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Thermal Processing of Thermogelling Nanoemulsions as a Route to Tune Material Properties

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Supplementary information

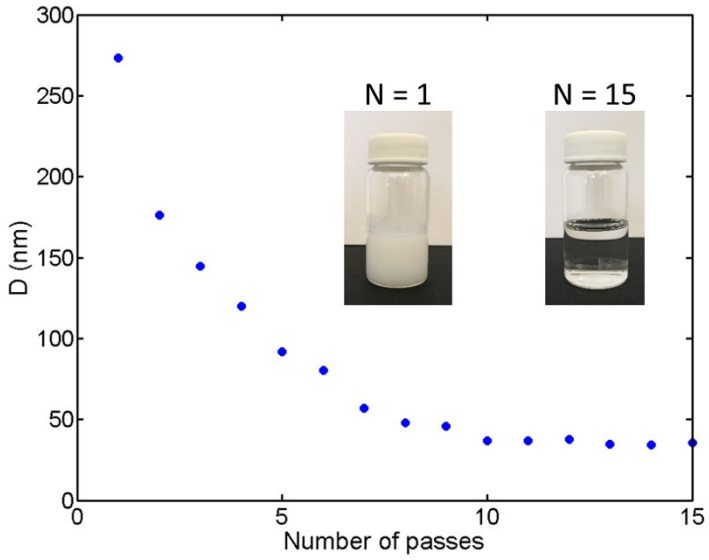

Figure S1. Oil droplet diameter (D) evolution with increasing number of pass (N) through the homogenization. Inset photos show the appearance of the emulsion with N = 1 (opaque) and N = 15 (transparent).

