference beam to create intensity variations.

Figure 5 shows the reference beam of frequency F_1 combined with scattered light arising from moving particles of frequency F_2. Combining the two frequencies together gives rise to a modulated beam due to constructive and destructive effects, which has a much smaller, measurable "beat" frequency. This "beat" frequency is the difference between F_1 and F_2 and is used to determine the mobility of the particles.

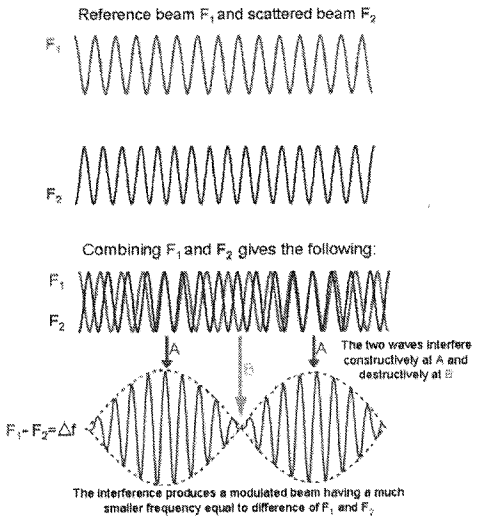

Figure 5 Reference beam (F_1) combined with scattered light of moving particles (F_2) gives rise to a "beat" frequency related to electrophoretic mobility.

The sign of the Doppler shift is determined by comparing this beat frequency with that of a reference frequency. This reference frequency is produced by modulating one of the laser beams with an oscillating mirror. The mobility of the particles in an applied field will therefore produce a frequency shift away from that of the modulator frequency. This gives an unequivocal measure of the sign of the zeta potential.

The optical configuration on the Zetasizer Nano for zeta potential measurements is shown in Figure 6. A helium-neon laser is used as a light source to illuminate the particles within the sample. The beam is split to provide an incident and reference beam. The incident laser beam passes through the center of the sample cell and the scattered light is detected at a forward angle.

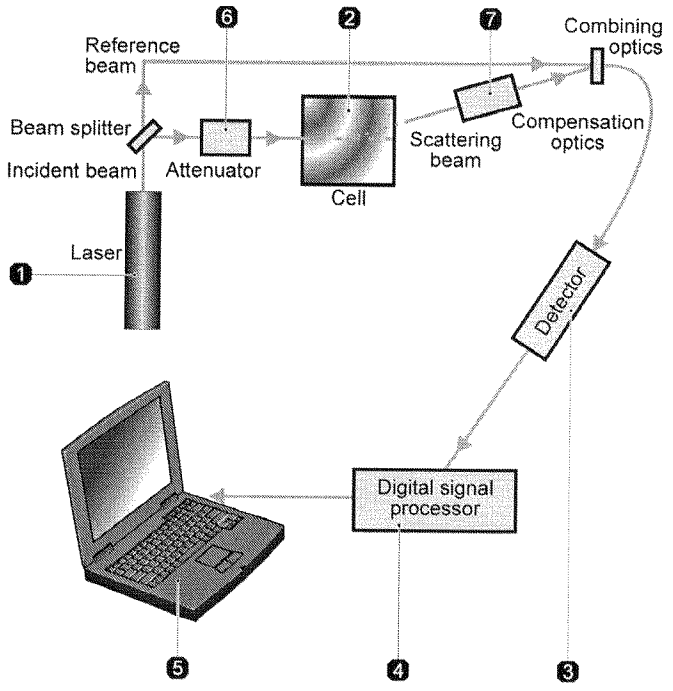

Figure 6 The Malvern ZetaSizer Instrument.

When an electric field is applied across the cell, any particles moving through the measurement volume will cause the intensity of light detected to fluctuate with a frequency dependent on the particle speed and this information is passed to a digital signal processor and PC. The software analyzes the data and calculates the electrophoretic mobility and zeta potential.

The Zetasizer uses a combination of laser Doppler velocimetry and phase analysis light scattering (PALS) in a technique called M3-PALS to measure particle electrophoretic mobility. This enables even samples of very low mobility to be analysed and their mobility distributions calculated. M3 stands for mixed mode measurement and consists of both fast field reversal (FFR) (to eliminate the effects of electro-osmosis) and slow field reversal (SFR) measurements (to find peak shape).

