Supporting Material

S1 Influence of the Type of Oil

Preliminary polymerisation studies revealed that polymerizing the system H_2O / NIPAm / BisAm – *n*-octane / 12-HOA – $C_{13/15}E_5$ will be much less complicated and more promising compared to the *n*-dodecane containing base system.[16] Replacing *n*-dodecane by *n*-octane does not change the general approach and can be considered as “optimization of the system” anticipating that the rheological properties are not influenced significantly. To prove – or disprove – this assumption we studied the influence of the type of oil on the viscoelastic properties of the gelled bicontinuous microemulsions. To be more precise, we gelled a microemulsion the oil of which was *n*-octane and compared our results with those obtained for the *n*-dodecane containing counterpart. Both systems were prepared at the same water-to-oil ratio of $\alpha = 0.6$, the same gelator concentration of $\beta = 0.041$ and the same monomer concentration of $\psi = 0.14$. However, different surfactant concentrations γ and experimental temperatures T were needed due to the shift of the phase diagram as will be explained below. The rheological data (left) and the phase diagrams (right) for the systems with two different oils are shown in Fig. S1 and the sample compositions are listed in Table S1.

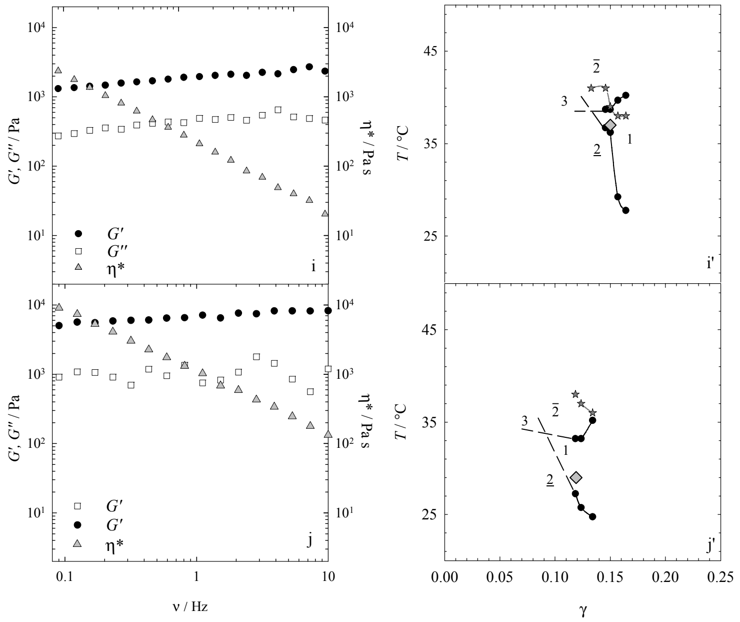

Fig. S1 Storage modulus *G*’, loss modulus *G*’’, and complex viscosity η* as a function of the frequency ν (left) and phase diagrams (right) of the system H_2O/NIPAm/BisAm – oil/12-HOA – $C_{13/15}E_5$ at $\alpha = 0.6$, $\beta = 0.041$, and $\psi = 0.14$ measured for two different oils, namely *n*-dodecane (sample i) and *n*-octane (sample j). The stars in the phase diagrams represent the sol-gel transition temperatures T_g and the diamonds the surfactant concentration γ and temperature T_{exp} of the samples used for the rheological measurements (see section 2.2.1 and Table 1).

Table S1 Compositions and phase transition temperatures of the system H_2O / NIPAm / BisAm – oil / 12-HOA – $C_{13/15}E_5$. The definitions of α, β, γ, and ψ are given in eqn 1-4. T_{min} is the lower and T_{max} the upper phase transition temperature for the given composition, $T_{\text{middle}} = (T_{\text{min}} + T_{\text{max}})/2$, and T_{exp} indicates the temperature at which the rheological measurements were carried out. The oil phase is *n*-dodecane (sample i) and *n*-octane (sample j), respectively.

