

Electronic Supplementary Information

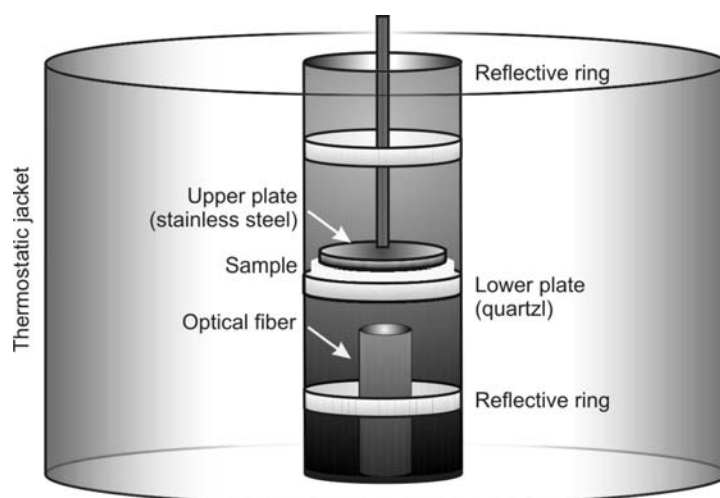


Figure 1SI. Scheme of the assembly used for performing photopolymerization experiments; in a Bohlin rheometer the lower plate was replaced by a transparent quartz window. Two Teflon white inserts (reflective rings) were employed to minimize the loss of light from the reaction chamber.

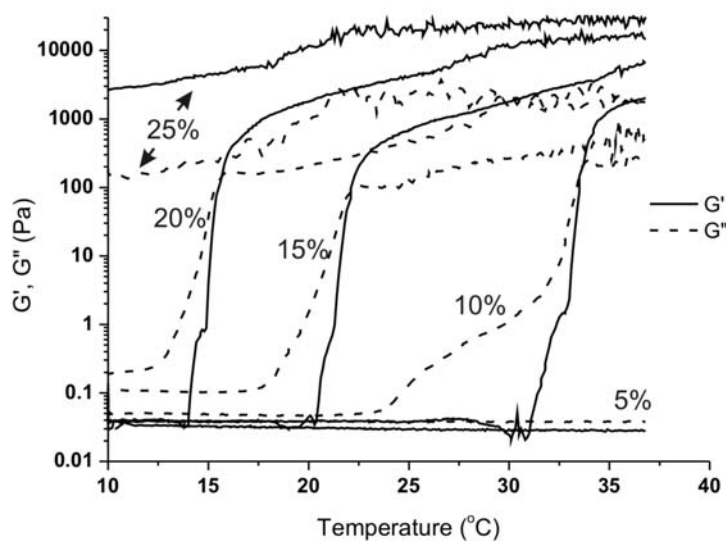


Figure 2SI. Storage (G') and loss (G'') moduli recorded at a stress of 10 Pa and a frequency of 1 Hz for F127DA solutions in deionized water at different concentrations.

