# Supporting information for

Synthesis and Directed Self-Assembly of Patterned Anisometric Polymeric Particles

Zhenkun Zhang,† Patrick Pfleiderer,† Andrew B.Schofield,‡ Christian Clasen,† Jan Vermant,†,*

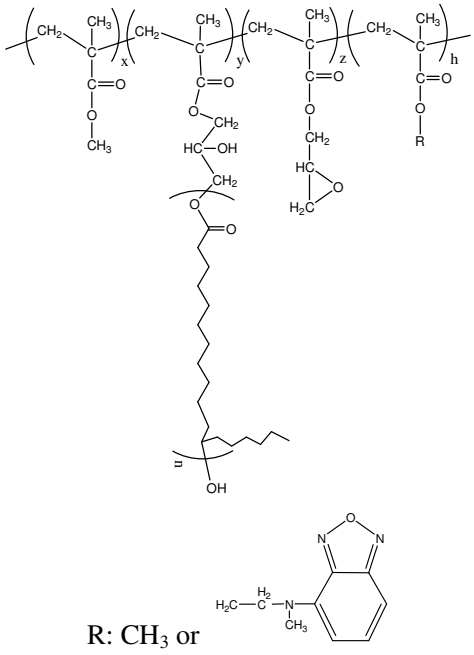
†*Department of Chemical Engineering, K.U.Leuven, Belgium,*

‡ *Department of Physics, University of Edinburgh, United Kingdom*

jan.vermant@cit.kuleuven.be

## Materials

Poly(methyl methacrylate) (PMMA) particles of diameter from 300 nm and 3 μm were synthesized following the method of ref. 1. The particles are covalently grafted with comb-like polymeric stabilizers which consists of linear PMMA as the backbone and poly(12-hydroxy-stearic acid) (PHSA) as the teeth (Scheme S1).[1] For the fluorescent comb-like polymeric stabilizer, units containing 7-nitrobenzo-2-oxa-1,3-diazol (NBD) were incorporated as the fluorescent source. A small fraction of glycidyl groups on the backbone can be used as anchors for covalently binding the stabilizers to the surface of the particles. To prepare the stabilizer solution, 1g of (fluorescent) stabilizer was dissolved in 2 mL ethyl acetate/butyl acetate (2:1 in w/w). The resulting solution was then diluted with 10 mL decalin. Hereafter we refer to this solution as the stabilizer solution. Materials for the mechanical stretching to prepare PMMA ellipsoids are: hydroxy-terminated poly(dimethylsiloxane) (PDMS, average $M_n$ ~110,000, viscosity ~50,000 cSt) for the matrix, poly(dimethylsiloxane-co-methylhydrosiloxane) (trimethylsilyl-terminated, average $M_n$ ~950, 50 mol % methylhydrosiloxane) as the cross-linker, and stannous 2-ethylhexanoate as the catalyst. The degrading solution consists of 0.2% (w/w) sodium methoxide in isopropyl alcohol (IPA). All the chemicals were supplied by Sigma-Aldrich in the highest purity and used as received without further purification.




Scheme S1. Chemical structure of the (fluorescent) polymeric stabilizer.

# Methods

**Transmission optical and fluorescence microscopy**

Most of the microscope observations were performed on a bright field video microscope (BX51WI, Olympus) equipped with long working distance 20x (SLMPlan, NA 0.35, Olympus) and 50x (SLMplan, NA 0.45, Olympus) air objectives and a CCD camera (C8800-21C, Hamamastu). For the fluorescence microscopy, light from a Hg lamp was filtered by a blue fluorescent cube (NIB, Olympus) to excite the samples. This whole system with a long working distance is highly tuned for investigating directed self-assembly of colloidal particles in the bulk and at the liquid-liquid interface. In addition, some samples were cross-checked with an inverted epifluorescence microscope (IX71, Olympus) equipped with a 100x oil-immersion objective (1.3 NA, Plan Fluorite Olympus) and a highly sensitive cooled CCD camera with 512 × 512 pixels (Hamamatsu EM-CCD ImagEM model C9100-13) with a pixel size of 16x16 $\mu m^2$ after being excited with 100 $Wcm^{-2}$ of the 488 nm line from an $Ar^+$ laser (Stabilite 2017, Spectra-Physics). Unless otherwise noted, samples were directly put on cover slides or sealed into 0.1x1.0 mm flat glass capillaries (VitroCom).

