

Supporting Information

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S1

The longitudinal relaxation rate of a material with dissolved oxygen can be expressed as

$$\frac{1}{T_{1,measured}} = \frac{1}{T_{1,intrinsic}} + \frac{1}{T_{1,oxygen}}$$

The oxygen contribution to relaxation rate can be modeled with the following equation first proposed by Sandhu (1):

$$\frac{1}{T_{1,oxygen}} = \frac{16\pi^2}{15} \cdot \langle \mu^2 \rangle \cdot \frac{\gamma^2}{kT} \cdot N_{oxygen} \cdot \eta,$$

where μ is the net magnetic moment of oxygen, γ is the hydrogen gyromagnetic ratio, η is the solution viscosity, and k is the Boltzmann constant. Oxygen solubility is represented by N_{oxygen} , the concentration of dissolved oxygen. The equation can be rewritten as a function of oxygen partial pressure using Henry's law:

$$\frac{1}{T_{1,oxygen}} = \frac{16\pi^2}{15} \cdot \langle \mu^2 \rangle \cdot \frac{\gamma^2}{kT} \cdot \frac{\eta}{H} \cdot P_{O_2},$$

where H is Henry's law constant, the reciprocal of gas solubility. Oxygen contribution to the relaxation rate is thus greatest when oxygen solubility and viscosity are both high.

1. Sandhu H (1966) Effect of paramagnetic impurities on proton spin-lattice relaxation time in methane. *J Chem Phys* 44(6):2320.

S2

The sensitivity of 70% dodecamethylpentasiloxane (DDMPS) sensors to changes in oxygen partial pressure is estimated from the calibration curve (Fig. S2). The relaxation time was measured at different oxygen partial pressures at 37 °C. The SD of the fit residues suggests that the sensors can distinguish changes of 15 mmHg near hypoxic levels using the described pulse sequence. The calibration curves were obtained using the same pulse sequences and numbers of measurements as the in vivo measurements to ensure the best representation. Therefore, we expect the sensitivity of the in vitro and in vivo experiments to be similar. The sensitivity is limited by how accurately relaxation times can be measured, and techniques for improving SNR, such as additional averaging or increasing voxel size, will improve sensitivity.

The distance to capillary vessels would play a role in the measured oxygen partial pressure. Perfusion-related information can be obtained with dynamic contrast-enhanced MRI (for tumor studies) or magnetic resonance (MR) angiography to help put measured oxygen values in the correct context.

The minimal size of the sensor that can be reliably measured would depend on the signal-to-noise ratio (SNR) of the measurements. The SNR depends on both the static field strength of the MR scanner and the number of repetitions performed for the measurement. Thus, the size of the detectable sensor is not fundamentally limited by the measurement technique; instead, a tradeoff between scan time and spatial resolution needs to be made based on the application. Clinical MRI scanners tend to operate at the 1.5–3 T range, and typical clinical MRI scans have resolutions of roughly 1 mm × 1 mm at reasonable SNR values.

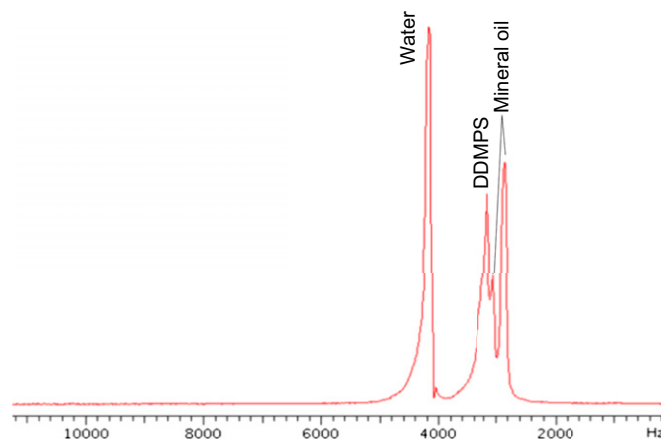


Fig. S1. Spectrum of DDMPS, DI water, and mineral oil obtained using the Varian 7-T small animal imager. The two peaks on the right belong to mineral oil, which contain several different hydrocarbons. PDMS and DDMPS both have chemical shifts of roughly 4 ppm from water, which translates to about 1.2 kHz at 7 T. Protons in all of the materials are excited by the excitation pulse, which has a bandwidth of 3 kHz.

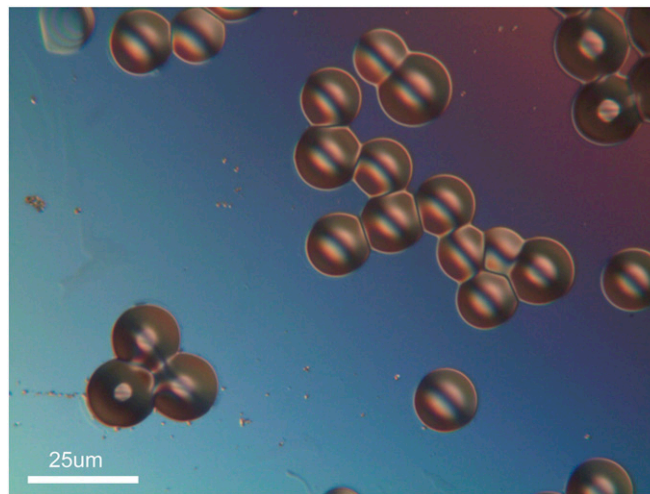


Fig. 54. An optical micrograph of 70% DDMPs microparticles shows no phase contrast within the particles. This suggests a uniform composition where DDMPs is randomly dispersed within the PDMS polymer matrix. We examined the structure of these microparticles with optical microscopy under Nomarski contrast and found that no core-shell structures were present. These imaging conditions are sensitive to gradients in index of refraction that would exist if a core-shell structure were present. The images seem to indicate that the particles are uniform. The index of refraction of DDMPs and PDMS are $n_{20/D}$ 1.392 (1) and 1.41, respectively (2). We believe the composition of these microparticles to be uniform, which can be explained by the similar chemical structure between DDMPs and PDMS.

1. O'Neil MJ (2006) *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals* (Merck, Whitehouse Station, NJ), 14th Ed.
2. Rahong S, et al. (2010) Modification of the optical properties of polydimethylsiloxane (PDMS) for photonic crystal biosensor application. *In: 2010 3rd International Nanoelectronics Conference*, Vols. 1 and 2, pp 1303–1304.