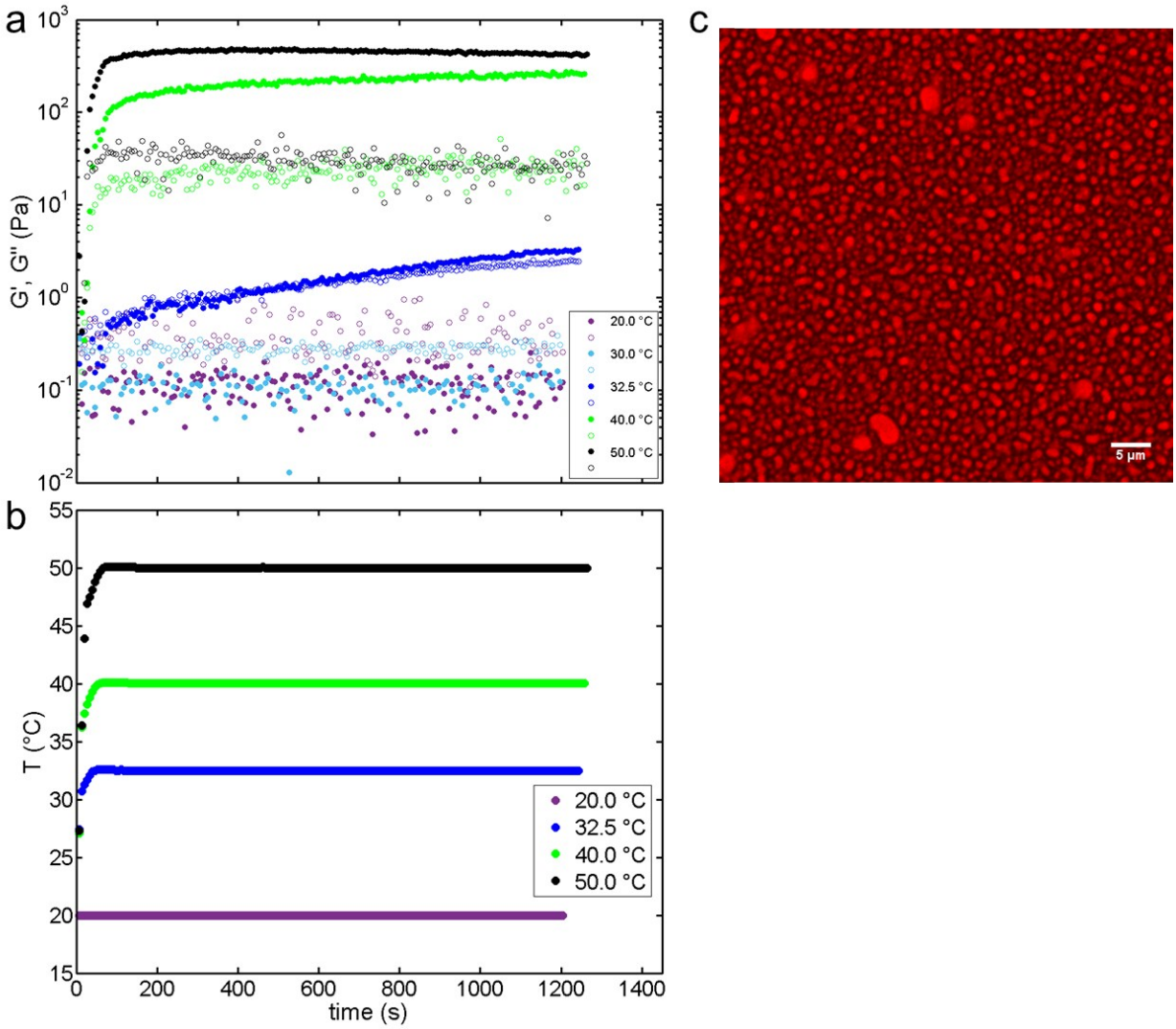

Figure S2. (a) Rheological response of the nanoemulsion with one-step temperature jump. The plot shows the measurements with initial temperature increasing from T = 20.0 ºC to the target temperature. Closed symbols denote G' and open symbols denote G". (b) Complete temperature history during the rheology measurement. (c) Confocal image of the nanoemulsion at T = 30.0 ºC. The image shows the microstructure is composed of freely-suspended clusters and the rheology at T = 30.0 °C shows liquid-like behavior without increase in viscoelasticity in (a). Therefore, we believe that the freely-suspended clusters at T = 32.5 °C (quantified as $L_{C,2}$ in this work) are not stress-bearing structures.

