Electronic Supplementary Information

Figure 1SI. Scheme of the assembly used for performing photopolymerization experiments; in a Bohlin rheometer the lower plate was replaced by a transparent quartz window. Two Teflon white inserts (reflective rings) were employed to minimize the loss of light from the reaction chamber.

Figure 2SI. Storage ($G'$) and loss ($G''$) moduli recorded at a stress of 10 Pa and a frequency of 1 Hz for F127DA solutions in deionized water at different concentrations.
Figure 3SI. Frequency and shear stress dependence of storage (G') and loss (G'') moduli as a function of concentration for F127DA in deionized water at a temperature of 10°C. The data were obtained subjecting the samples to increasing and then decreasing frequency and stress. Left: Stress = 10 Pa. Right: frequency = 1 Hz. Please realize that G’ or G’' values below 10⁻¹ Pa are purely indicative since they are substantially out of the measurable range of the rheometer utilized.

At 25%wt. F127DA showed a rather clear gel point in the frequency sweep and a gel-like behaviour acquired at high frequency, which suggests an anti-thixotropic behaviour. The border-line nature of this sample is confirmed that in temperature scans (Figure 2SI) it showed G’>G’'' at all temperatures.
Figure 4SI. Frequency and shear stress dependence of storage ($G'$) and loss ($G''$) moduli as a function of concentration for F127DA in deionized water at a temperature of 37°C. **Left:** stress = 10 Pa. **Right:** frequency = 1 Hz. Please realize that $G'$ or $G''$ values below $10^1$ Pa are purely indicative since they are substantially out of the measurable range of the rheometer utilized.

At 5% wt. F127DA showed a stress dependent behaviour upon increasing stress, which was substantially lost in the decreasing stress sweep. The 5% wt. polymer solution does not appear to gel by the end of the temperature scan (Figure 2SI), whereas gels are recorded in the amplitude and frequency sweeps at 37°C. This can be due to either a kinetic factor, due to the shorter time spent at that temperature during the temperature scan (the samples for stress and frequency sweeps were first equilibrated for 10 minutes at 37°C, while the temperature scan is a dynamic measurement), but the influence of water evaporation in the stress sweep cannot be completely ruled out.
Figure 5SI. Frequency and shear stress dependence of storage ($G'$) and loss ($G''$) moduli for F127DA photopolymerized at a concentration of 15% wt., as a function of the temperature at photopolymerization (vertical axis) and of the temperature during the rheological measurement. Samples polymerized at 20°C ("viscous gel"→gel), 30 and 37°C (gel→gel) retained an elastic gel behaviour also when cooled at 10°C. Stress = 10 Pa in the frequency sweeps, frequency = 1 Hz in the stress sweeps.
Figure 6SI. Number (left) and volume (right) size distribution of a dispersion of Pluronic F127DA photopolymerised at a concentration of 5% wt. and at a temperature of 37°C. The intensity size distributions of the 50 mg/mL samples are reported in Figure 6, left.