# Permanently Linked Rigid Superparamagnetic Chains

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Magnetorheological (MR) fluids are suspensions of paramagnetic colloidal particles that self-assemble to form chains under the application of an external magnetic field. This aggregation is reversible and, owing to Brownian motion, the colloidal particles return to their freely dispersed state once the magnetic field is removed. Such chaining of MR fluids in the presence of an external magnetic field has a significant effect on the fluid rheology, including inducing a finite yield stress. Permanently linked chains of these polarizable particles have several interesting potential applications since their suspensions have a dynamic structure both in the presence and absence of a magnetic field [1]. They can be used as micromechanical sensors [2], for shock absorption in automobiles, headrests and ballistic events [3], and in DNA and other bio-separation processes that use rigid obstacles (e.g., columns of aligned magnetic particles) to impede the convective transport of these species [4]. The rheological properties of these suspensions under different shear and magnetic field conditions may also have unique applications. To date, only *flexible* chains of superparamagnetic particles, linked permanently by a flexible polymer or other linker, have been reported in the literature [1, 2]. Herein we demonstrate a technique whereby sol-gel chemistry is used to link these polarizable particles permanently, once they have been aligned within a microchannel by an external magnetic field, to yield *rigid* superparamagnetic chains. These rigid chains are responsive to applied magnetic fields and have unique dynamic response characteristics and rheological properties. The particles used to form these chains were polystyrene (PS) beads that were coated with polyelectrolyte layers and maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticles. Once formed, the chains were linked together with titanium dioxide to create a new class of magnetoresponsive materials. The extra strength imparted by the bonding material (titania in this case) ensures that the permanently linked rigid magnetic chains will be much stronger than those formed from free particles in suspension under a magnetic field, and hence will affect the shock absorption and other mechanical properties of the magnetic fluid suspensions quite considerably. In addition to bonding the linked chains permanently, the titania coating can be exploited in a range of other applications that include photocatalysis, sensor technology, and antimicrobial resistance. These rigid magnetic rods can also have potential microfluidic applications where they could be used, for example, as microstirrers, microvalves and micropumps [5].

Figure 1 outlines the procedure for making the rigid magnetic chains. Positively charged superparamagnetic PS beads were prepared using a layer-by-layer (LbL) strategy as described by Caruso et al. [6, 7]. First, poly (diallydimethyl) ammonium chloride (PDAMAC) was adsorbed onto negatively charged sulfonated polystyrene (PS) beads (790 nm). This step was followed by the adsorption of a negatively charged polyelectrolyte, polystyrene sulfonate (PSS) and, finally, of a second layer of PDAMAC to leave the coated particles positively charged. The reversal of surface charge was monitored by measuring the zeta potential (Zeta Pals, Brookhaven) after each coating. The measured zeta potential was 50 mV when PDAMAC was the outer layer and -60 mV when the outer layer was PSS. The positively charged beads (PS coated with PDAMAC/PSS/PDAMAC) were then coated with negatively charged citrate-stabilized magnetic nanoparticles (Zeta potential = -20 mV) followed by a layer of PDAMAC so that the final surface charge was positive. These positively charged beads were recovered