**Confocal laser scanning microscopy (CLSM)**

A Zeiss Axiovert microscope equipped with a VT-infinity II multi-point 2D array confocal scanner (VisiTech International Ltd., United Kingdom) with a pinhole size of 50 μm was used for confocal microscopy observations. The NBD was exited at 488 nm with an Ag-Kr mixed gas laser. Apart from the high time resolution of this system, the main advantage of using this multi-pinhole system is that it reduces bleaching of the dyes used here. A 100x oil immersion objective (Plan-apochromat, NA 1.4) was used.

**Transmission and scanning electron microscopy (TEM and SEM)**

TEM was performed with a Philips EM200 transmission electron microscope which is coupled with a side mounted (wide angle port) 11 MegaPixel TEM CCD camera (Morada, Olympus), providing a dynamic range of 14 bits and a range of 1 ms to 60 s in exposure time. The samples were prepared by dropping and evaporating the (diluted) ellipsoid suspension onto a carbon-coated copper grid. SEM is performed on a Philips FEG SEM XL 30 after depositing the particles on the surface of an aluminum stub and sputter coating with gold. Energy-dispersive X-ray spectroscopy (EDX) was conducted on the same setup.

**Preparation of PMMA ellipsoids by thermomechanical stretching**

We adapted the procedure developed by Keville and coworkers[2] and later on improved by Mohraz and Solomon.[3] A stock solution of hydroxy-terminated PDMS in hexane (1:2 in weight) was first prepared. For one film, 61.8 g of 6.1% (w/w) suspension of PMMA particles in hexane were mixed with 224 g of PDMS solution in a glass container to form a homogeneous solution. The crosslinker (224 mg) and catalyst (269 mg) were dissolved in 5 mL hexane each, and added to the mixture. After 2 min of vigorous shaking, the mixture was poured into a home made Teflon-coated mold and left at room temperature for >15 h. The levelness of the mold can be controlled to $10^{-4}$ radians to obtain films of homogeneous thickness, which reduces polydispersity. The pre-cured film, with the mold, was put into an oven at 120 $^oC$ for >6 h. A film of ~ 1 mm thickness was obtained and could be easily

removed from the mold. The film was cut into strips of 2-3 cm width and mounted on an aluminum stretching apparatus designed in-house for particle processing at the gram scale. The length of the strips depends on the desired aspect ratio of the ellipsoids and 12 cm was typical for an aspect ratio of 6. The strips were stretched in several steps with a velocity of 1 cm/mm and a 5-min waiting after each stretching step until a uniaxial extension factor of 3 was obtained. The stretching apparatus with the films was then put into an oven for >7h, with the temperature preset at ca. 160 $^{o}$C. After cooling, 3cm of each end of the film were rejected to avoid effects of clamping and inhomogeneous stretching at these areas. The films were then cut into pieces of about 1x1cm$^2$, weighted and finally swollen in hexane for about 24h.

For the film degradation to recover the ellipsoids, the swollen films were weighed into hexane to get 4.3% (w/w) mixture. The degrading solution was added to give a final reagent concentration (w/w) of 3.5% PDMS film, 78.8% hexane, 17.7% IPA, and 0.04% SM. The mixture was magnetically stirred. After 6-8 hrs the film was fully degraded and a uniform suspension was formed. The liberated particles were collected by centrifuging at ~2000 g, and washed with extensive amounts of hexane/IPA (4:1 v/v) to remove residual degrading agents. By this procedure, ca. 2 gram ellipsoids with well-defined morphology were obtained (Fig. S1). No silicon from the PDMS film can be found on the surface of the ellipsoids (in Fig. S1C, the strong peaks of Au and Al are from the gold-sputtering for SEM and the aluminum stub of the holder).