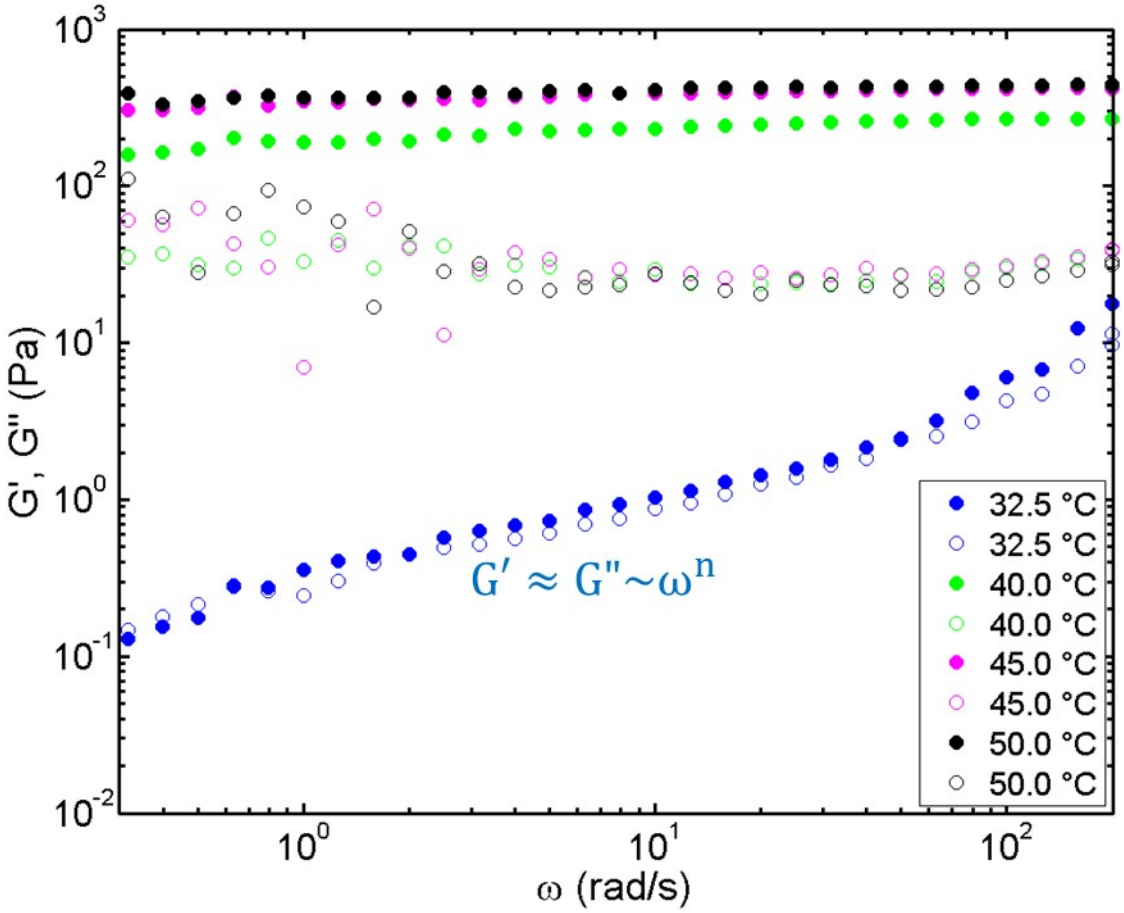

Figure S3. Frequency-sweep linear viscoelastic moduli of the nanoemulsion at various temperatures. The measurements start after T reaches the target temperature for 10 minutes. Closed symbols denote G' and open symbols denote G".

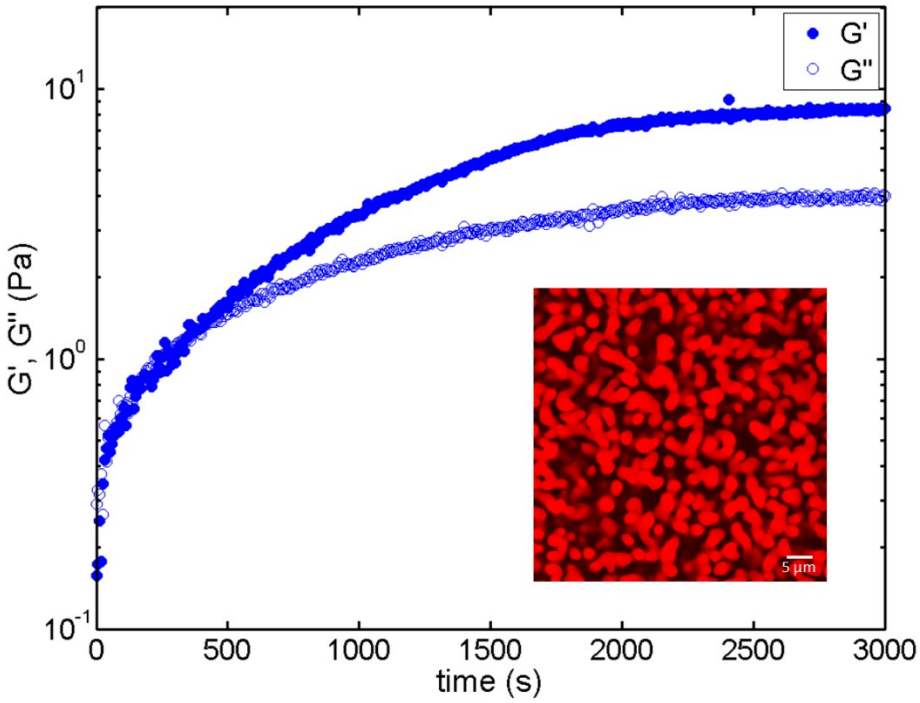

Figure S4. Time-dependent viscoelastic moduli (G' and G") of the nanoemulsion at T = 32.5 ºC. Both G' and G" become nearly constant after t = 45 min, suggesting a pseudo-steady state is achieved. The inset confocal image shows the microstructure captured at t = 50 min, where no discernible freely-suspended clusters are observed, suggesting the inclusion of every cluster in the network.

