Supplementary Material (ESI) for Polymer Chemistry

Hybrid biological spores wrapped in a mesh composed of interpenetrating polymer nanoparticles as "patchy" Pickering stabilizers

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Supporting Information

Experimental

Kinetic experiments

AIBN (375mg) and DVB (12.5ml) were diluted to 250ml in a volumetric flask with acetonitrile. 50ml of this solution was added to a schlenk tube containing varying amounts of lycopodium (0-5g) and deoxygenated thoroughly by bubbling nitrogen through the solution. The flasks were sealed with rubber seals attached using jubilee clips and placed in a rotary oven at 70°C. An initial sample was removed for a reference at time zero. Conversion was monitored by NMR by comparison of the vinyl peaks of the monomer to an ethyl acetate tracer. 1ml of the sample mixture was removed from the reaction vessel and cooled in ice. 0.3ml of this sample was added to 0.3ml of CDCl3 and 0.05ml ethyl acetate. In order to avoid the solvent peaks the range of the NMR spectrum was limited to between 3.5 and 8ppm.

Gel trapping technique

A 2wt% solution of phytagel was made up by dissolving in water at 80oC with vigorous stirring then left to cool to 50°C with light stirring until no bubbles remained in the system. This solution was placed in a Petri dish and where required oil at 50°C was layered on top. 0.5ml of a 1wt% particle suspension in isopropanol was injected at the air-water or oil-water interface by syringe and the Petri dish was left to cool for 30 minutes at which point the gel had set. The oil layer was gently removed by pipette and replaced by a Sylgard 184 elastomer at a ratio of 9:1 PDMS:curing agent ratio, which had previously been degassed in a vacuum. The liquid PDMS was gently poured over the gel surface and left to cure for 2 days at room temperature. At this point the PDMS layer was peeled from the hydrogel surface and immersed in hot water for two minutes to remove any residual phytagel. The PDMS layer could then be imaged by electron microscopy after sputter coating a thin layer of platinum onto the surface.

Interpenetrating polymer network

To confirm the interpenetrating structural newtwork of polymer nanoparticles we used scanning electron microscopy. The images below confirm the existence of nanoparticles on the surface of the spore ridges.

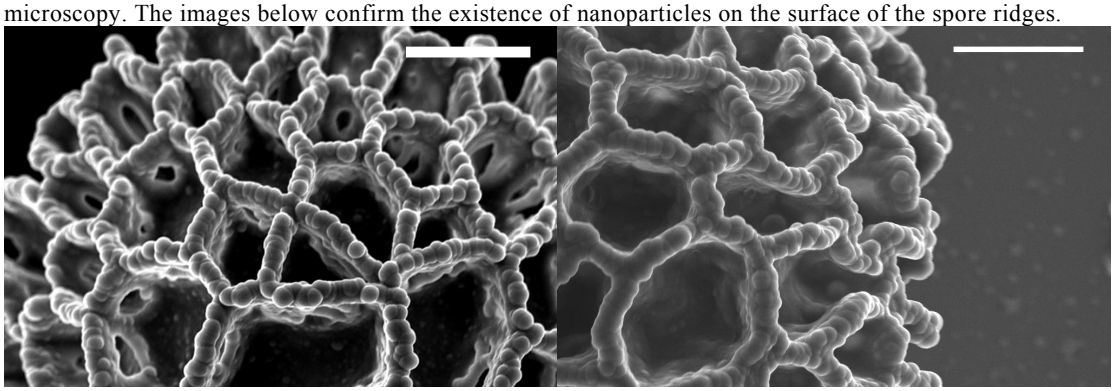

Figure S1 SEM images of lycopodium particles after polymerization at 70°C for 24h and L:M=2. The scale bar in both cases is 5μm.

Kinetic experiments results

The reaction was monitored as a function of monomer conversion. For the case of a free radical polymerization initiator decomposition is taken into account we can deduce the appropriate rate equation:

$$-\frac{d[M]}{dt} = k_p[M][R^\bullet]$$

Where k_p is the polymerization rate constant of divinylbenzene, [M] is monomer concentration and [$R^\bullet$] is the radical concentration.
The overall concentration of radicals, equated to 0 by the steady state approximation, in solution is given as the rate of production of radicals by decomposition of the thermal initiator minus the rate of consumption of radicals by termination

$$\frac{d[R^\bullet]}{dt} = 2k_d f[I] - 2k_t[R^\bullet]^2 = 0$$

Where k_d is the initiator decomposition constant, f is the initiator efficiency, [I] is the initiator concentration and k_t is the termination constant. The radical concentration is therefore given by

