Supporting Information

Dipolar Assembly of Ferromagnetic Nanoparticles into Actuating Microscopic Filaments

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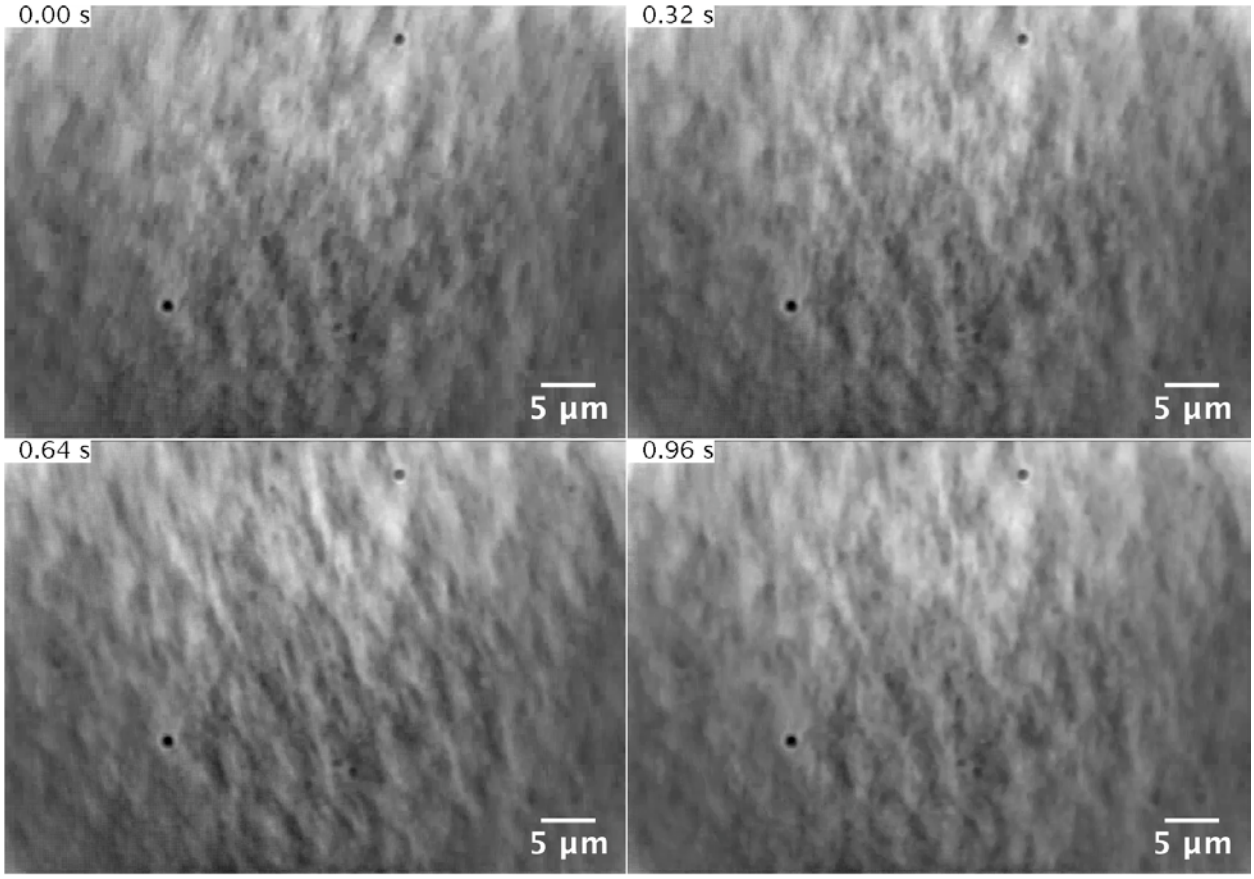
Copolymerization of styrene and 4-(vinylphenyloxy)benzaldehyde to prepare poly(Sty-r-BzAld). Into a 25 mL Schlenk flask was added with AIBN (0,152 g; 0.924 mmole), styrene (4.36 g; 41.9 mmole), 4-(vinylphenyloxy) benzaldehyde (1.00 g; 4.19 mmole) and toluene (4 mL). The flask was fitted with a glass stopper and the content was deoxygenated via 3 cycles of freeze-pump-thaw. The content of the flask was then backfilled with argon before placing the reaction flask into a thermostated oil bath at 60 °C. The polymerization reached 93% monomers conversion in 3.5 hours. The viscous polymer mixtures were precipitated into methanol (500 mL), filtered and dried to obtain a white powder (4.998 g; 98% yield. ^{1}H NMR (250 MHz, $CDCl_3$, δ): $Mn(_{SEC)}$ = 13000 g/mole; M_wM_n = 2.30.