Sample	α	β	γ	ψ	T_{min}	T_{max}	T_{middle}	T_{exp}
oil-variation (α = 0.6, β = 0.041, ψ = 0.14)								
i	0.60	0.041	0.150	0.140	36.21	38.70	37.46	37.0
j	0.60	0.041	0.119	0.140	27.24	33.21	30.26	29.0

A look at the phase diagrams (right) shows that replacing *n*-dodecane by *n*-octane shifts the 1-phase region, *i.e.* the region where a bicontinuous microemulsion is formed, to lower surfactant concentrations γ and temperatures *T*. This behavior is well-known and will not be discussed any further - the interested reader is referred to.[1] We like to emphasize that it is only because of the detailed phase studies that we were able to identify the concentration and temperature range of the 1-phase bicontinuous microemulsion in the *n*-octane system, which, in turn, explains why the rheological measurements of sample i and sample j had to be carried out at different γ- and *T*-values. The simultaneous shift of the sol-gel transition to lower temperatures is not only caused by the shift of the phase diagram of the microemulsion but also by the shift of the sol-gel transition of the binary system. We measured the sol-gel transition of three binary 12-HOA – oil systems and found that the sol-gel transition temperatures decrease with decreasing chain length of the oil. The results of the tabletop measurements are presented in Fig. S2.

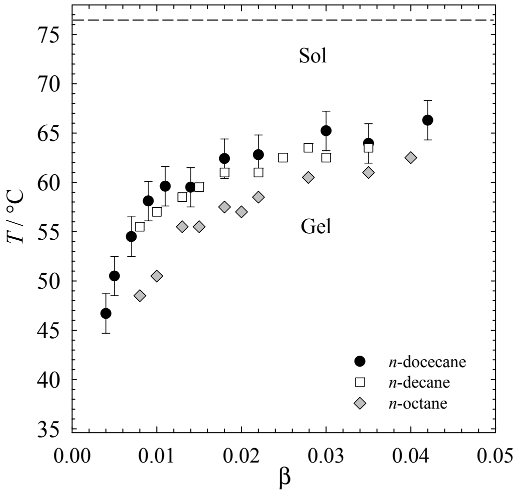

Fig. S2: Sol-gel transition temperature T_g versus gelator mass fraction β of the binary systems oil – 12-HOA for three different oils, namely *n*-dodecane (same data as in Fig.1), *n*-decane, and *n*-octane, obtained via the "tabletop" method. The horizontal dashed line represents the melting temperature of pure solid 12-HOA.

Regarding the rheological properties (left) one clearly sees that both systems exhibit a gel-like behavior. In both cases the storage modulus *G*' and the loss modulus *G*'' are frequency independent. Moreover, the *G'*:*G*'' ratio is roughly the same for both systems, namely 5:1. The absolute values of the moduli, however, are different. The *G*' and *G*'' values of the *n*-dodecane system (top) are about a factor 3 smaller than the corresponding data of the *n*-octane system (bottom). Note that the scales of the y-axes are different compared to those of Fig. 4 - 7 in the main manuscript. One reason for the formation of a stronger gel in the *n*-octane system could be the distance between the temperature at which the sample was measured and the sol-gel transition temperature. Looking at Fig. S1 (right) and Table S1 one sees that this distance is roughly 2 °C for the *n*-dodecane system, while it is around 4 °C for the *n*-octane system. In other words, the *n*-dodecane sample was closer to the sol-gel transition than the *n*-octane sample which explains the smaller *G*' and *G*'' values. Another reason for the different *G*' and *G*'' values may be the absolute temperature at which the samples were measured. Comparing the two samples one sees that that *n*-octane sample was measured at a temperature which was 8°C lower than that of the *n*-dodecane sample. A temperature study (see below, section S2) revealed that it is indeed a combination of these two points which causes the different behavior.