and resuspended in anhydrous ethanol.  The outer PDAMAC layer on the PS beads was highly hygroscopic and retained some of its water of hydration even when suspended in anhydrous ethanol.  From a Karl Fischer titration, the partition coefficient for water between the bead surface and the bulk ethanol was measured to be ~60.
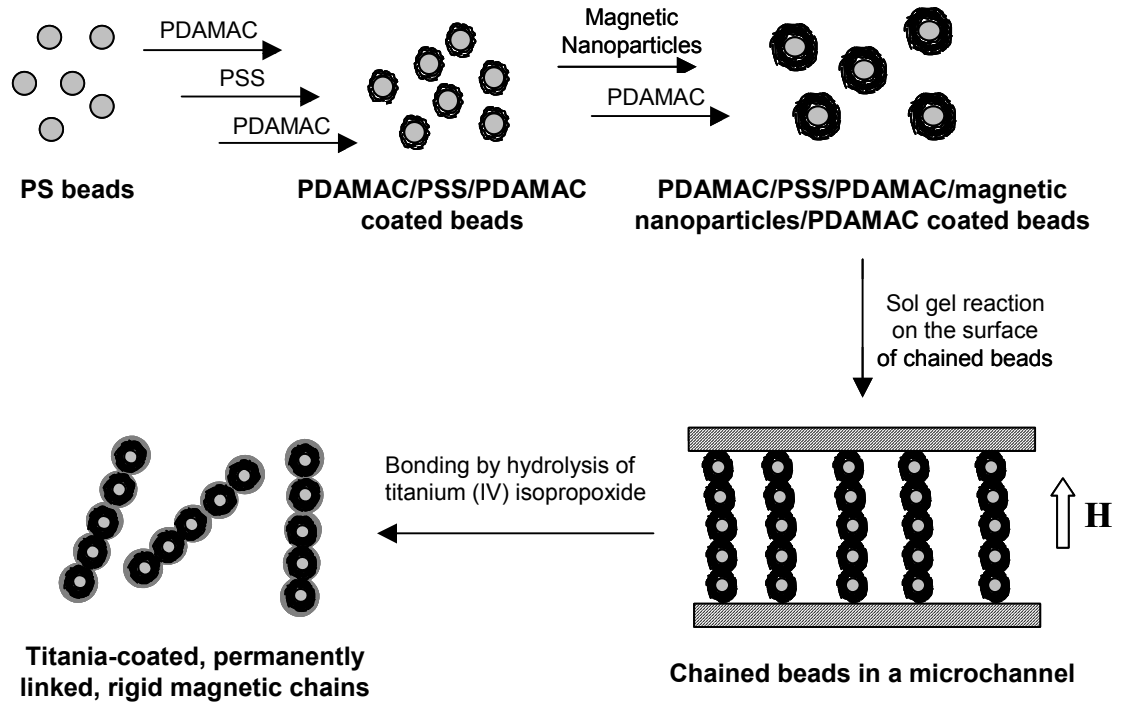


**Figure 1: Process for producing permanently linked rigid magnetic chains.**

The adsorption of the magnetic nanoparticles on the positively charged PS beads produced completely covered beads, as observed by scanning electron microscopy (JEOL-6060SEM) (Figure 2).  The thickness of the magnetic nanoparticle coating was 25 nm, in close agreement with our estimate of 27 nm based on the quantity of PS beads and magnetic nanoparticles added to the suspension.  Magnetization experiments on these coated beads indicated that they had zero remanence, thus verifying the superparamagnetic nature of the particles.  The beads, which were well dispersed as individual particles in the absence of an applied magnetic field (Figure 3A), aggregated reversibly as chains under an applied magnetic field (Figure 3B).
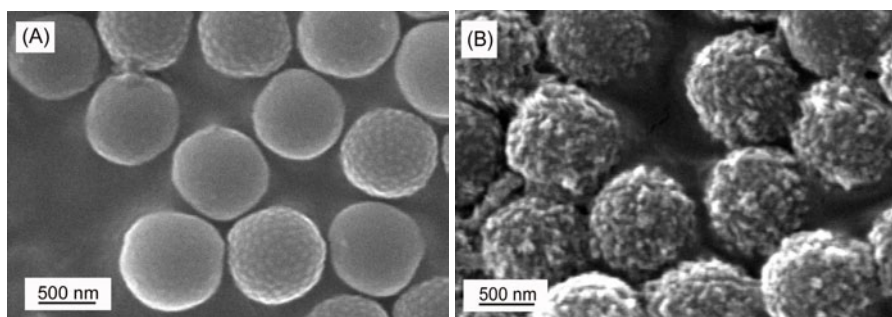
**Figure 2: SEM micrograph of (A) plain PS beads and (B) magnetic nanoparticle-coated beads. The samples were sputter coated with gold for better contrast. The thickness of the magnetic coating was estimated to be 25 nm based on the difference in the diameters of the coated and the uncoated beads.**
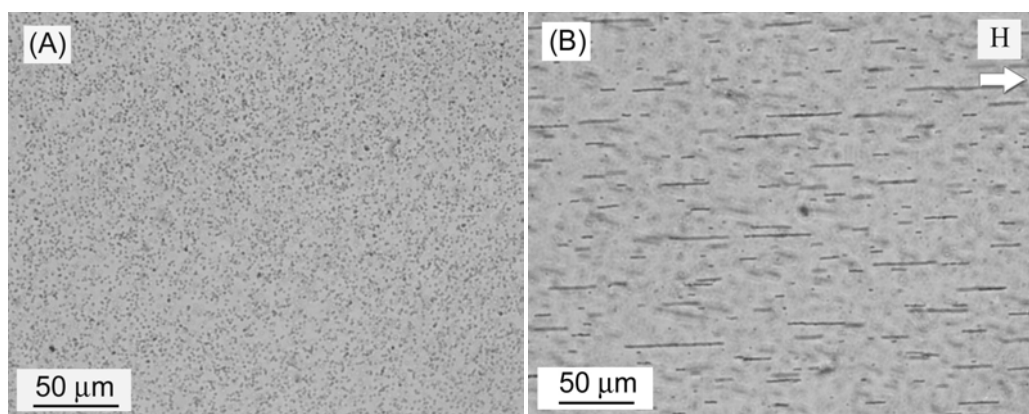