F127DA at 10°C

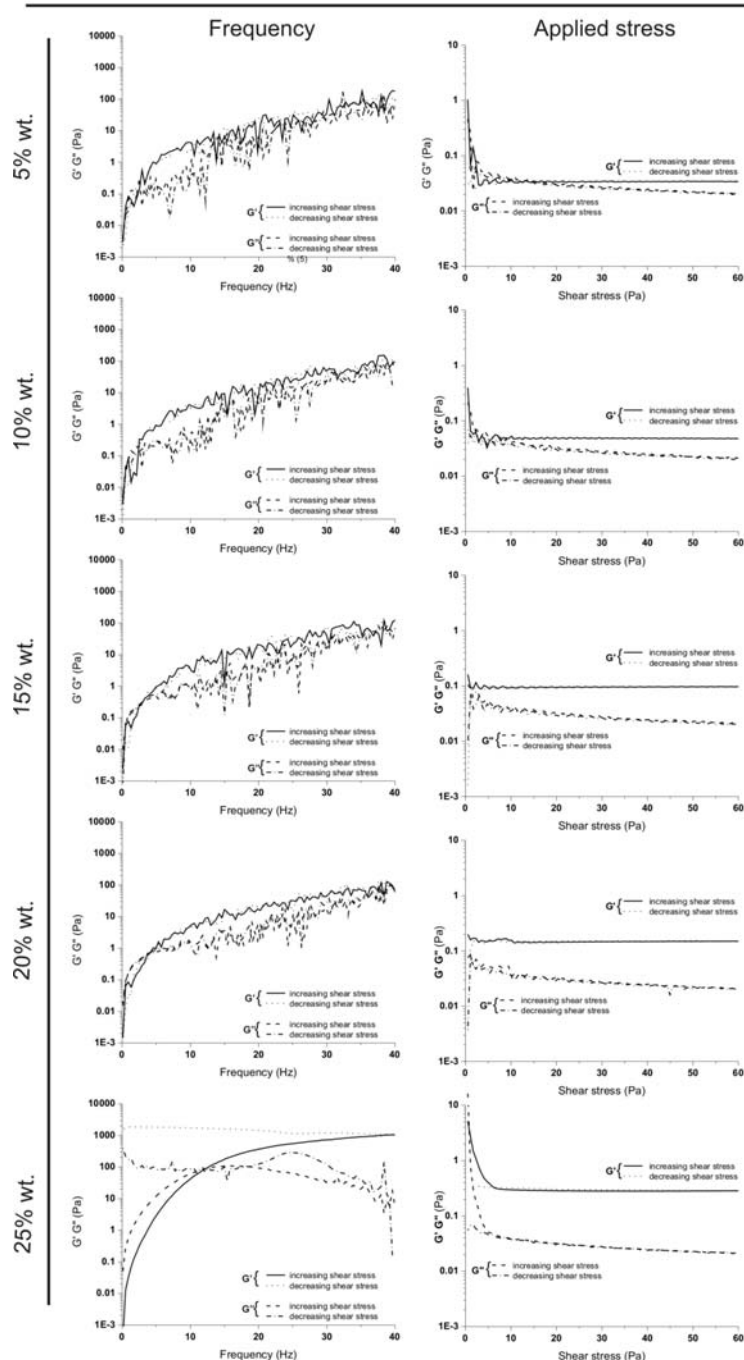


Figure 3SI. Frequency and shear stress dependence of storage (G') and loss (G'') moduli as a function of concentration for F127DA in deionized water at a temperature of 10°C. The data were obtained subjecting the samples to increasing and then decreasing frequency and stress. *Left:* Stress = 10 Pa. *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.