S2 Influence of the Temperature

The influence of the temperature on the rheological properties of gelled microemulsions consisting of H_2O / NIPAm / BisAm – oil / 12-HOA – $C_{13/15}E_5$ where the oil was *n*-octane and *n*-dodecane, respectively, was studied in more detail. For that purpose we carried out a temperature scan along the 1-phase region and measured the values *G*', *G*'' and η* as a function of the temperature at a constant frequency of 1Hz. The resulting rheological parameters are presented in Fig. S3 and the temperature ranges of the 1-phase region are listed in Table S1.

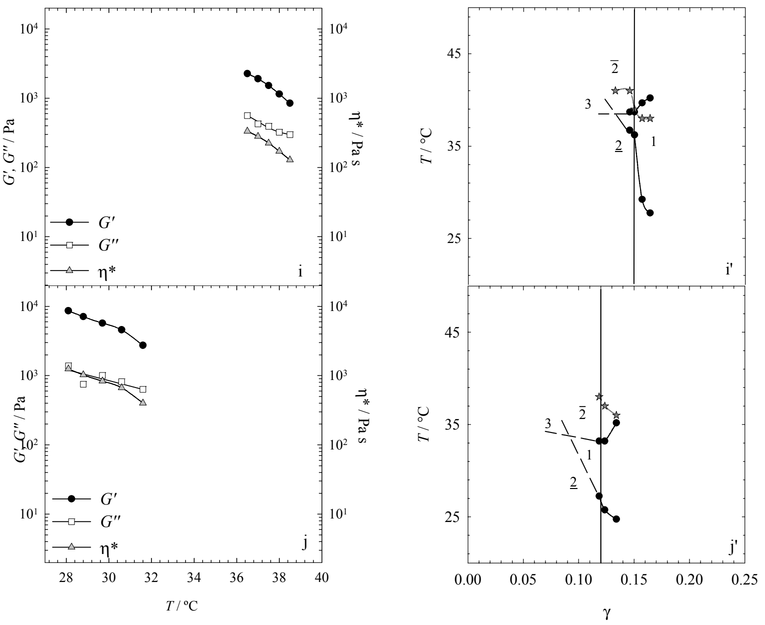

Fig. S3: Storage modulus *G*', loss modulus *G*'', and complex viscosity η* as a function of the temperature *T* obtained for 1 Hz (left) and phase diagrams (right) of the system H_2O/NIPAm/BisAm – oil/12-HOA – $C_{13/15}E_5$ at $\alpha = 0.6$, $\beta = 0.041$, and $\psi = 0.14$ measured for two different oils, namely *n*-dodecane (sample i) and *n*-octane (sample j). The stars in the phase diagrams represent the sol-gel transition temperatures T_g and the vertical lines the surfactant concentration γ of the samples used for the rheological measurements (see section 2.2.1 and Table 1). The samples were studied only between the upper and the lower phase boundary of the 1-phase region.

As can be seen in Fig. S3 a small temperature increase causes a significant decrease of all parameters for both microemulsions – note that the parameters are plotted on log-scales. Reductions up to a factor of 4-5 are obtained for a temperature increase of 3-5 ºC. The main reason for the decrease of the rheological parameters is the fact that the systems approach the sol-gel transition at which the gel network collapses. Looking at the upper end of the 1-phase regions one sees that the parameters of the *n*-octane system are still higher than those of the *n*-dodecane system. Two explanations can be given for this observation. Firstly, the absolute temperature is about 7°C lower than that of the *n*-dodecane system. Secondly, the distance between the $1 - \bar{2}$ phase boundary and the sol-gel transition is larger in the *n*-octane system, *i.e.* the system is farer away from the temperature at which a collapse of the gel is expected. In conclusion one can say that approaching the sol-gel transition decreases significantly the rheological parameters. With respect to the gelled bicontinuous microemulsions one can say that the gels are the stronger the larger the distance between the 1-phase region and the sol-gel transition boundary. Note that the thermal behavior may be important for the control of the polymerization process.