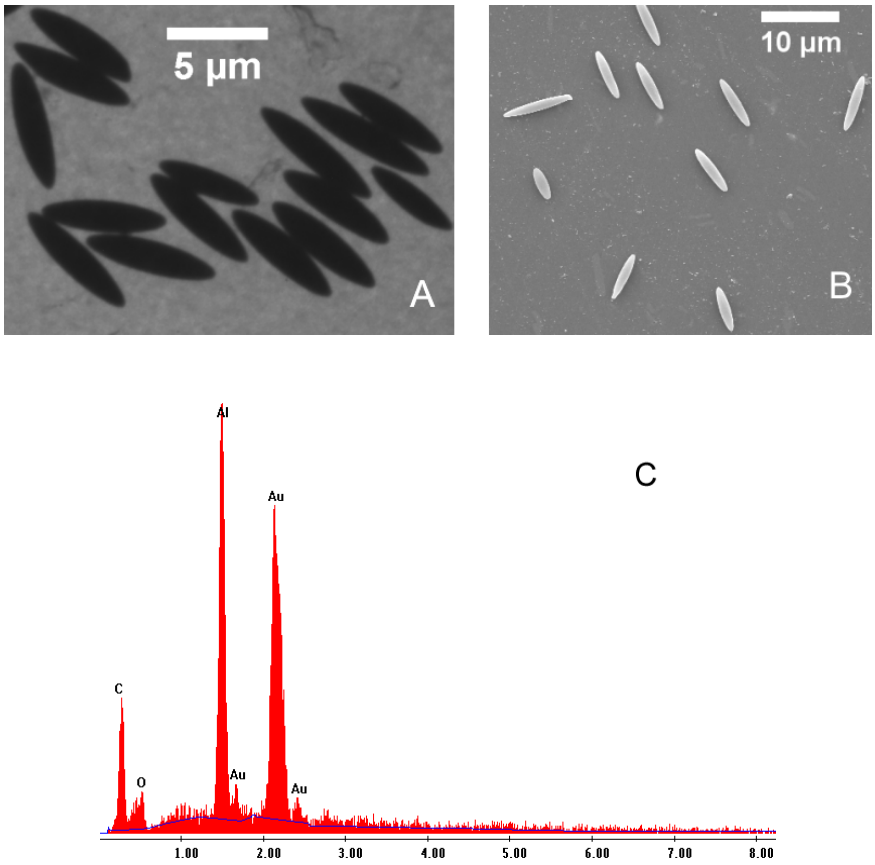



Figure S1 TEM (A) and SEM (B) characterization of PMMA ellipsoids prepared by thermo-mechanical stretching. (C) EDX by SEM.

**Monitoring the curvature-dependent wet chemical etching by negative staining TEM**

For the negative staining, aliquots of the mixture of ellipsoids and the degrading agent in hexane/IPA at varied stage were washed with hexane/IPA (4:1 v/v) by three cycles of centrifugation and redispersion. A copper grid covered with a carbon film was put on a drop of the ellipsoid suspension for 30s, and then washed three times by putting on one drop of ultrapure water (MilliQ) for 10s. Finally, the grid was put on a drop of 2% (w/v) uranyl acetate solution for 10s and then dried at room temperature. The images were recorded following the procedure described in the instrumental section. The results are shown in Fig. S2.

