

Electronic Supplementary Information

“Mixed-mode interpenetrating polymer networks from polymerizable eutectics”

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NMR characterization of bis(carbonate) crosslinker

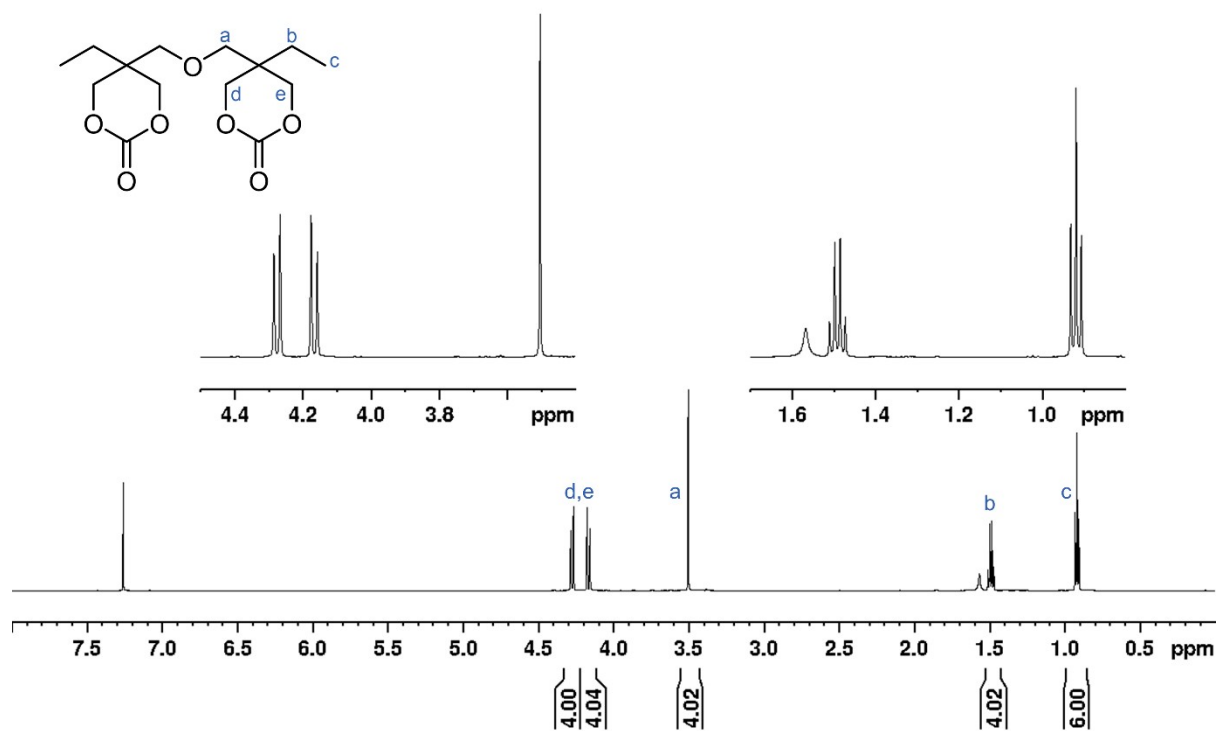


Figure S1. ¹H NMR spectrum of purified bis(carbonate) crosslinker in CDCl₃ with insets showing the regions from 4.5-3.4 ppm and 1.7-0.8 ppm.

Characterization of polymerizable eutectics

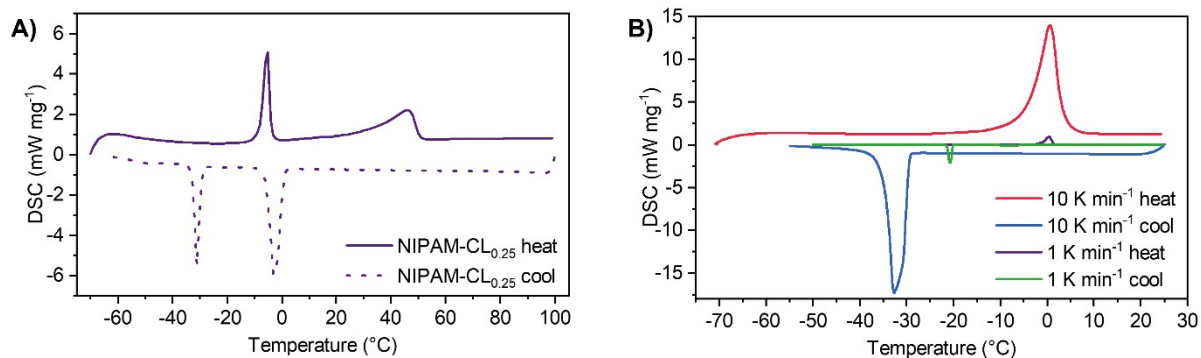


Figure S2. A) DSC thermogram of NIPAM-CL_{0.25} displaying multiple melt and freeze transitions. B) Comparison of heating and cooling rates for pure CL with clear freezing point hysteresis.

