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Impact of Swelling on Macroscopic and Nanoscopic Mechanical Properties of Amphiphilic Polymer Co-Networks in Non-Selective and Selective Solvents

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Supporting Information

Impact of Swelling on Macroscopic and Nanoscopic Mechanical Properties of Amphiphilic Polymer Co-Networks in Non-Selective and Selective Solvents

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2.2. Swelling properties

2.2.1. Non-selective solvent

Table S1: Equilibrium swelling degrees of PEG-PCL and PEG-PEG networks in toluene prepared at different concentrations and temperatures.

c (g·L ⁻¹)	PEG-PCL		PEG-PEG	
	T (°C) ¹	Q_1 ²	T (°C) ¹	Q_1 ²
70	25	17.8 ± 0.6	25	13.4 ± 0.7
	60	16.0 ± 0.1		
140	25	12.8 ± 0.1		
	60	12.5 ± 0.2		
210	25	10.6 ± 0.5	25	8.3 ± 0.2
	60	10.1 ± 0.3		
280	25	9.3 ± 0.2		
	60	9.3 ± 0.1		
350	25	8.7 ± 0.5	25	6.7 ± 0.2
	60	8.4 ± 0.3		

¹ Synthesis temperature

² First swelling directly after synthesis without drying.

2.2.2. Effect of Drying

Table S2: Equilibrium swelling degrees of PEG-PCL networks in toluene before (Q_1) and after drying (Q_2). The drying was performed at room temperature for five days, if not stated otherwise.

c (g·L ⁻¹)	T (°C) ¹	Q_1	Q_2
70	25	17.58	9.60 ²
	25	18.62	15.90
	60	16.00	15.40
210	25	10.94	10.93
	60	10.16	9.96
350	25	7.94	7.61
	60	8.40	8.21

¹ Synthesis temperature.

² Drying was performed at 60 °C.

2.2.3. Selective solvent

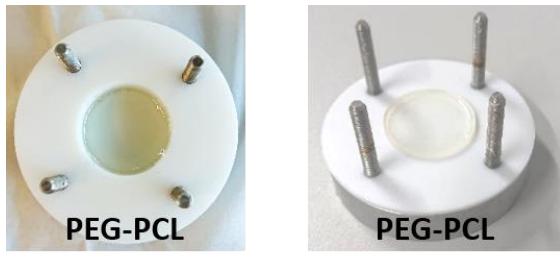


Figure S1: Pictures of PEG-PCL networks after preparation in toluene. This method of gelation in teflon molds was used for the rheology setup to obtain gels with the correct geometry. The gels were then swollen to equilibrium in excess toluene.

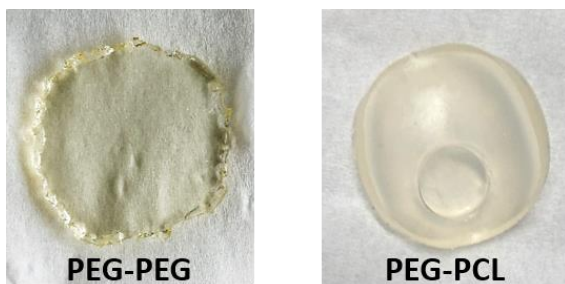


Figure S2: Pictures of a PEG-PEG network and a PEG-PCL network swollen in water. The transparent appearance of the PEG-PEG networks is due to the good solvent quality of water for PEG. In contrast, water is not a good solvent for PCL, resulting in contraction of PCL domains and a cloudy appearance.