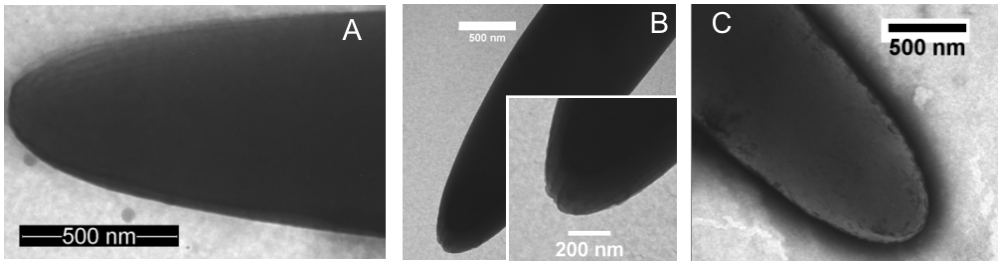



Figure S2 Surface morphology of PMMA ellipsoids at different degrading times: (A) 8hrs; (B) 12hrs; (C) >48 hrs.

**Controlling the wet chemical etching processes and preparation of fluorescently patterned ellipsoids**

The stretched films (9 g) obtained from the above stretching procedure were mixed with 198g hexane. To the mixture, various amounts of the degrading agent were added under vigorous magnetic stirring which was kept for the whole degrading procedure. Starting from the moment of adding the degrading agent, the degrading reaction was monitored at a defined interval. For this purpose, 3 mL of the degrading mixture were taken out at preset time and immediately washed three times with large amounts of hexane/IPA (4:1 v/v) and twice with decalin. During the last round of washing, the particles were resuspended in 1 mL of the fluorescent stabilizer solution (see the material section) and the readsoprtion was allowed to proceed for at least 30 min. The ratio of the fluorescent stabilizer to the particle was kept at 4:1 in weight. After this, the particles were separated from the residual fluorescent stabilizers and washed extensively with hexane and decalin before investigation with the fluorescent microscope.

The speed of the degradation procedure depends mainly on the concentration of sodium methoxide (SM) if other parameters are constant. With high concentration of SM, the PDMS film disappears quickly. However, the stabilizers on the particles were also instantaneously removed, resulting in fully naked particles. A SM concentration of 0.04% (w/w) gave the optimal results for dissolving away the films while keeping the original stabilizer on the particles during around 8 hrs. With the knowledge from these experiments, preparation at large scale was repeated for each specific degradation time, which produces ca. 1 g of patterned particles.

In Fig. S3, contaminated spheres were used as the internal control to demonstrate that there no curvature-dependent etching effect for spheres of constant curvature as revealed by a homogeneous fluorescent shell after different degrading times.

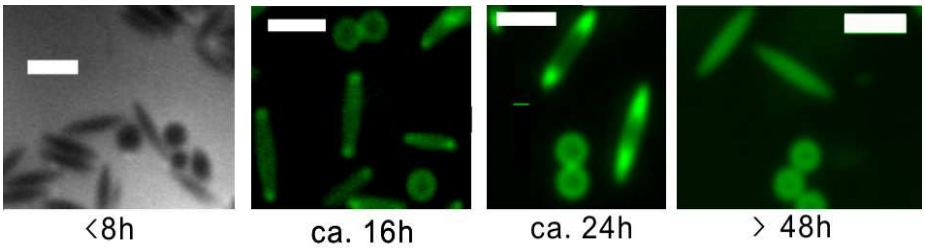



Figure S3 Fluorescent microscopy images of PMMA sphere at different stage of degradation after readsoprtion of the fluorescent stabilizers. Scale bar: 5 μm.

**Optical sectioning by the fast scanning confocal microscopy**

In order to investigate of the fluorescently patterned ellipsoidal particles by confocal microscopy, we fixed the particles in a thin layer of PDMS film. The main goal was to obtain some particles oriented vertically with their long axis to the substrate and along the *z*-direction of the scanning, in order to utilize a higher resolution of the microscope in the x-y plane. We followed the principles to prepare a film embedded with PMMA particles described as above (see the section of "Preparation of PMMA ellipsoids by thermo-mechanical stretching"). A diluted suspension of fluorescently patterned particles in hexane (20 μL) was mixed with the PDMS, crosslinker and catalyst solution. The homogeneous mixture was poured onto a cover slide and pre-cured at room temperature in dark for 24 hrs. A transparent thin film of PDMS with the particles was formed on the cover slide, with the embedded particles orienting against the substrate at different angles (Fig. S4). An example of *z*-scanning on a particle standing against the x-y plane with an angle of ca. 70 degree is shown in Fig. S4C. The slice thickness is approximately 700nm. The insets of Fig.1 in the main text were taken by focusing at the middle plane of the particles oriented parallel to the substrate (B in Fig. S4).