GOAL OF OUR RESEARCH GROUP: HAP PROTECTIVE COATINGS ON TITANIUM IMPLANTS

The goal of our research group is to prepare chemically stable, homogeneous, well-characterized hydroxyapatite bioceramic coatings (HAP; inorganic component of bone) on titanium-based implants using the technique of electrophoretic deposition (EPD). The preparation of HAP bioceramic surface coatings has been carried out extensively using numerous production routes including solid state reactions or dry processing,[10] plasma techniques,[11] spray pyrolysis,[12] ultrasonic spray pyrolysis,[13] pulsed-laser deposition,[14] freeze-drying,[15] hydrothermal processing,[16,17,18,19] wet chemical methods

(precipitation)[20,21] sol-gel crystallization,[22,23] microwave processing,[24] sonochemical synthesis,[25] and the simple hydrolyzation of calcium phosphate.[26] In fact, in our laboratory at ATU, we have synthesized stoichiometric and non-stoichiometric HAP using aqueous co-precipitation methods and have characterized these powders at the UALR Center for Nanotechnology using Raman spectroscopy,[27] FT-IR,[28] and X-ray diffraction.[29]

In contrast to the aforementioned deposition techniques, electrophoretic deposition (EPD) [30] is a simple and low-cost method for depositing high-quality and reproducible coatings on metallic substrates, and has recently been used to deposit HAP coatings on pure titanium metal and medical-grade titanium, TiAl6V4.[31] Briefly, an HAP suspension (precipitation or gel) is prepared using a conventional aqueous or non-aqueous process. The pH is adjusted to achieve the desired charge on the colloidal particles (depending on cathodic or anodic deposition). The ***only way*** of knowing the charge (positive or negative) and stability (zeta potential in mV; i.e., to prevent unwanted clumping or aggregating) of the colloid is to make zeta potential measurements on the suspension as a function of pH. Zeta potential is a physical property which is exhibited by any particle in suspension; it is the potential that exists at the solid/solution interface and determines its stability. If particles have a sufficiently high repulsion (high zeta potential), the dispersion will resist coagulation and the colloidal system will be stable. This information is used to optimize the suspension, long-term stability, and the electrophoretically deposited thin film. The recently acquired Zetasizer Nano Z calculates the zeta potential by determining the electrophoretic

mobility (using Laser Doppler Velocimetry) and applying a mathematical relationship (called the Henry equation).

PRELIMINARY RESULTS: ZETA POTENTIAL MEASUREMENTS OF COLLOIDAL HYDROXYAPATITE (HAP) AND TITANIUM DIOXIDE (TiO_2)

Before the actual deposition of hydroxyapatite (HAP) and titanium dioxide (TiO_2) films on titanium metal subtrates, the pH versus zeta potential curves (see Figure 2) must be generated for HAP and TiO_2 nano-particle suspensions. This work is currently in progress. In this section, we present some preliminary results.

Figure 7 shows the results of a zeta potential measurement on nanoparticles of TiO2 (Degussa, P-25 titania) in ethanol; these particles have a diameter of about 23 nanometers.

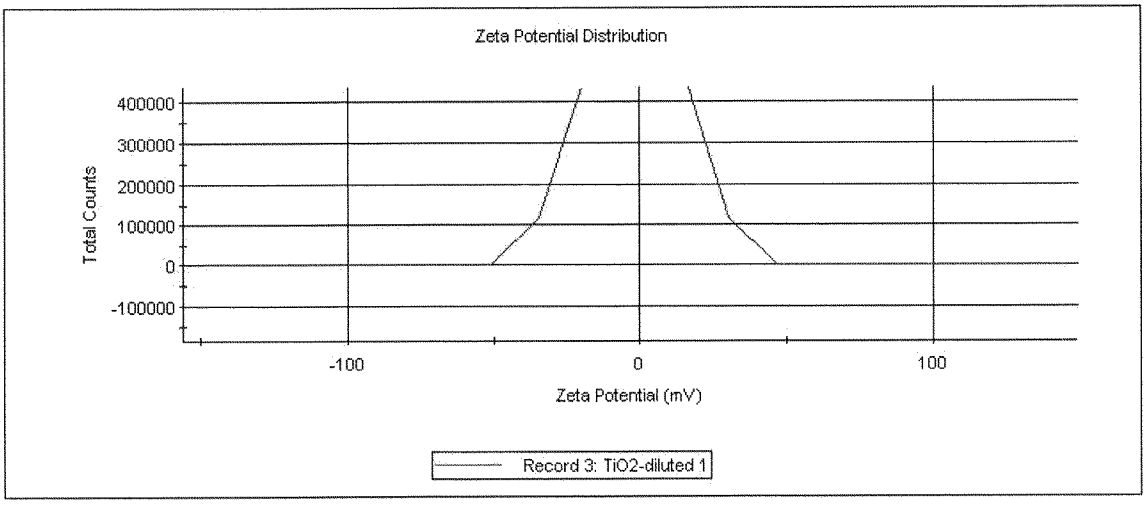

Figure 7 Zeta potential distribution of Degussa TiO_2 nano-particles at a pH of about 6.5.