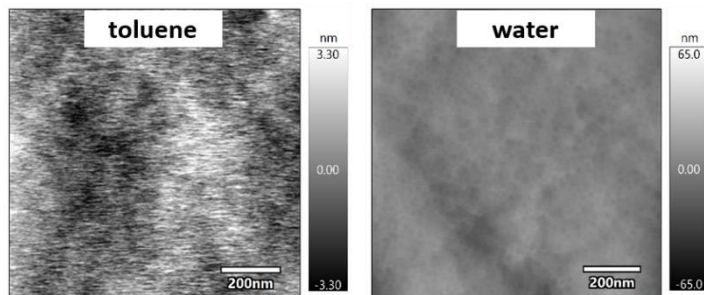


Figure S3: Height images measured with AFM in tapping mode of PEG-PCL networks swollen in either toluene or water. Whereas the gels show smooth surfaces in toluene without any noticeable structures, they show a rather rough surfaces in water. Further structural information is hidden in the surface roughness, but can be visualized via phase imaging.

Table S3: Equilibrium swelling degrees of PEG-PCL and PEG-PEG networks in water prepared at different concentrations and temperatures. The networks were prepared in toluene, dried at room temperature for five days and reswollen in water.

c (g·L ⁻¹)	PEG-PCL		PEG-PEG	
	T (°C) ¹	Q_2	T (°C) ¹	Q_2
70	25	3.0 ± 0.2	25	14.5 ± 0.3
	60	3.2 ± 0.1		
140	25	2.99 ± 0.08		
	60	2.9 ± 0.2		
210	25	2.9 ± 0.1	25	11.0 ± 0.2
	60	3.1 ± 0.1		
280	25	2.98 ± 0.04		
	60	3.0 ± 0.1		
350	25	2.7 ± 0.1	25	8.9 ± 0.2
	60	2.8 ± 0.1		

¹ Synthesis temperature

2.3. Mechanical Properties

2.3.2. Non-selective solvent

Table S4: Storage modulus of PEG-PCL networks swollen in toluene (non-dried) converted with a Poisson's ratio of $\mu = 0.25$ and $\mu = 0.5$ from AFM measurements with tip (radius ≈ 8 nm) and colloidal probe (CP33: $3.3 \mu\text{m}$) as well as storage modulus directly from rheological measurements. The error of the converted modulus corresponds to the percentage error of the original data.

c ($\text{g} \cdot \text{L}^{-1}$)	G'_1 (kPa)					
	$\mu = 0.25$		$\mu = 0.5$		rheometry	
	tip	CP33	tip	CP33	25 °C	60 °C
70	11 ± 4	10 ± 2	9 ± 3	8 ± 1	6.3 ± 0.2	6.5 ± 0.1
140	29 ± 5	18 ± 4	25 ± 4	15 ± 3	13.91 ± 0.09	15.3 ± 0.2
210	37 ± 20	25 ± 7	31 ± 16	20 ± 6	22 ± 2	23.3 ± 0.2
280	52 ± 24	30 ± 9	43 ± 20	25 ± 7	34 ± 1	34.9 ± 0.3
350	95 ± 17	42 ± 9	79 ± 14	35 ± 7	46.2 ± 0.2	47 ± 1

Table S5: Comparison of experimentally found and theoretically calculated elastically effective network strands, ν_{exp} and ν_{theo} , based on the AFM measurements for PEG-PCL networks in toluene using a tip and colloidal probes.

c ($\text{g} \cdot \text{L}^{-1}$)	ν_{theo} ($\text{mmol} \cdot \text{L}^{-1}$)	tip		CP33	
		ν_{exp} ($\text{mmol} \cdot \text{L}^{-1}$)	$\nu_{\text{exp}}/\nu_{\text{theo}}$	ν_{exp} ($\text{mmol} \cdot \text{L}^{-1}$)	$\nu_{\text{exp}}/\nu_{\text{theo}}$
70	12.2	7.4	0.6	6.6	0.5
140	18.0	19.8	1.1	12.3	0.7
210	22.9	24.9	1.1	16.5	0.7
280	27.4	34.8	1.3	19.9	0.7
350	30.8	64.1	2.1	28.6	0.9