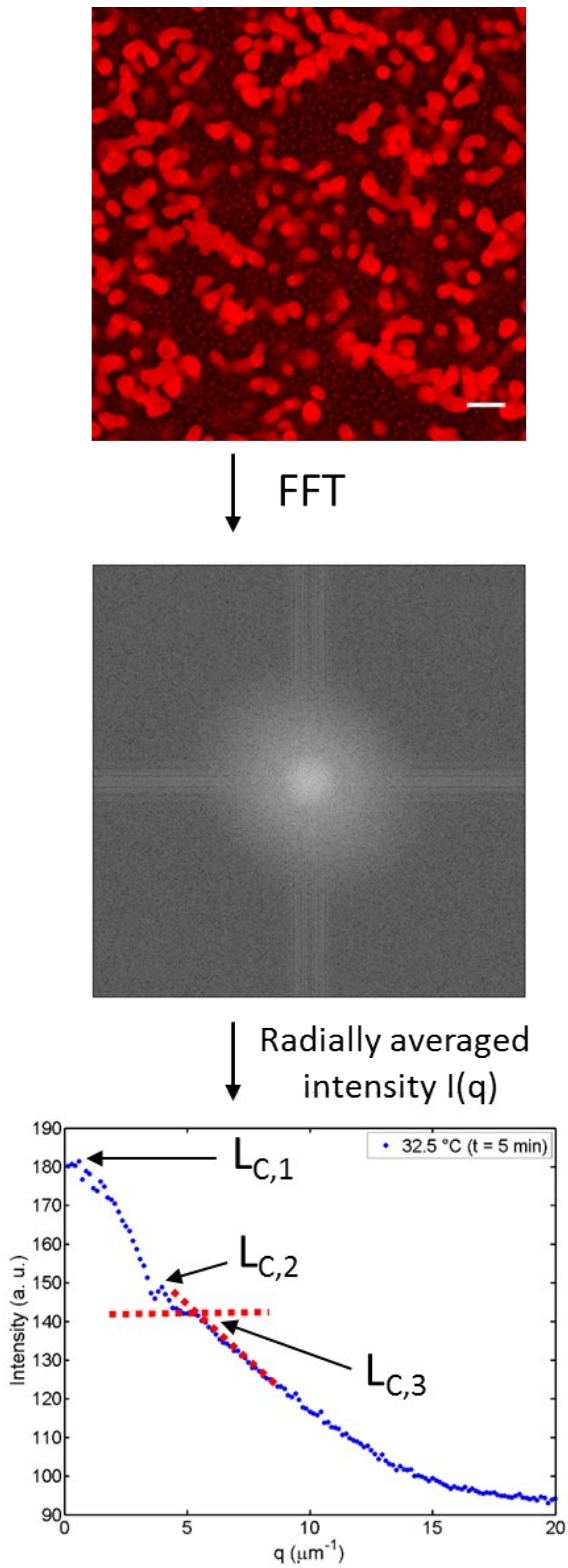

Figure S5. An example to show the procedure to determine L_C using the software ImageJ. Scale bar = 5μm. Dashed red lines are local fits to the data. The inflection point is then determined by the intersection of the fitted lines.