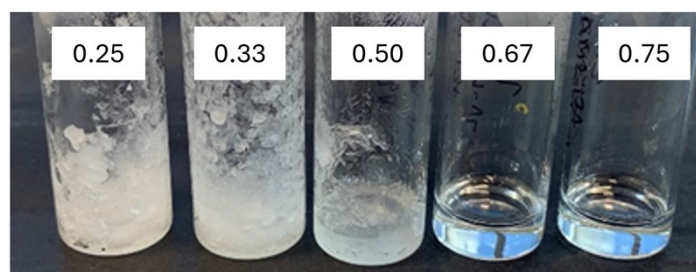


Figure S3. Photo of NIPAM-VL eutectic mixtures with x_{VL} indicated for each vial.

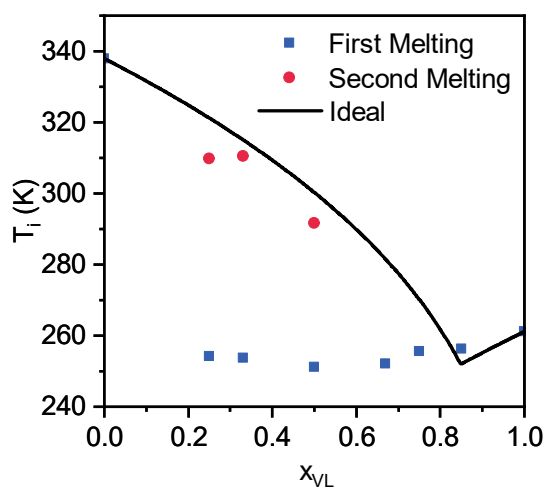


Figure S4. NIPAM-VL phase diagram showing experimental onset melting temperatures, in addition to ideal melting point curve (calculated using Equation 1, main manuscript).

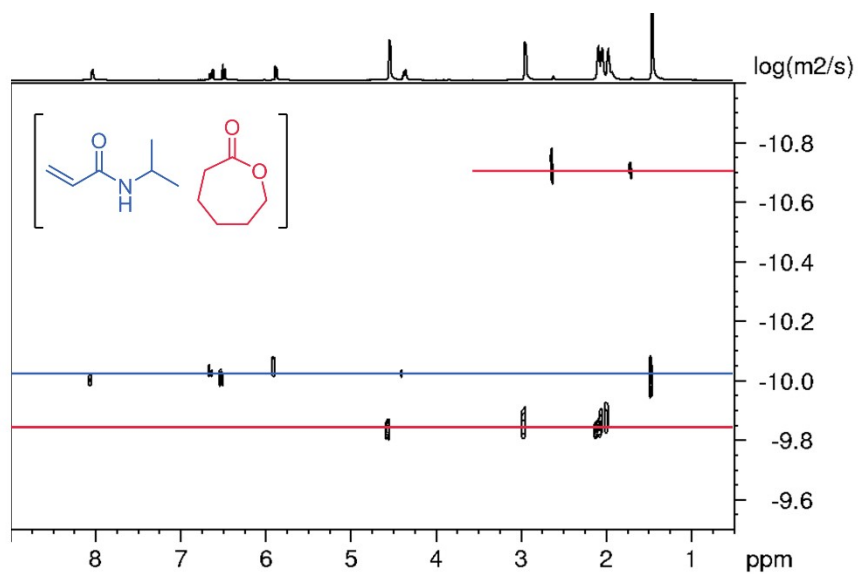


Figure S5. NIPAM-CL_{0.67} neat 2D DOSY NMR spectrum with approximate diffusion coefficients indicated for NIPAM (blue) and CL (red). PCL is sometimes observed in the mixture prior to the addition of ROP catalysts, as seen by the appearance of resonances with self-diffusion coefficients $\sim 10^{-10.7} \text{ m}^2 \text{ s}^{-1}$

