Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Oil-in-Water Microemulsion Droplets of TDMAO/Decane Interconnected by the Telechelic C_{18}-EO_{150}-C_{18} – Clustering and Network Formation

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1. Analysis of the SANS data

Table S1: Molecular formula, molecular weight, mass density and scattering length density of all the components present in the microemulsions as they were employed in analysing the SANS data.

Molecule	Strucure	M_W / gmol^{-1}	d / gml^{-1}	ρ_{SLD} / 10^{10} cm^{-2}
D_2O	D_2O	20	1.1056	6.36
Decane	$C_{10}H_{22}$	142.29	0.73	-0.49
TDMAO	$C_{16}H_{35}NO$	257.46	0.891	-0.23
Rewopal	$C_{2n}H_{4n}O_{n-1}$	6592	1.07	0.603
	$C_{18}H_{35}O_2$	283.5	0.85	-0.061

For Rewopal 6000DS the scattering contribution was divided into the PEG part and the C_{18} chain, such that the C_{18} chain was considered to be part of the aggregate and the PEG to be part of the aqueous solution, thereby modifying volume fractions and contrasts correspondingly.

<u>Calculation of cg</u>

Cg is the mass per volume concentration of droplets and stickers, assuming that all the stickers incorporate into the droplets.

$$C_g = (C_{i,TDMAO} + C_{i,decane}) * (1 - \phi_{Rewopal}) + C_{stickers}$$

$$C_g = \left(0.1\frac{mol}{l} * 247.46\frac{g}{mol} + 0.035\frac{mol}{l} * 142.29\frac{g}{mol}\right) * (1 - \phi_{Rewopal}) + C_{rewopal}\frac{g}{l} * 2 * \frac{M_W(stickers)}{M_W(rewopal)}$$

Calculation of the volume fraction

Initial TDMAO volume fraction:

$$\phi_{i,TDMAO} = 0.1\frac{mol}{l} * 257.46\frac{g}{mol} * \frac{1}{891}\frac{l}{g} = 0.0289$$

Initial decane volume fraction:

$$\phi_{i,decane} = 0.035\frac{mol}{l} * 142.29\frac{g}{mol} * \frac{1}{730}\frac{l}{g} = 0.0068$$

Rewopal volume fraction at a given Rewopal weight per cent concentration, C_{pol}

$$\phi_{Rewopal} = \frac{C_{pol}g}{100g} * \frac{d(solution)^{g}/_{ml}}{d(polymer)^{g}/_{ml}} \sim \frac{C_{pol}}{100}$$

Sticker volume fraction

$$\phi_{stickers} = \frac{C_{pol}g}{100g} * \frac{2 * 283^{g}/_{mol}}{7159^{g}/_{mol}} * \frac{\sim 1.07^{g}/_{ml}}{0.85^{g}/_{ml}}$$

Sphere volume fraction:

$$\phi = (\phi_{i,TDMAO} + \phi_{i,decane}) * (1 - \phi_{Rewopal}) + \phi_{stickers}$$

PEG volume fraction:

$$\phi_{PEG} = \frac{C_{pol}g}{100g} * \frac{6592^{g}/_{mol}}{7159^{g}/_{mol}} * \frac{\sim 1.07^{g}/_{ml}}{1.07^{g}/_{ml}}$$

Calculation of the scattering length density variation

Sphere scattering length density:

$$\rho_{sphere} = (\phi_{i,TDMAO} * \rho_{TDMAO} + \phi_{i,decane} * \rho_{decane}) * (1 - \phi_{Rewopal}) + \phi_{stickers} * \rho_{stickers}$$

Sample average scattering length density:

$$\bar{\rho}_{sample} = (\phi_{i,TDMAO} * \rho_{TDMAO} + \phi_{i,decane} * \rho_{decane}) * (1 - \phi_{Rewopal}) + \phi_{stickers} * \rho_{stickers} + \phi_{PEG} * \rho_{PEG}$$

Contrast :

$$\Delta\rho = \bar{\rho}_{sample} - \rho_{sphere}$$

Table S2. Volume fraction of the sticker, the PEG chains and the spheres and the scattering length densities for all the samples as they were used in the analysis of the SANS data.