Formation of Dense, Cilia-Mimetic Arrays: S1-S3

The first movie corresponds to the image sequence shown in Figure 5.

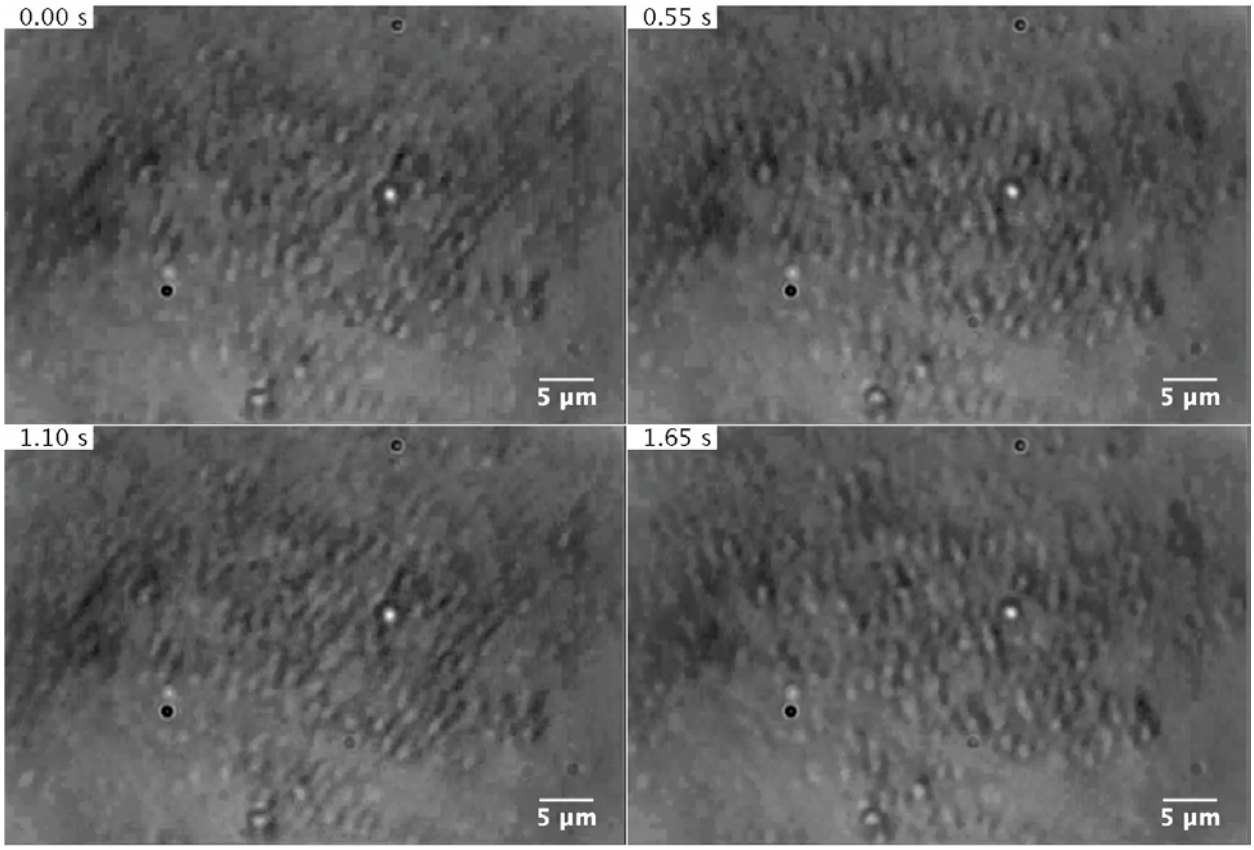


S1: Real time movie captured using an Olympus BX2 microscope with a 100x objective. The sample was made from a 1000 µg/ml solution of PS-CoNPs in DMF. The filaments appear thicker than their actual diameter since it was necessary to under-focus in order to maximize contrast. First the amplitude of the alternating magnetic field is decreased and increased. Then the frequency changes from 0.6 Hz up to 10 Hz and then back down to 0 Hz.

This movie clearly shows that the pivot points of the magnetic filaments are at their bases. Since this behavior was observed even in the absence of crosslinker, we deduce that some combination of the downward pull of the magnetic field and possibly friction with the lower

coverslip is holding the base of the filament in place. Indeed, movies taken during the early stages of array formation show many filaments pinned to the surface while free-flowing filaments continue on their journey toward the magnet tips.