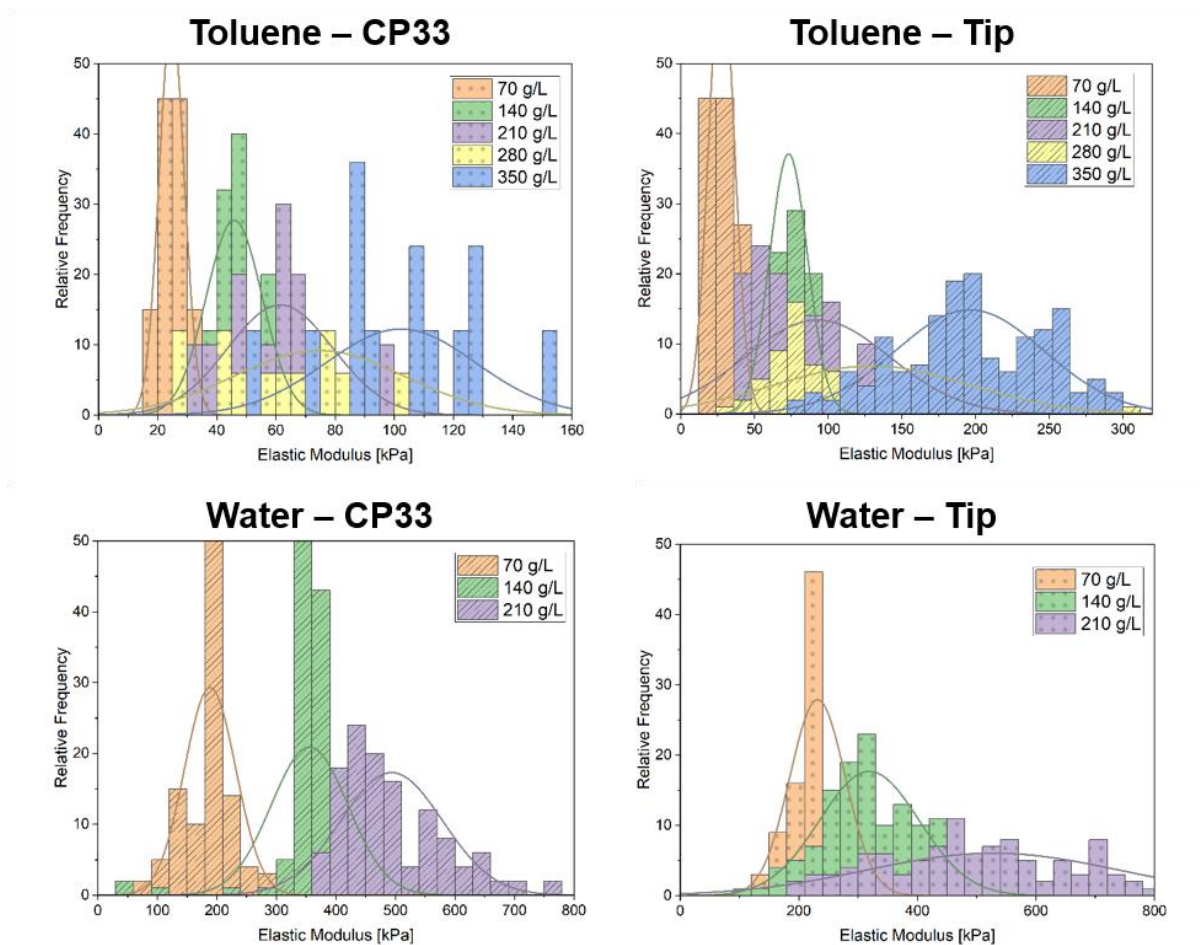


Figure S4: Elastic moduli of PEG-PCL networks swollen in toluene and water obtained from AFM measurements with colloidal probe (CP33: radius 3.3 μm) or tip (radius \approx 8 nm). Elastic moduli are higher for gels that have been synthesized at higher network concentrations. Both tip and colloidal probe measurements demonstrate wider distributions of obtained moduli with increasing network concentrations. Gel networks swollen in water are stiffer than in toluene.