C_{pol} / wt %	$\phi_{stickers}$	ϕ_{PEG}	ϕ_{sphere}	$\bar{\rho}_{sample}/10^{10}cm^{-2}$	$\rho_{sphere}/10^{10}cm^{-2}$	$\Delta\rho/10^{10}cm^{-2}$
0	0	0	0.0357	6.12303	-0.27733	6.40036
0.25	2.48568E-4	0.0023	0.03586	6.10878	-0.27583	6.38461
0.5	4.97135E-4	0.00461	0.03601	6.09454	-0.27434	6.36888
0.75	7.45703E-4	0.00691	0.03617	6.08029	-0.27287	6.35316
1	9.9427E-4	0.00921	0.03633	6.06604	-0.27141	6.33745
1.25	0.00124	0.01151	0.03649	6.05179	-0.26996	6.32175
1.5	0.00149	0.01382	0.03664	6.03755	-0.26853	6.30607
1.75	0.00174	0.01612	0.0368	6,0233	-0. 2671	6.2904
2	0.00199	0.01842	0.03696	6.00905	-0.26569	6.27474
2.25	0.00224	0.02072	0.03712	5.9948	-0.26429	6.2591
2.5	0.00249	0.02303	0.03727	5.98056	-0.2629	6.24346
2.75	0.00273	0.02533	0.03743	5.96631	-0.26153	6.22784
3	0.00298	0.02763	0.03759	5.95206	-0.26016	6.21223

Structure factor of the sticky hard sphere model, $S_{SHS}(q)$

The structure factor for the sticky hard sphere model according to Baxters approximative solution [1] depends on the magnitude q of the wave vector, the hard sphere radius R_{HS}, and the stickiness parameter α, according to:

$$\frac{1}{S_{SHS}(q,R_{HS},\phi_{HS},\alpha)} = 1 + \frac{24\cdot\phi_{HS}}{x^6}\cdot\Big\{C_1\cdot x^3\cdot(\sin x - x\cdot\cos x) + C_2\cdot x^2\cdot[\,2\cdot x\cdot\sin x -$$

$$\left(x^2-2\right)\cos x - 2\,] + 0.5\cdot\phi_{HS}\cdot C_1\cdot\Big[\left(4\cdot x^3 - 24\cdot x\right)\sin x - \left(x^4 - 12\cdot x^2 + 24\right)\cos x + 24\Big]\Big\} -$$

$$2\cdot{\phi_{HS}}^2\cdot\lambda^2\cdot(1-\cos x)/x^2 + 2\cdot\phi_{HS}\cdot\lambda\cdot\sin x/x$$

with:

$$C_1 = \frac{(1+2\cdot\phi_{HS}-\mu)^2}{(1-\phi_{HS})^4}$$

$$C_2 = -\frac{3\cdot\phi_{HS}\cdot(2+\phi_{HS})^2 - \cdot 2\cdot\mu\cdot\left(1+7\cdot\phi_{HS}+{\phi_{HS}}^2\right) + \mu^2\cdot(2+\phi_{HS})}{2\cdot(1-\phi_{HS})^4}$$

$$\mu = \lambda\cdot\phi_{HS}\cdot(1-\phi_{HS})$$

$$\lambda = \frac{6}{\phi_{HS}}\cdot\left(\varepsilon - \sqrt{\varepsilon^2-\gamma}\right)$$

$$\varepsilon = \alpha + \frac{\phi_{HS}}{1-\phi_{HS}}$$

$$\gamma = \phi_{HS}\cdot\frac{1+\phi_{HS}/2}{3\cdot(1-\phi_{HS})^2}$$

$$x = q\cdot 2\cdot R_{HS}$$

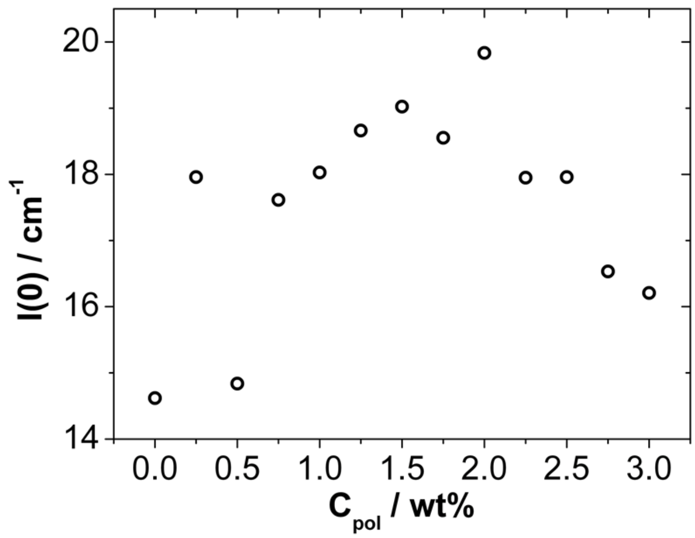

Figure S1: Intensity extrapolated to zero scattering angle for SANS (I(0)).