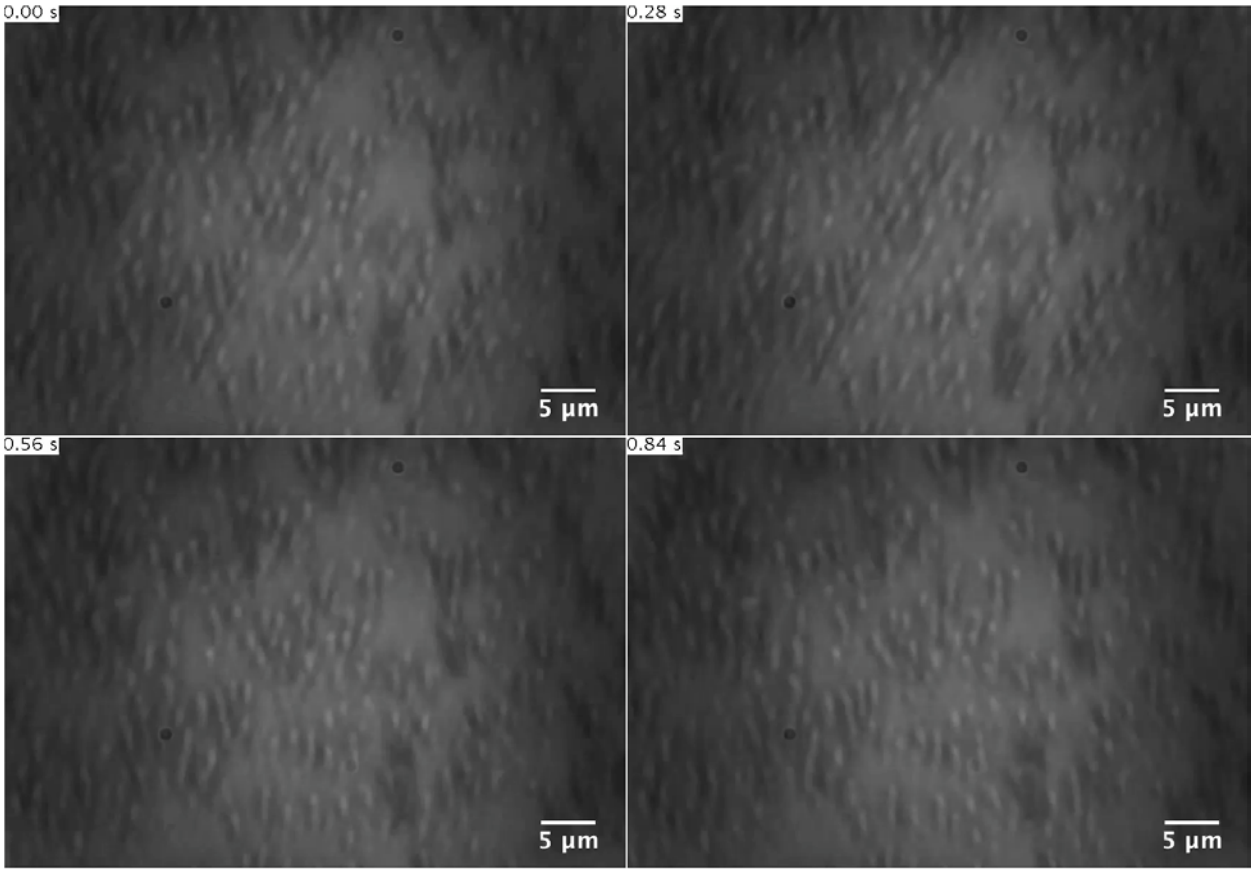
Another question regarding the imaging of the filaments has to do with their thickness. At 25 nm in diameter, the PS-CoNPs are too small to resolve in an optical microscope. However, chains of NPs appear to scatter light sufficiently to provide enough contrast for imaging. SEM images have been collected for samples made on the magnetic stage, and in each case we observed only NP chains that were one particle wide. To further emphasize this point, we added 1 ng/ml of 250 nm magnetite colloids provided by Micromod Partikeltechnologie GmbH. One can see in the following movie that the white dot near the center of the image moves along with the magnetic field. This 250 nm particle appears much brighter than the neighboring filaments and appears to be much thicker. Although this does not serve as an accurate measurement of filament diameter, it demonstrates that the thickness is much less than 250 nm.