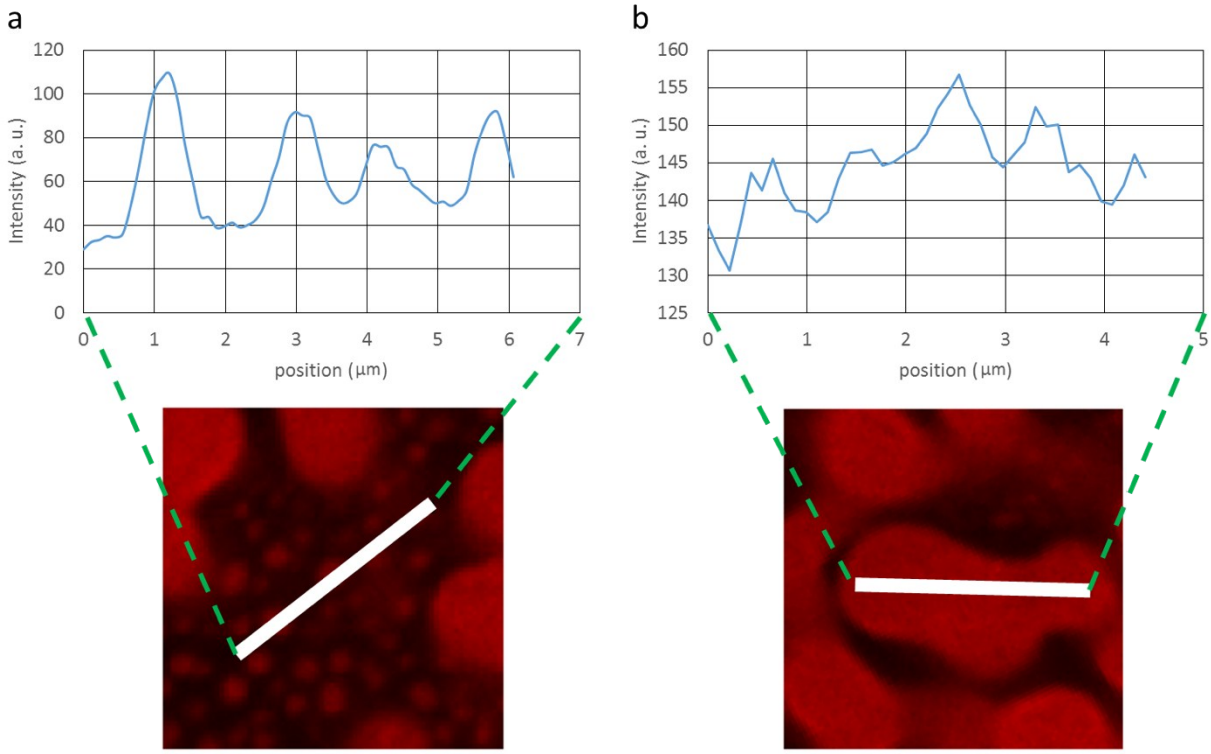

Figure S6. (a) Intensity profile of the region where only freely suspended clusters are present. (b) Intensity profile inside the droplet-rich phase for $L_{C,3}$ validation. Profiles are taken from the nanoemulsion held at T = 32.5 ºC for 20 minutes.