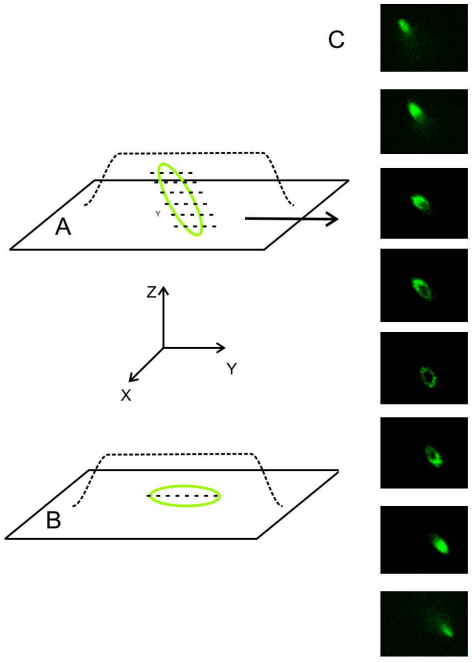



Figure S4 Trapping of fluorescently patterned ellipsoidal particles in PDMS film and the *z*-scanning by the confocal microscopy. (A) and (B): Schematics of two typical configurations of the particles in the PDMS film (not drawn to scale): with

certain angle (A) and parallel to (B) the substrate (the cover slide). (C) Typical *z*-scanning sequences by CLSM of a particle standing with an angle to the substrate.

**Self-assembly of the inverse pom-pom ellipsoids into chains in bulk**

To monitor the suspension state of the particles, the clean ellipsoids collected from different degradation stage were resuspended in decalin to form suspensions of ca. 1.68 mg/mL. Aliquots of the suspension was kept in a glass container or sealed in a flat capillary and then investigated with the microscope. The size of the bare area at the tips was estimated from readsorption with fluorescent stabilizers as discussed above. In this way, connection between the tip-tip assembly of the inverse pom-pom particles and the size of the bare area at the tips can be linked.

**Self-assembly of ellipsoids fully covered with stabilizers at the oil/air interface**

For spreading the ellipsoid particle at the oil/air interface, we used the protocol developed in ref. 4 with some modifications. When decalin was used as the oil phase, particles were resuspended in hexane and injected at the interface using a microsyringe. We waited for at least 5 mins after the initial spreading process and until there is no apparent interfacial flow. It was also found that, when the suspension of ellipsoids in decalin was directly put into a glass container, particles were trapped at the decalin-air interface and directly assemble into stripes in a side-by-side way. The structure details of the assembled stripes formed by these two methods shows no difference. We utilized this feature to investigate the fine structure of the assembly by the above fast scanning confocal microscope by placing the suspension into a cubic plastic container of hydrophobic interior walls and focusing at the interface.

## Reference


1. Antl, L.; Goodwin, J. W.; Hill, R. D.; Ottewill, R. H.; Owens, S. M.; Papworth, S.; Waters, J. A., *Colloids and Surfaces* **1986,** 17, 67-78.
2. Keville, K. M.; Franses, E. I.; Caruthers, J. M., *J. Colloid Interface Sci.* **1991,** 144, 103-126.
3. Mohraz, A.; Solomon, M. J., *Langmuir* **2005,** 21, 5298-5306.
4. Madivala, B.; Fransaer, J.; Vermant, J., *Langmuir* **2009,** 25, 2718-2728.