F127DA at 37°C

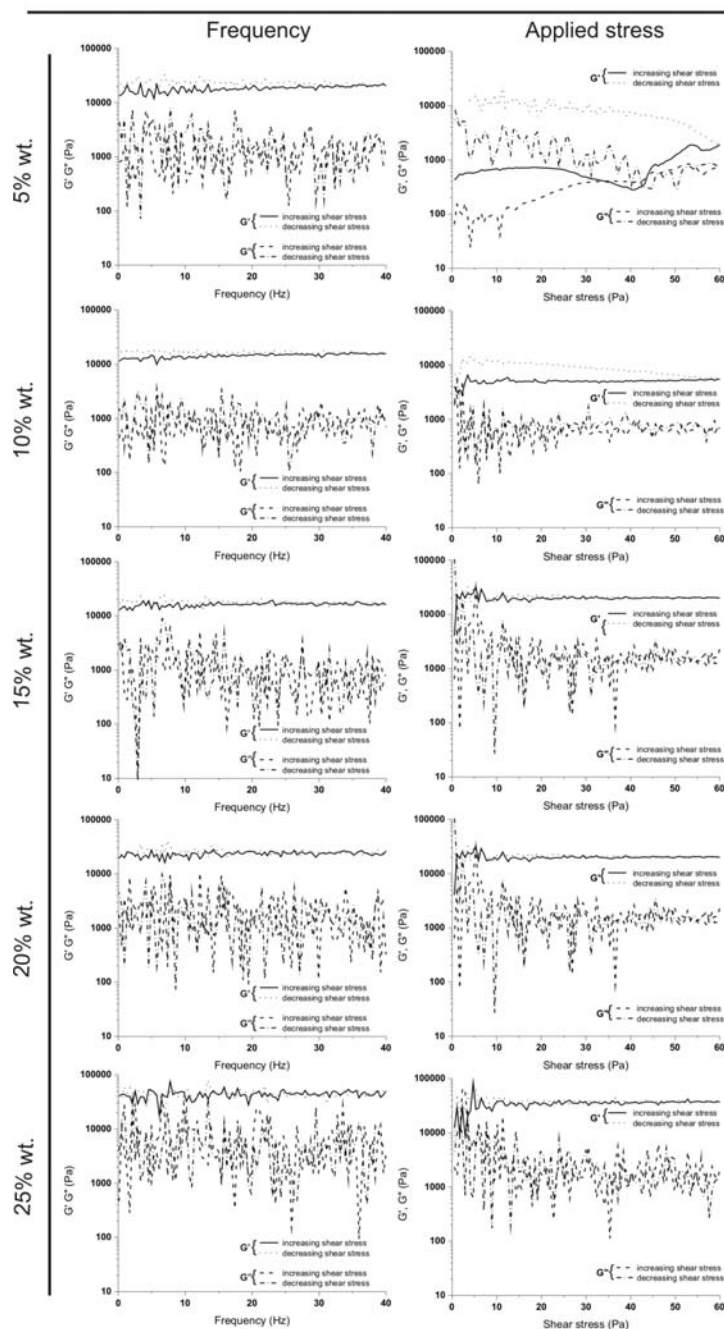


Figure 4SI. Frequency and shear stress dependence of storage (G') and loss (G'') moduli as a function of concentration for F127DA in deionized water at a temperature of 37°C. *Left:* stress = 10 Pa. *Right:* frequency = 1 Hz. Please realize that G' or G'' values below 10^{-1} Pa are purely indicative 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.