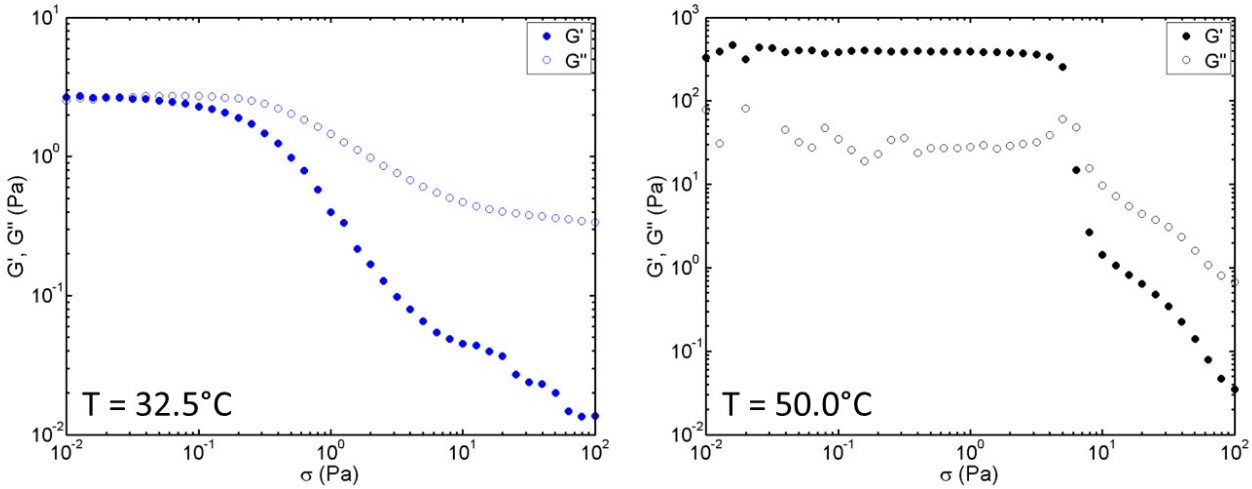

Figure S7. Large amplitude oscillatory shear rheology of viscoelastic moduli (G' and G") versus oscillatory shear stress (σ) of the nanoemulsion at T = 32.5 ºC and 50.0 ºC. At T = 50.0 ºC, the measurement shows a typical two-step yielding with a maximum in G", suggesting the gel network is of a hierarchical nature (primary: droplet-rich strands and secondary: 'building blocks' clusters, as shown in Fig. 2e). At T = 32.5 ºC, the nanoemulsion only shows a weak two-stage yielding in G", while a simple yielding is present in G", which may be because this temperature is at the critical gel point where the stress-bearing network is just established.

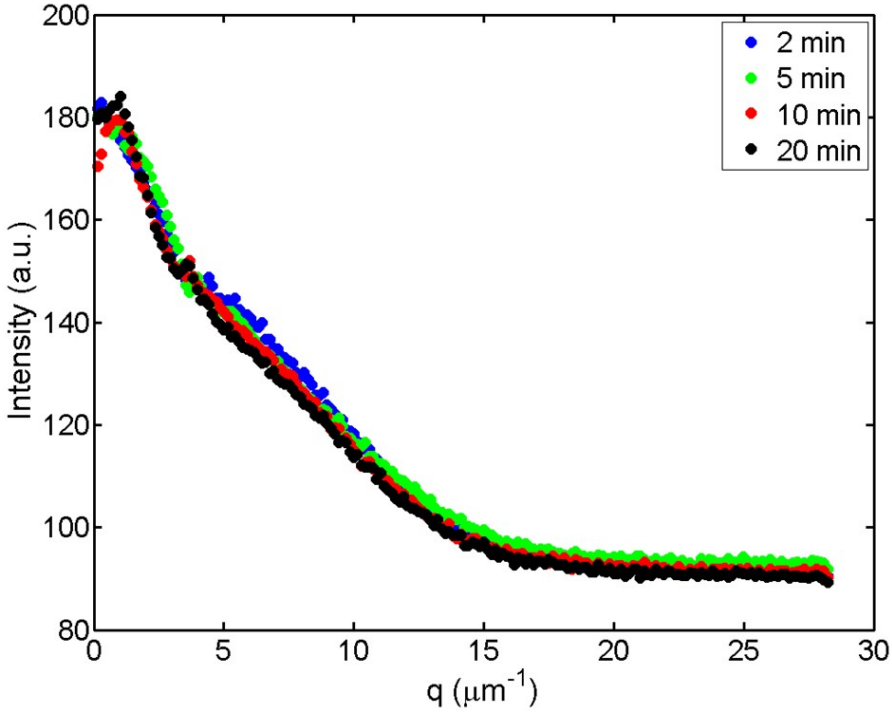

Figure S8. Scattered intensity as a function of the wave vector, q, at T = 32.5 ºC at various times. For q smaller than ≈ 2μm^{-1}, which corresponds to primary length scale ($L_{C,1}$), the intensity increases with time. This is consistent with more droplet-rich strands formed with time, as shown in Fig. 1d. For 3 μm^{-1} ≤ q ≤ 5 μm^{-1}, which corresponds to secondary correlation length ($L_{C,2}$), the intensity decreases with time. This is consistent with fewer freely suspended clusters present with time, as shown in Fig. 1d.