**Figure 3: Magnetic beads in (A) the absence, and (B) the presence of an external applied magnetic field (H) as observed under an optical microscope.**

The coated bead suspension in ethanol was mixed with a titania precursor (titanium (IV) isopropoxide, TIP) and injected into a microchannel (25 $\mu m$ x 50 mm x 25 mm). The beads aligned into chains upon application of a magnetic field across the channel, the height of which determined the length of the chains formed. The hydrolysis reaction was allowed to proceed in the presence of the magnetic field for 24 h. The controlled nucleation of titania on the surfaces of the aligned beads cemented the particles within the chains together and produced permanently linked rigid superparamagnetic chains. The localized concentration of water on the outer PDAMAC ensured preferential hydrolysis of TIP on the bead surface. A small degree of hydrolysis was observed in the bulk due to the low concentration of water in the solvent, but this did not have an effect on the properties of the chains formed during this process.

The positive charge on the PS beads also contributed to the efficient capture of the nucleated titania. Titania is negatively charged at neutral pH [8], and the positive charge on the magnetic beads from the outermost PDAMAC layer ensured that the nucleated titania associated with the particle surface. The charge on the bead surface reversed from positive to negative as the adsorption of titania continued. During this process of charge

reversal, some of the beads became negatively charged, while others were positively charged. The aggregation of such oppositely charged beads, which inhibited the formation of chains, was prevented by adding poly(vinylpyrrolidone) (PVP) to the suspension, which adsorbed on both titania particles and the magnetic bead surfaces to impart a steric stabilization against bead aggregation [9]. At the end of the reaction, permanently linked rigid magnetic chains were formed. These chains were stable and could be recovered and stored for months without degradation. Transmission electron microscopy (JEOL 200CX, 200kV) indicated a titania coating thickness of 30 nm (Figure 4), that was close to the thickness (32 nm) calculated based on the concentrations of TIP and PS beads used in the experiments. The titania-coated magnetic rods aligned in the direction of an externally applied magnetic field.
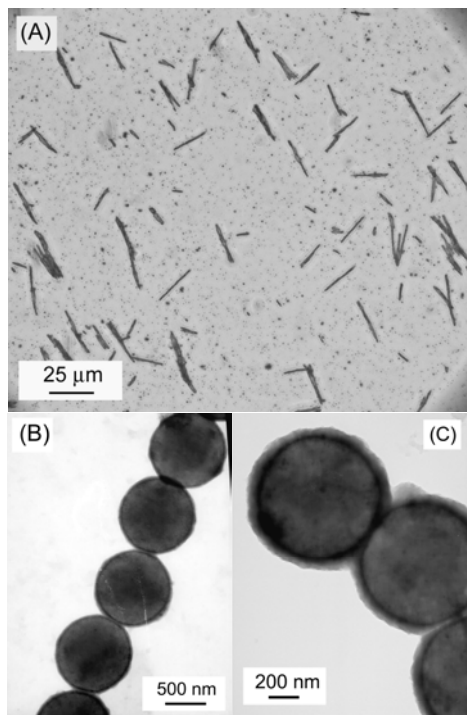


**Figure 4: TEM micrographs of titania–coated magnetic chains. The thickness of the titania coating was estimated to be 30 nm.**
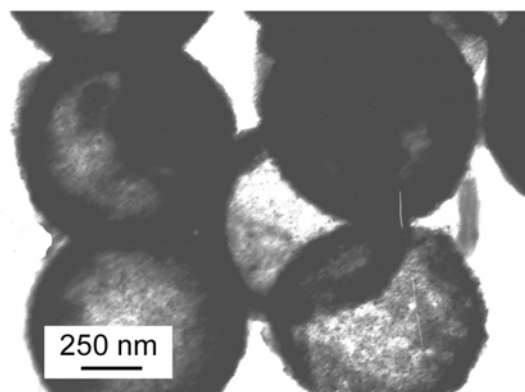
**Figure 5: TEM micrograph of hollow titania-linked magnetic chains after calcination. The transparency of the beads in the micrograph provides evidence of their hollow structure.**

The permanently linked magnetic chains were calcined at 600 $^{o}$C to convert the amorphous titania to its crystalline anatase form, as confirmed by X-ray diffraction. The anatase form of titania has a higher mechanical strength and a much wider range of application possibilities [10] than does the amorphous form of this oxide. During the calcination process, the PS beads burned off to yield magnetic chains that consisted of hollow spherical cores linked together by the titania coating (Figure 5).