The surface charge was measured at about 0 mV indicating surface charge neutrality and that at this pH we are very near the isoelectric point. In fact, the isoelectric point of TiO_2 has been reported to occur at about pH = 6.

Figure 8 shows the measured zeta potential distribution of in-house hydroxyapatite synthesized using an acid-base precipitation method and air-dried.

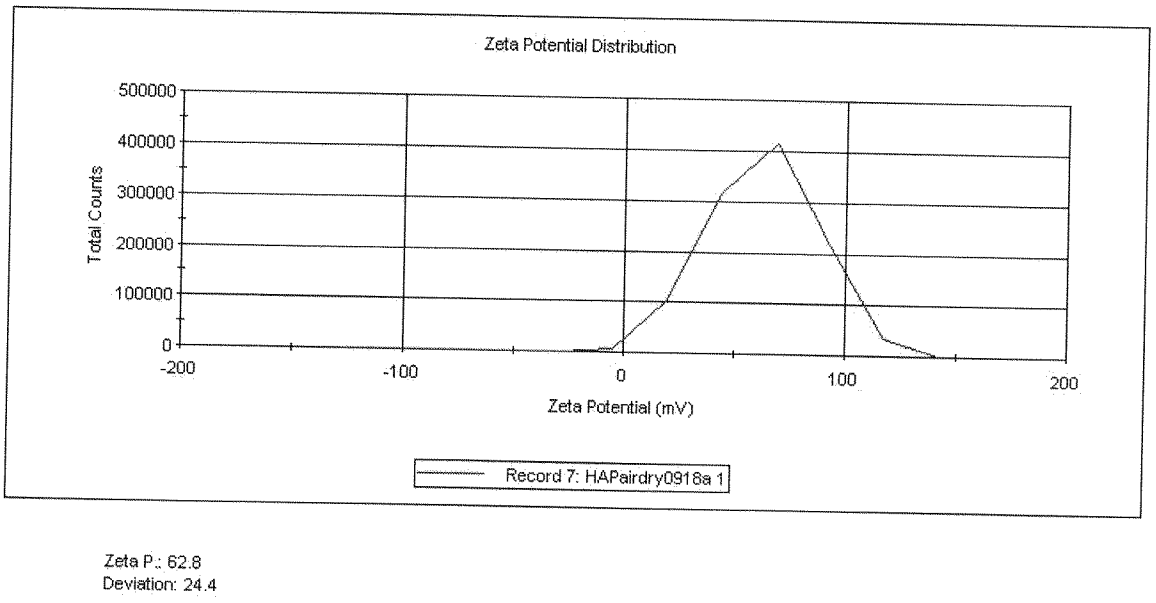

Figure 8 Zeta potential distribution of in-house hydroxyapatite measured with the ATU Malvern Zeta-Sizer potentiometer.

These results, showing an average zeta potential of +63 mV, indicate that the HAP particles are very stable at a pH of about 6.5. Depending on the results of the particle size measurements, these conditions may be suitable for deposition

of HAP onto the negatively charged electrode as a stable and homogeneous coating.

CONCLUSION AND FUTURE STUDIES

A Malvern model Zetasizer Nano Z zeta potentiometer was recently purchased, installed, and tested at Arkansas Tech University (McEver Building, Instrument Lab). One important function of the zeta potentiometer is to measure the stability of colloids in solution (suspended particles) as a function of temperature and surface charge (a function of solution pH). This information is required for effective electrochemical deposition of these colloids as films onto metal substrates, a process known as electrophoretic deposition (EPD).

Our group at ATU is interested in the EPD of hydroxyapatite (synthetic bone, synthesized in our laboratory) onto titanium substrates (mimicking titanium implants). Preliminary results for in-house HAP and commercial TiO_2 are promising and demonstrate the feasibility of using both HAP, TiO_2 and composite thereof as materials for the electrophoretic deposition onto titanium implants.

Eventually, with appropriate funding, this instrument will be upgraded (by adding components) to a state-of-the-art model Zetasizer Nano ZS for the simultaneous and automated determination of zeta potential (using an auto titrator), particle size distribution analysis, and molecular weight.

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