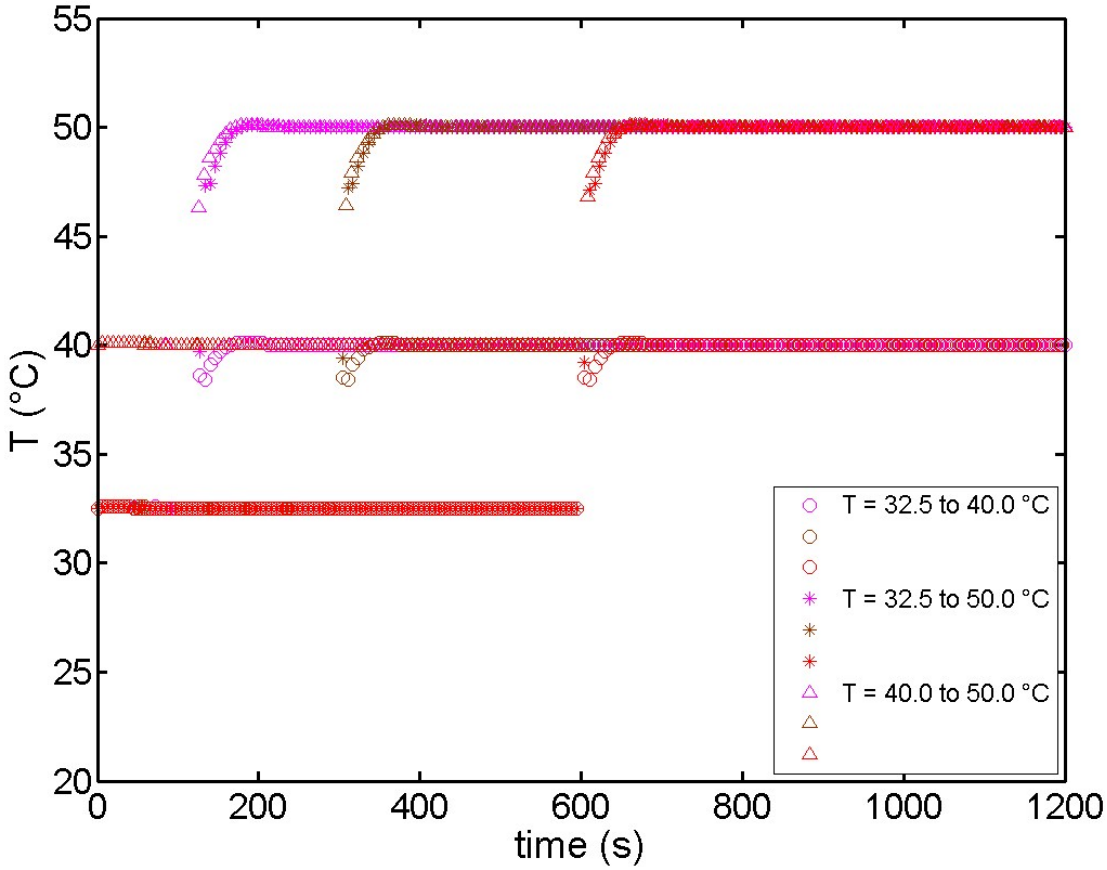

Figure S9. Complete temperature history of thermally processed samples during the rheology measurement. The shape indicates the different thermal processing route. Circle: 32.5 to 40.0 ºC. Star: 32.5 to 50.0 ºC. Triangle: 40.0 to 50.0 ºC. The color indicates the different holding time. Purple: T_{hold} = 2 min. Brown: t_{hold} = 5 min. Red: T_{hold} = 10 min.