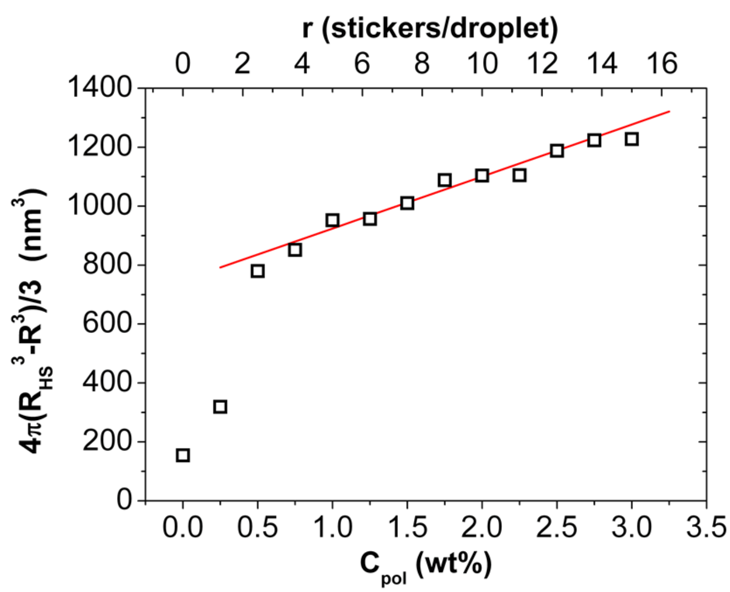

Figure S2: Hard sphere volume minus the nominal particle volume, which is the volume of the interactions shell.

2. Rheology and dynamic properties.

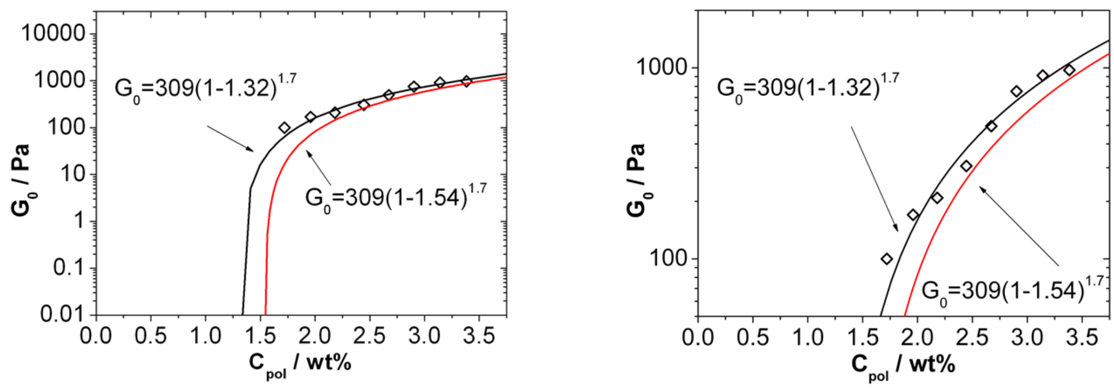

Figure S3: Shear modulus G_0 at 25 °C of the mixtures of microemulsions as a function of the concentration of C_{18}-EO_{150}-C_{18} (Rewopal 6000DS) measured with the instrument AR-G2. Solid lines: scaling laws with a scaling exponent of 1.7 but different critical concentrations of 1.32 or 1.54 wt% Rewopal 6000DS.

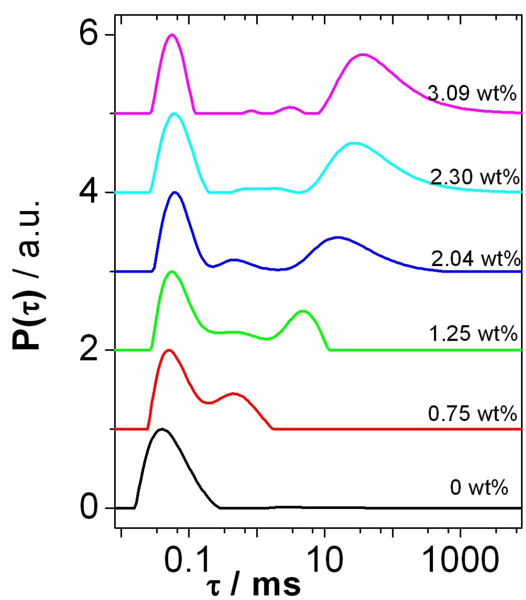

Figure S4: Intensity weighted decay time distributions of microemulsion with C_{18}-EO_{150}-C_{18} determined by dynamic light scattering (measured at 90°) for polymer concentrations of 0, 0.75, 1.25, 2.04, 2.30 and 3.09 wt%.