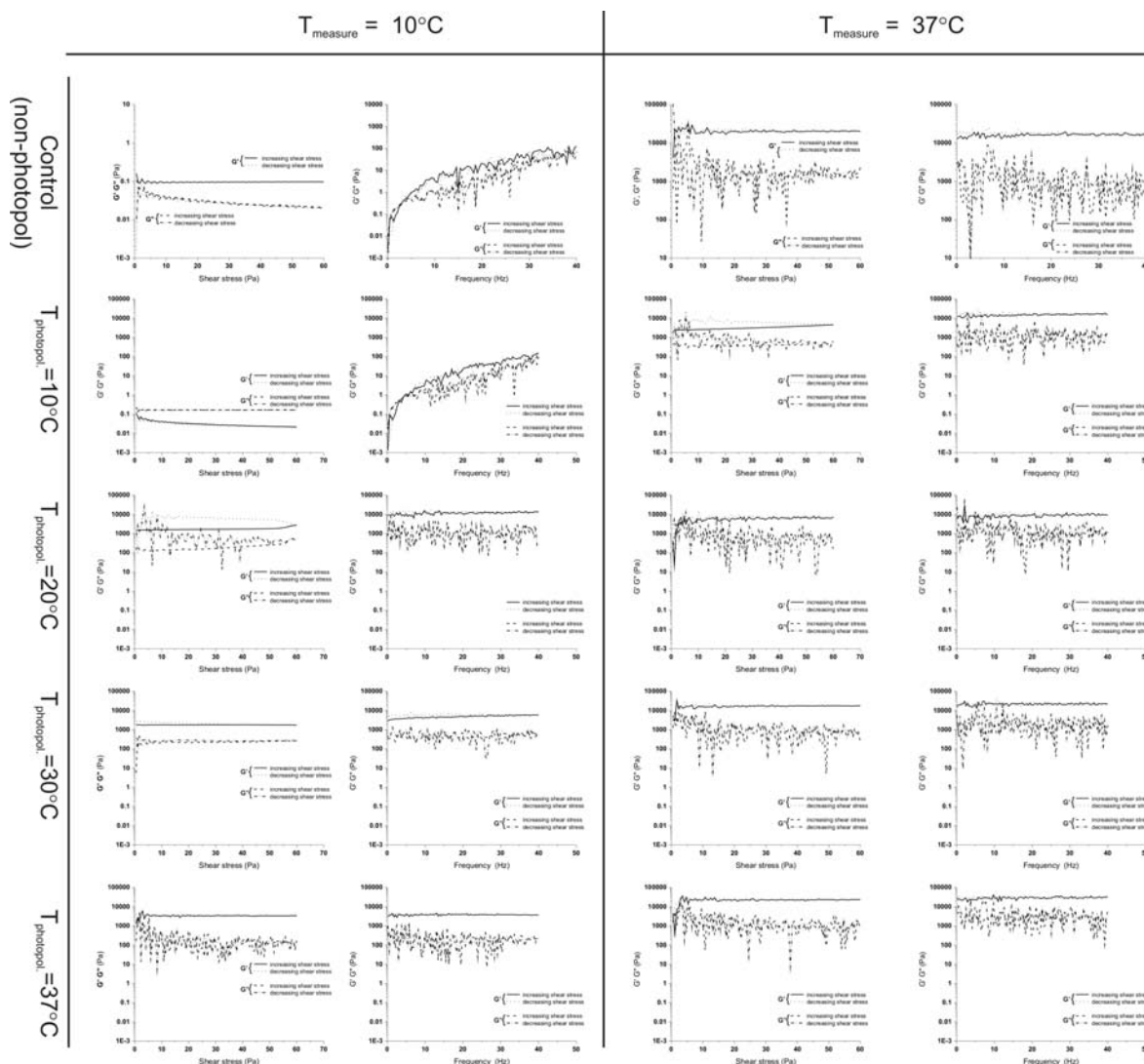


Figure 5SI. Frequency and shear stress dependence of storage (G') and loss (G'') moduli for F127DA photopolymerized at a concentration of 15% wt., as a function of the temperature at photopolymerization (vertical axis) and of the temperature during the rheological measurement. Samples polymerized at 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.

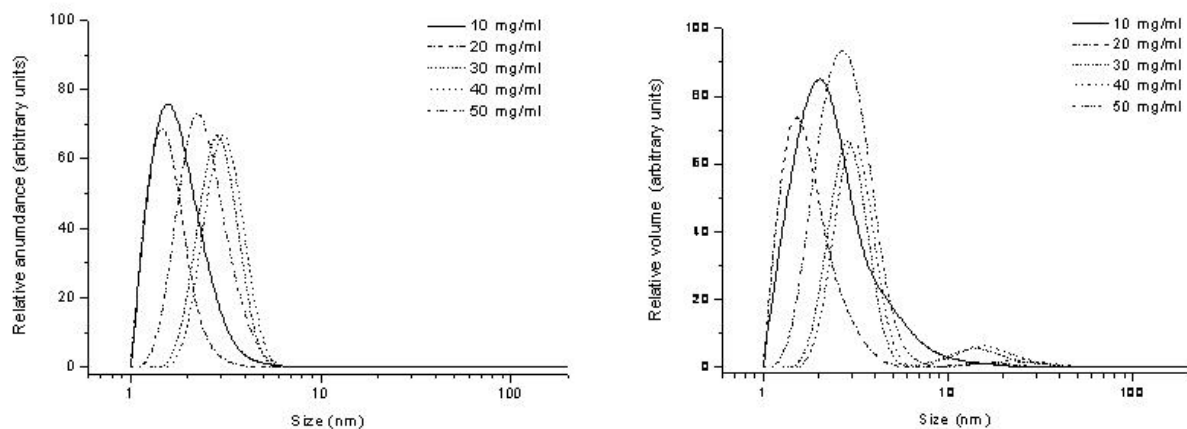


Figure 6SI. Number (left) and volume (right) size distribution of a dispersion of Pluronic F127DA photopolymerised at a concentration of 5% wt. and at a temperature of 37°C. The intensity size distributions of the 50 mg/mL samples are reported in Figure 6, left.