The approach used here for making rigid magnetic chains is quite versatile, as it should allow the synthesis of magnetoresponsive rods using a variety of sol-gel precursors and a variety of magnetic nanoparticles. The intrinsic and extrinsic properties of the chain can also be readily manipulated. The diameter and length of the chains can be controlled by changing the PS bead diameter and the height of the microchannel, respectively. The magnetization of the beads can be enhanced by depositing additional magnetite layers on the particle surfaces, following the established layer-by-layer technique. Our current focus is on the dynamic response of these rigid magnetic chains to applied magnetic fields, and on methods for the production of these chains on a continuous basis.

## Experimental Method

### Positively charged PS beads

Commercially available negatively charged sulfonated PS beads (average diameter 790 nm, Spherotech) were made positively charged using a layer-by-layer polyelectrolyte adsorption technique [7]. In a typical process, 0.5 mL of a 0.5 wt% solution of PS beads was suspended in an aqueous solution of 0.5 mL of 1 mg/mL PDAMAC (poly (diallydimethyl) ammonium chloride, MW 150,000, Aldrich, 0.5 M NaCl). After 30 min of adsorption, the beads were separated by centrifugation at 7000g for 10 min and resuspended in water. This process was repeated three times. The beads were then coated with a negatively charged polyelectrolyte by suspending them in a 1

mg/mL of polystyrene sulfonate (PSS, MW 70,000, Aldrich, 0.5 M NaCl) solution using the same process outlined above. These negatively charged PS beads were finally coated with a second layer of PDAMAC by the above method to obtain positively charged particles.

**Synthesis of magnetic nanoparticles and subsequent adsorption**

Citrate-coated magnetic nanoparticles with an average diameter of 10 nm (as estimated by TEM) were synthesized using Massart's method [11]. An aqueous solution of magnetic nanoparticles (150 $\mu L$, concentration 0.005 wt % in water) was added to the positively charged PDAMAC/PSS/PDAMAC coated PS beads (1 mL, concentration 0.25 wt% in water). After continuous shaking for 30 min, maghemite-coated PS beads were recovered by centrifugation at 7000g for 10 min. They were again coated with PDAMAC using the same procedure as above to yield positively charged magnetic beads. These beads were then centrifuged and washed with anhydrous ethanol four times with, and finally resuspended in anhydrous ethanol.

**Linking of magnetic beads**

In a typical reaction, a mixture of 0.5 mL (10 mg/mL) of PDAMAC-coated magnetic PS beads in anhydrous ethanol, 3 $\mu L$ of TIP (99 wt%, Aldrich), and 5 mg of PVP (MW 150,000, Aldrich)) were injected into a microchannel (25 $\mu m$ x 50 mm x 25 mm). The microchannel was prepared using two glass microslides separated by a teflon spacer. Two neodymium-boron-iron magnets (McMaster Carr) of 200 mT each placed on opposite faces of the microchannel were used to provide a uniform magnetic field. The reaction was run for 24 h under the applied magnetic field in an ethanol-saturated chamber to prevent evaporation from the microchannel reaction mixture.

**Sample Preparation**

TEM samples were prepared by drying a drop of sample on a carbon substrate grid. SEM studies were performed by drying the sample on a carbon tape grid. The zeta potentials of the samples were measured in water (MilliQ, conductivity 18 M$\Omega$). Karl Fisher titrations (Mettler Toledo DL31) of the positively charged magnetic beads were conducted by centrifugation of a suspension in anhydrous ethanol, analysis of the supernatant and the centrifuged beads, and a partition coefficient calculated based on the water content difference between the two samples. For calcinations, samples were first dried in a refractive crucible in a furnace, heated to 600 $^o$C at a rate of 5 $^o$C /min, held at 600 $^o$C for 8 h, and then cooled to room temperature at a rate of 5 $^o$C /min.

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