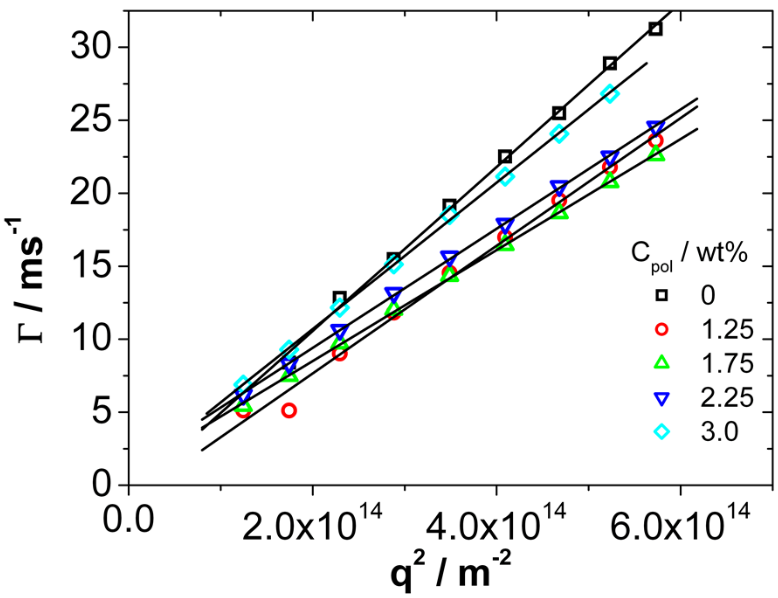

Figure S5: q-dependence of the relaxation rate of the fast mode for different polymer concentrations, that demonstrates diffusive behavior.

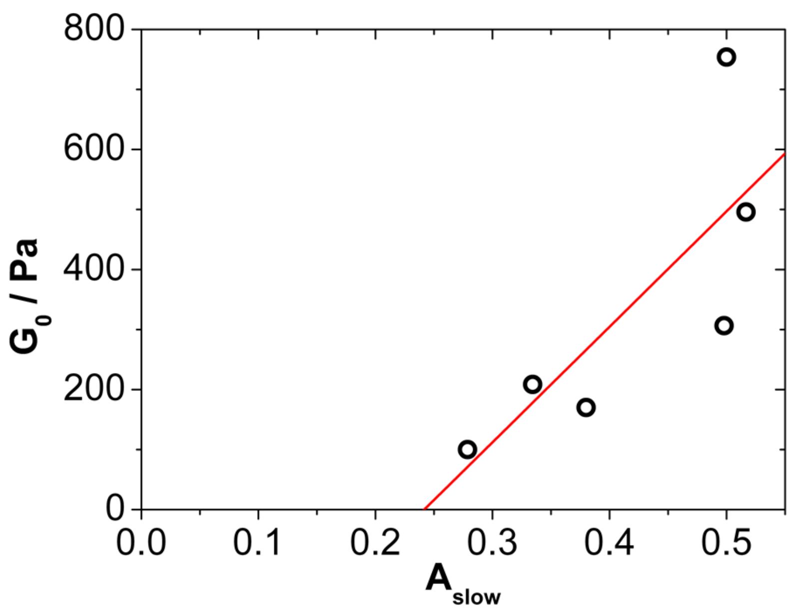

Figure S6: Relation between the shear modulus G_0 and the amplitude A_{slow} of the slow DLS relaxation mode.

Table S2: FCS fit parameters for microemulsion/ HM-polymer obtained by fitting the FSC autocorrelation functions with Eq. 6. Concentration of C_{18}-EO_{150}-C_{18} c_{pol}, diffusion time τ_D, anomalous diffusion exponent γ and self-diffusion coefficient D_s.

C_{pol} /wt%	τ_D /ms	γ	D_s /$10^{-11} m^2 s^{-1}$
0	0.15	0.99	8.99
0.25	0.2	0.94	6.74
0.49	0.28	0.99	4.81
0.74	0.42	0.97	3.21
0.99	0.67	0.98	2.01
1.22	1.44	0.96	0.94
1.47	1.38	0.88	0.98
1.96	3.41	0.83	0.40
2.18	4.34	0.8	0.31
2.41	3.2	0.74	0.42
2.64	2.69	0.74	0.50
2.87	3.98	0.8	0.34
3.1	3.12	0.64	0.35
3.33	3.81	0.7	0.43

References

[1] R. J. Baxter, J. Chem. Phys. 49, 2770-2774 (1968); Percus–Yevick Equation for Hard Spheres with Surface Adhesion