S2: Real time movie of PS-CoNP filaments formed from a 100 µg/ml solution with the addition of 1 ng/ml 250 nm magnetite colloids to indicate scale. Note that both the filaments and colloids appear larger than their actual size since the image was defocused to improve contrast. The white dot near the center of the image is a 250 nm particle, and it demonstrates that the filaments are much thinner. SEM images support this conclusion, and further suggest that the filaments are only one particle wide (25 nm).

Although the majority of the filaments remain at fixed locations, it is clear from the gliding filaments that they can lower their magnetic potential by continuing towards the magnet. Furthermore, the packing is not so dense that filament translation is sterically prevented. The

fact that most filaments remain in a fixed position strongly indicates that they are bound to the surface. The fact that the chemical functionality of the surface did not affect the binding indicates that binding was the result of some combination of downward magnetic forces, van der Waals attraction, and friction rather than covalent bonding.



S3: Real time movie captured for a 1000 µg/ml PS-CoNP solution with a 100x objective. This movie taken during the early stages of array formation shows. Note that the majority of the filaments are pinned at fixed locations but are still free to rotate with the alternating magnetic field. Also note how many filaments glide into the field of view and work their way through the dense array of magnetic filaments as they are pulled towards the magnet tips by the field gradient.

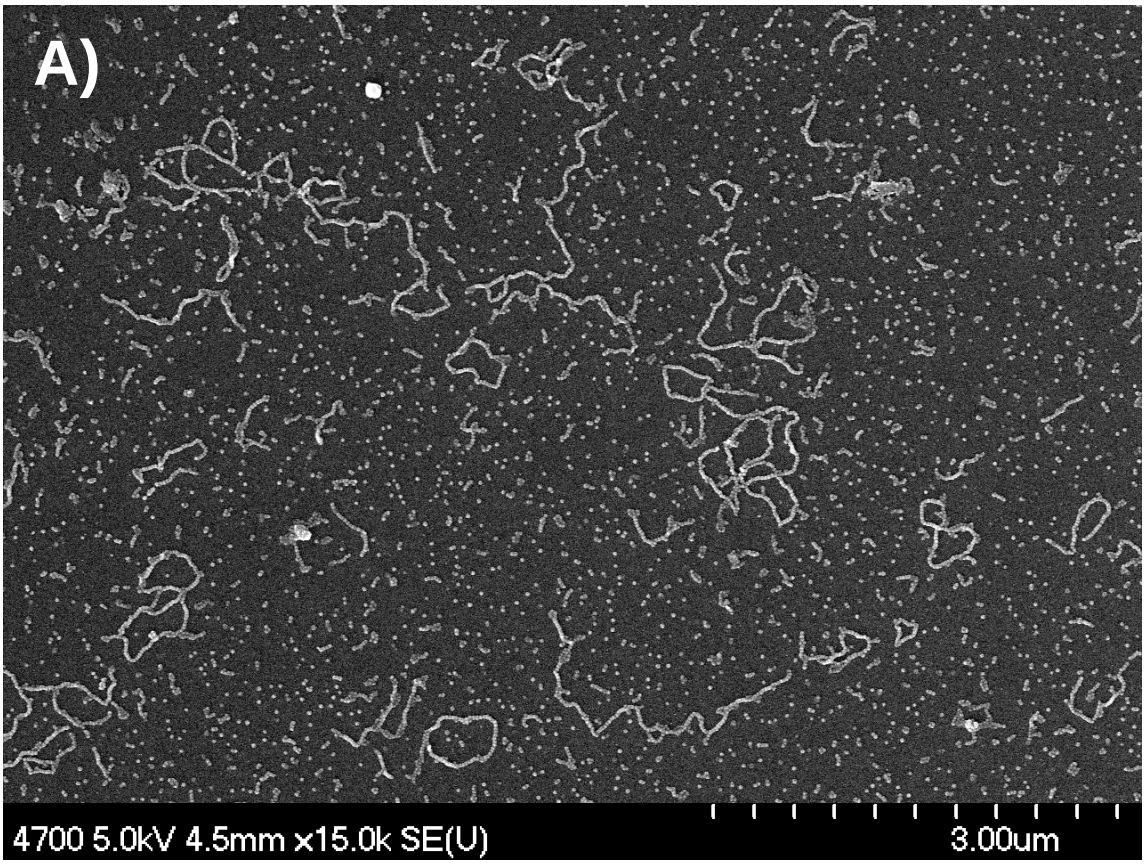
Effect of Crosslinker: S4, S5

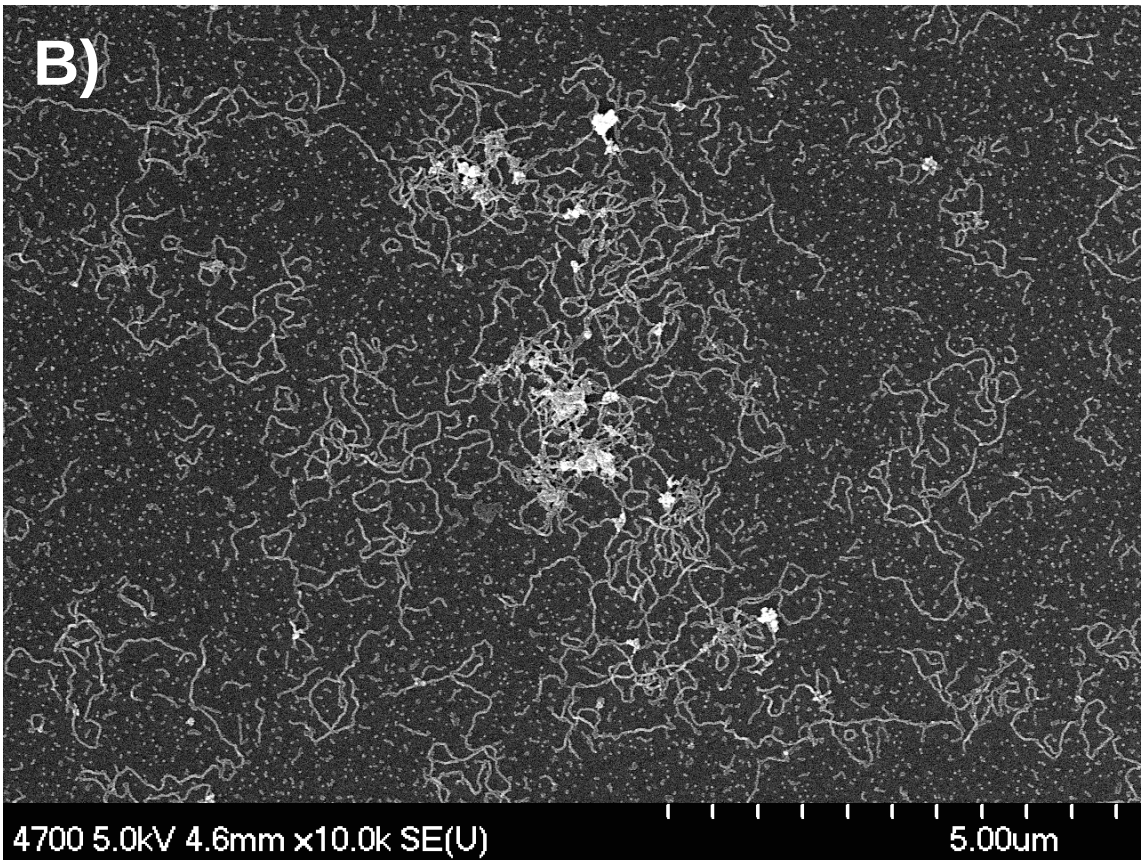
The magnetic filaments were assembled from a dimethylformamide (DMF) solution with cobalt nanoparticles ranging from 0.1 - 1000 μg/ml in concentration. Jeffamine XTJ-502 (H_2N-PEG-NH_2) was also added in concentrations ranging from 0 – 1000 μg/ml. The 2000 g/mol H_2N-PEG-NH_2 is a diamine-terminated polyethylene glycol used to chemically crosslink the Co nanoparticles (PS-CoNPs) together. The amine groups react with pendant benzaledyde groups of the end-grafted polystyrene to form imine bonds. 40 μl of the solution was placed atop a microscope cover slip after which it was covered by a second cover slip. The lower cover slip was chemically treated to one of the following three conditions: clean glass, epoxy functionalized, and fluorinated. Whereas the clean glass was hydrophilic and the fluorinated surface was hydrophobic, the epoxy-functionalized surface could react with the H_2N-PEG-NH_2 and therefore potentially form chemical bonds with the PS-CoNPs.