$$[R^\bullet] = \sqrt{\frac{k_d f[I]}{k_t}}$$

Substitution of this value back to the original rate equation gives us

$$-\frac{d[M]}{dt} = k_p[M]\sqrt{\frac{k_d f[I]}{k_t}}$$

The concentration of initiator at a given time is related to the initial concentration of initiator and the initiator decomposition rate at the reaction temperature

$$[I] = [I]_0 e^{-k_d t}$$

Where $[I]_0$ is the initiator concentration at time zero. Substituting this back into the rate equation we obtain

$$-\frac{d[M]}{dt} = k_p[M]\sqrt{\frac{k_d f[I]_0 e^{-k_d t}}{k_t}}$$

$$-\frac{d[M]}{[M]} = k_p\sqrt{\frac{k_d f[I]_0}{k_t}}\sqrt{e^{-k_d t}}\,dt$$

Integration of this equation leads to the final rate equation

$$-\ln\frac{[M]}{[M]_0} = 2k_p\sqrt{\frac{f[I]_0}{k_d k_t}}(1-\sqrt{e^{-k_d t}})$$

$$-\ln(1-X_M) = 2k_p\sqrt{\frac{f[I]_0}{k_d k_t}}(1-\sqrt{e^{-k_d t}})$$

Where X_M is the conversion of monomer expressed as a fraction.
We conducted experiments at varying values of L:M in order to determine if the spore concentration had any effect on the rate of polymerization.

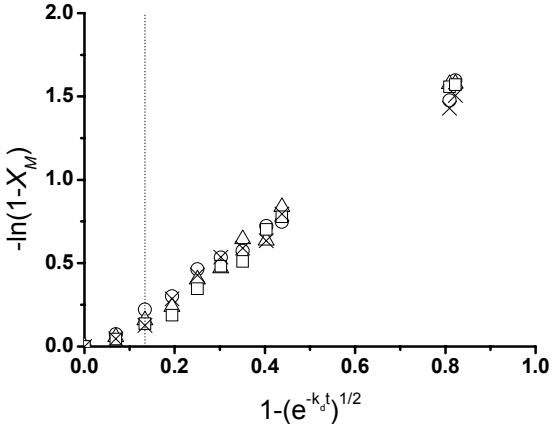

Figure S2 Rate of reaction of divinylbenzene in the presence of varying amounts of lycopodium spores monitored by NMR (no spores and L:M ratio of ∀ 0.5, 8 1, – 2). The vertical line indicates where the reaction temperature is reached.

As expected, the rate of reaction is not affected by the lycopodium content and in all cases is in good agreement with literature values[1] of $k_p/k_t^{1/2}$, determined from the gradient of the graph, which gave $k_p/k_t^{1/2}$ values of $6.0\text{-}6.5\times10^{-2}$(L/mol.s)$^{1/2}$ using an initiator efficiency of 1 compared to literature values of 4.85×10^{-2}(L/mol.s)$^{1/2}$ for *para*-DVB and 7.28×10^{-2}(L/mol.s)$^{1/2}$ for *meta*- DVB polymerized in toluene at 70°C, whereby an initiator efficiency of 1 was assumed. Note the graph in figure S2 shows an induction period when the temperature is equilibrating in the reaction vessel.

Figure S3 shows the growth of the spore ridges as a function of conversion. Approximately 50 different measurements were used from SEM images in each case to determine an approximate value for the width of the spore ridge with the adsorbed polymer particles. The error bars donate one standard deviation from the measured size. Where the spore concentration was low growth on the ridges occurred rapidly and nucleating particles were observed in SEM images. Where the spore concentration was high compared to monomer we observed no secondary nucleation and growth occurred in a controlled manner.

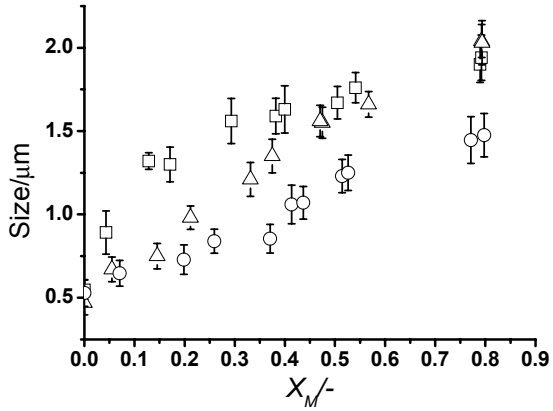

Figure S3 Growth of polymer particles on the surface of lycopodium as a function of time (L:M ratio of ∀0.5, 8 1, – 2).

[1] A. K. Nyhus, S. Hagen, A. Berge, *J. Polym. Sci. Part A-Polym. Chem.*, 1999, **37**, 3345-3359.