Supporting information

NMR spectroscopy

Poloxamer 407 macromonomers were dissolved in deuterated chloroform and their 1H NMR spectra recorded on a Varian 400 MHz NMR spectrometer. From the resulting spectra, shown in figure S1, oligomerization of α-hydroxy acids and conversion of hydroxyl to methacrylate were quantified by comparing oligoester and methacrylate proton peaks to PEG and PPG peaks. The integral at 4.29 ppm was assigned a value of 4, corresponding to the 4 protons at the terminal esters of each chain. The number of caprolactone monomers, lactide dimers and glycolide dimers per polymer chain was subsequently calculated according to (1), (2) and (3), respectively. Equation (4) was used to calculate conversion of hydroxyl moieties to methacrylates. In each equation, I_x denotes the value of integral I at a ppm value of x.

$$P_{CL} = \frac{I_{1.22-1.85}}{10} \tag{1}$$

$$P_{LA} = \frac{I_{1.57} + 3 \cdot I_{5.15}}{24} \tag{2}$$

$$P_{LG} = \frac{I_{4.7}}{4} \tag{3}$$

$$DM = \frac{I_{1.96} + 3 \cdot I_{5.57} + 3 \cdot I_{6.13}}{18} \tag{4}$$

Degrees of polymerization observed for the chain-extended poloxamers were found to be less than 2 repeating units per polymer chain end for P-CL-MA and P-LA-MA. For P-LG-MA up to 2 repeating units were present per polymer chain end as shown in table S1. More than 91% conversion of hydroxyl end groups to methacrylates was observed for all the four different macromers.

Table S1. List of the 4 different macromers, the type of lactone and their corresponding feed ratios.

Name	Lactone	Feed[a]	Block Length[a]	Feed MA[b]	Conversion[c]
P-MA	-	-	-	4	95%
P-CL-MA	ϵ-caprolactone	1	0.73	4	Full
P-LA-MA	D,L-lactide	2	0.71	4	Full
P-LG-MA	L-lactide	2	0.75	4	91%
	Glycolide	2	1.34	4	91%

[a] Lactone feed ratios and calculated average block lengths are given in mole repeat units per mole hydroxyl groups on P-407.
[b] Methacrylic anhydride (MA) feed ratio is given as mole MA per mole hydroxyl groups on P-407.
[c] Conversion is shown as the percentage of hydroxyl groups converted to methacrylates.

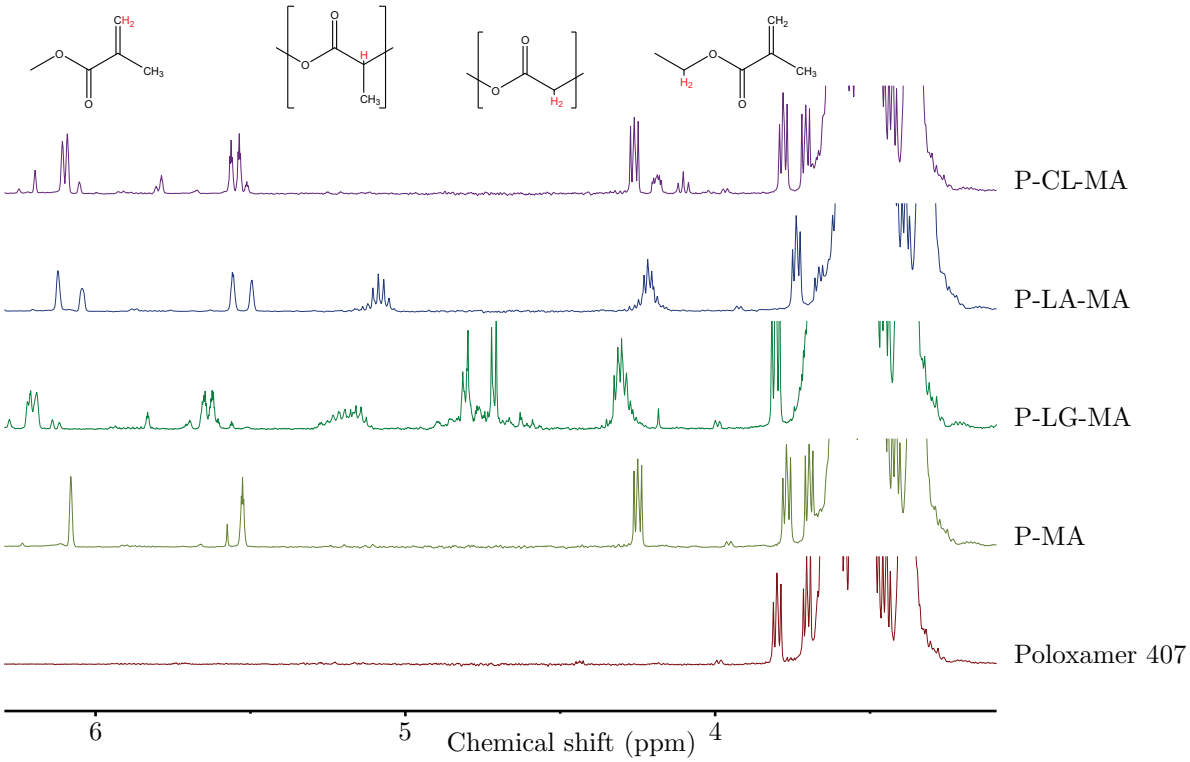

Figure S1. NMR spectra of the modified poloxamer macromonomers, compared to the NMR spectrum of unmodified poloxamer 407. Structural formulas are shown with protons in red over the range in the spectra where their peaks can be found. From left to right: protons from the vinyl group of methacrylate (5.5 and 6.0 ppm), single proton of lactyl (5.1 ppm), two protons of glycolyl (4.8 ppm) and protons adjacent to the terminal esters (4.3 ppm).

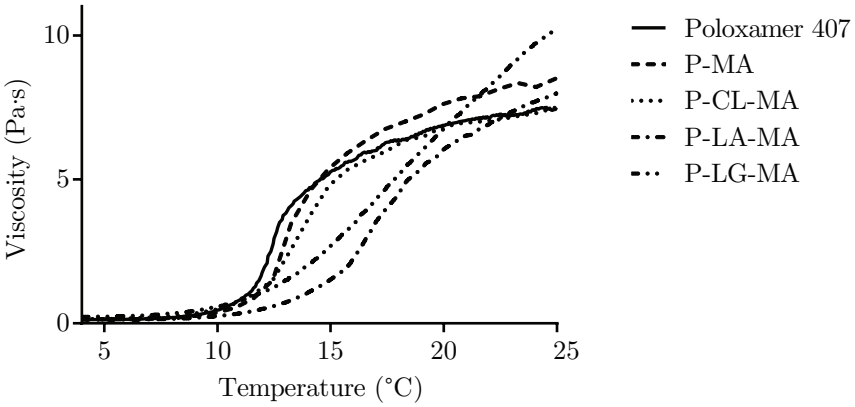

Figure S2. Viscosity measured as a function of increasing temperature from 4 to 25 °C for 28.6% gels based on modified and unmodified poloxamer. The applied shear rate was 100 s^{-1}