Untreated glass slides were cleaned prior to use using a Harrick plasma cleaner. For the 5 min exposure, the chamber was pumped down to 500 millitorr with 10 W supplied to the RF coil. Epoxy-functionalized cover slips were prepared by immersing them in a 1 vol % solution of (3-glycidoxypropyl)trimethoxy silane in toluene. The cover slips were immersed overnight before rinsing with toluene and drying with nitrogen gas. Fluorinated cover slips were prepared by exposing them to a saturated vapor of (heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane for three hours. Excess silane was removed by first rinsing with acetone followed by a gentle wash with soap and water.

Microscopic inspection did not reveal strong correlations between the extent of crosslinking and the observed structure and organization. With the exception of perhaps a greater degree of

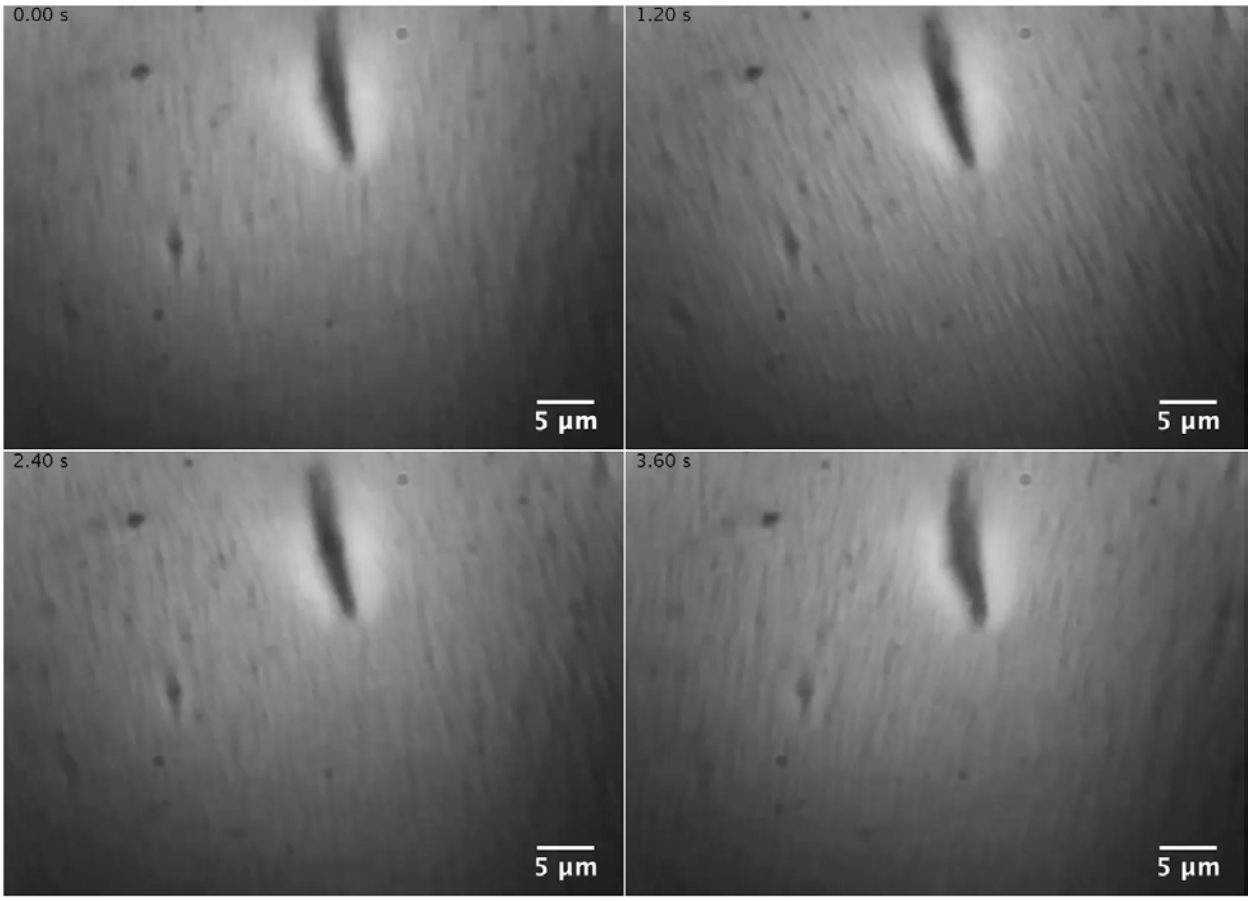
chain agglomeration in the presence of crosslinker, the samples with and without H_2N-PEG-NH_2 appeared nearly identical. The two micrographs shown below illustrate the minor differences.


A)
4700 5.0kV 4.5mm x15.0k SE(U)
3.00um


B)
4700 5.0kV 4.6mm x10.0k SE(U)
5.00um

S4: A) SEM micrograph showing a sample with a 500 μg/ml PS-CoNP concentration made under zero-field conditions with no crosslinker present. B) Shows a sample with the same PS-CoNP concentration and with the addition of 100 μg/ml H_2N-PEG-NH_2 crosslinker under zero-field conditions. Note the presence of agglomerates near the center of the micrograph.

The clumping shown in the SEM micrographs could occasionally be observed when capturing movies with the optical microscope. An example is shown below:

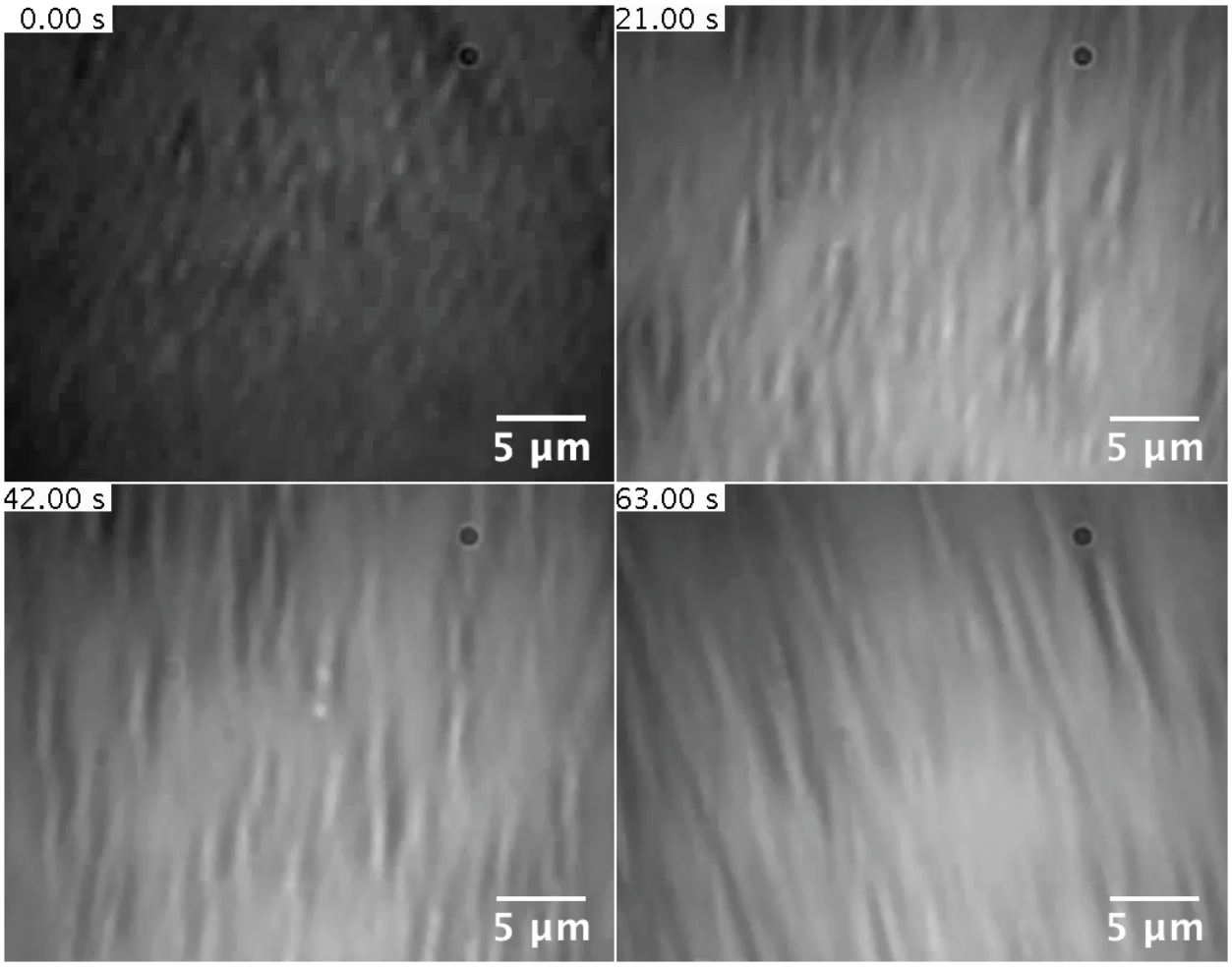


S5: A) Real time movie captured for a 1000 μg/ml PS-CoNP solution using an Olympus BX2 microscope with a 100x objective. The large clump of chains towards the top of the image progressively moves downwards towards the tip of the permanent magnet, collecting additional

filaments as it moves through. Such events were extremely rare, but were primarily observed when H_2N-PEG-NH_2 crosslinker was present.

Orientation Vs. Position: S6

The final movie shows the effect of moving away from the ends of the permanent magnets. Taken continuously as the stage is slowly moved, the movie shows the filament arrays becoming less dense and less perpendicular to the surface. The angle with the surface cannot be measured directly, but one can see that the filaments appear longer as the distance from the magnet tip increases. Observe also that the filaments appear "V" shaped in some instances. This shape is actually an artifact of the limited depth of focus. The V shape inverts to a Λ if the focal plane is moved upwards.



S6: Real time movie captured for a 1000 μg/ml PS-CoNP solution with a 100x objective. This movie taken while the magnetic stage was manually moved so that the field of view moved away from the end of the permanent magnet. Note that the filaments are not growing longer as one moves away from the magnet, but rather they appear longer since their alignment is becoming increasingly parallel to the surface.