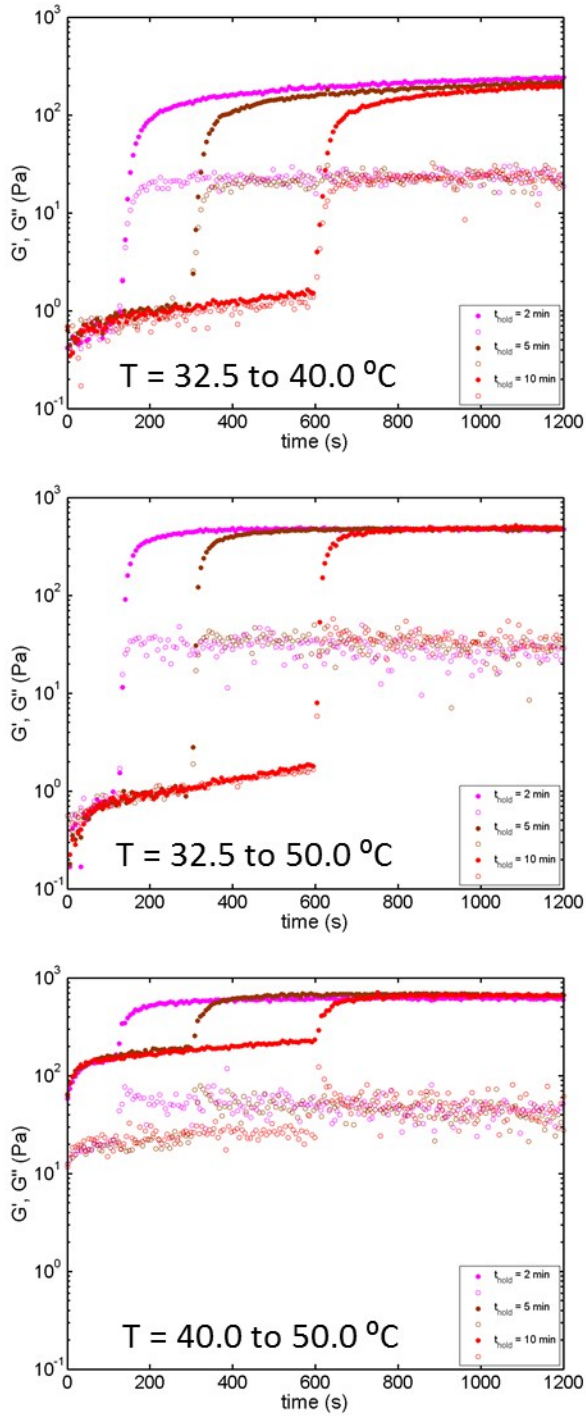

Figure S10. Temporal viscoelastic moduli, G' (closed symbols) and G" (open symbols), of the nanoemulsion undergoing two-step temperature jump.

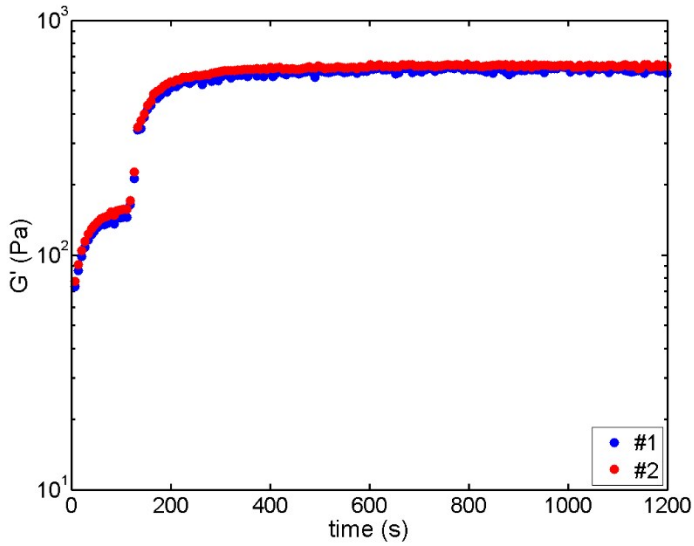

Figure S11. Rheological response of thermal processing sample (T = 40.0 to 50.0 °C, t_{hold} = 2 min) is reproducible. Freshly loaded nanoemulsion was used for each measurement.