Characterization of linear polymers

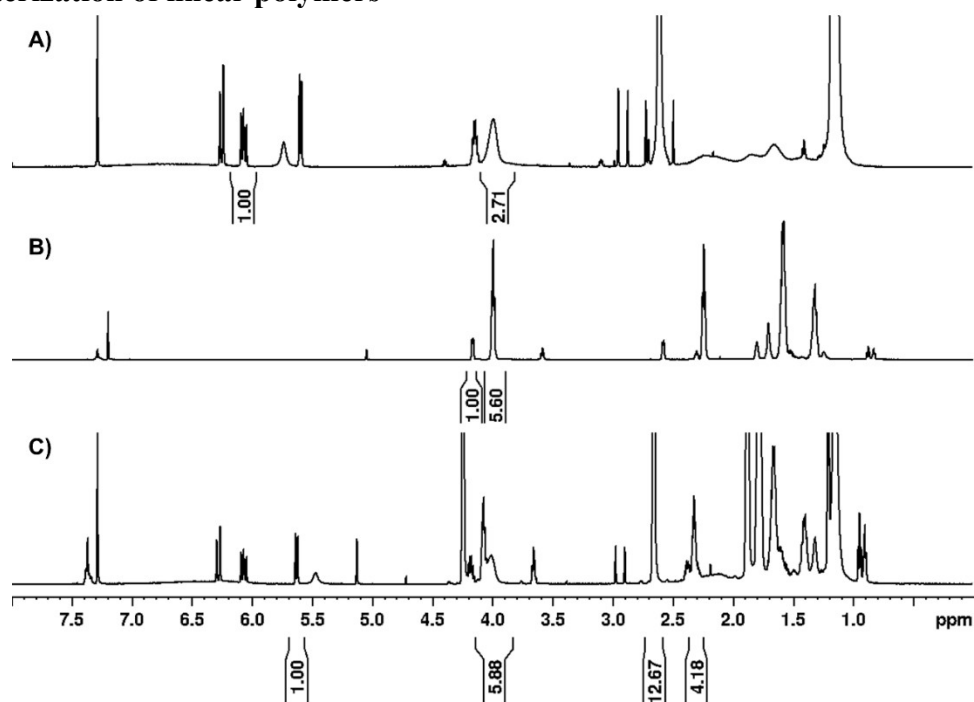


Figure S6. Example ^1H NMR spectra showing integration regions used to calculate the conversion of A) NIPAM homopolymer (NIPAM-DMSO TPO/UV 2 mins), B) CL homopolymer (CL neat, TEHA 3.75 hrs heat) C) NIPAM & CL blend (sequential NIPAM, CL R1 TPO/TEHA 5 mins UV + 5 hrs heat).

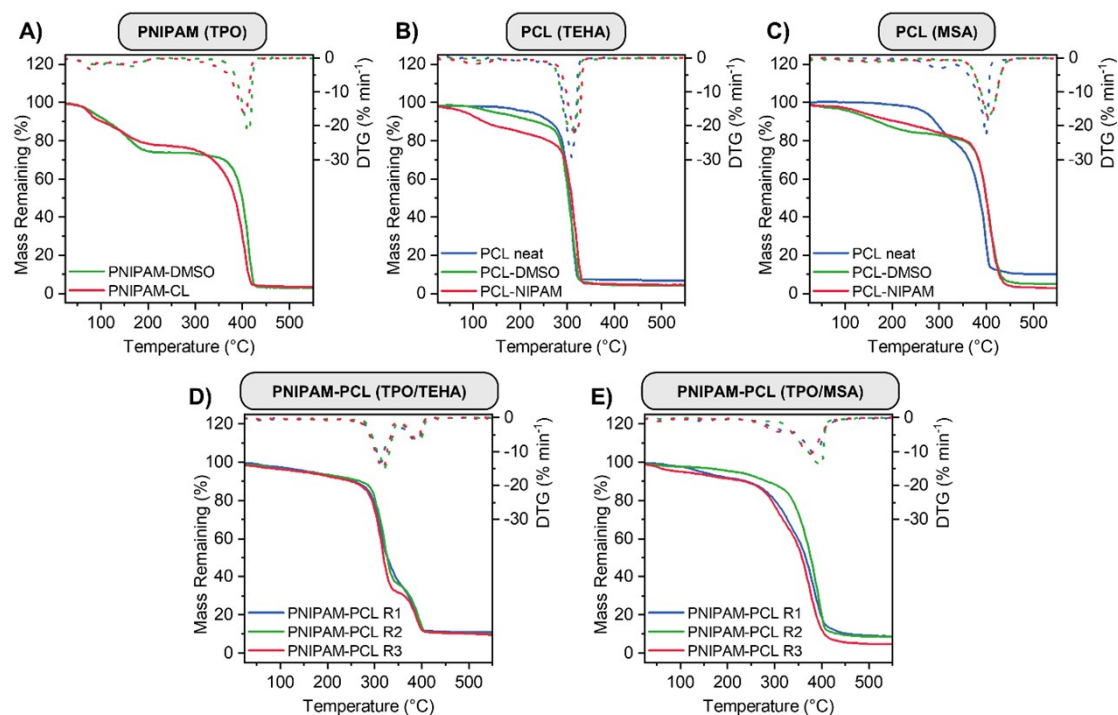


Figure S7. TGA thermograms for all homopolymer and PNIPAM-PCL blend samples with differential TGA traces (dotted lines). A) PNIPAM initiated by TPO, B) PCL catalysed by TEHA, C) PCL catalysed by MSA, D) PNIPAM-PCL catalysed by TPO/TEHA, E) PNIPAM-PCL catalysed by TPO/MSA.

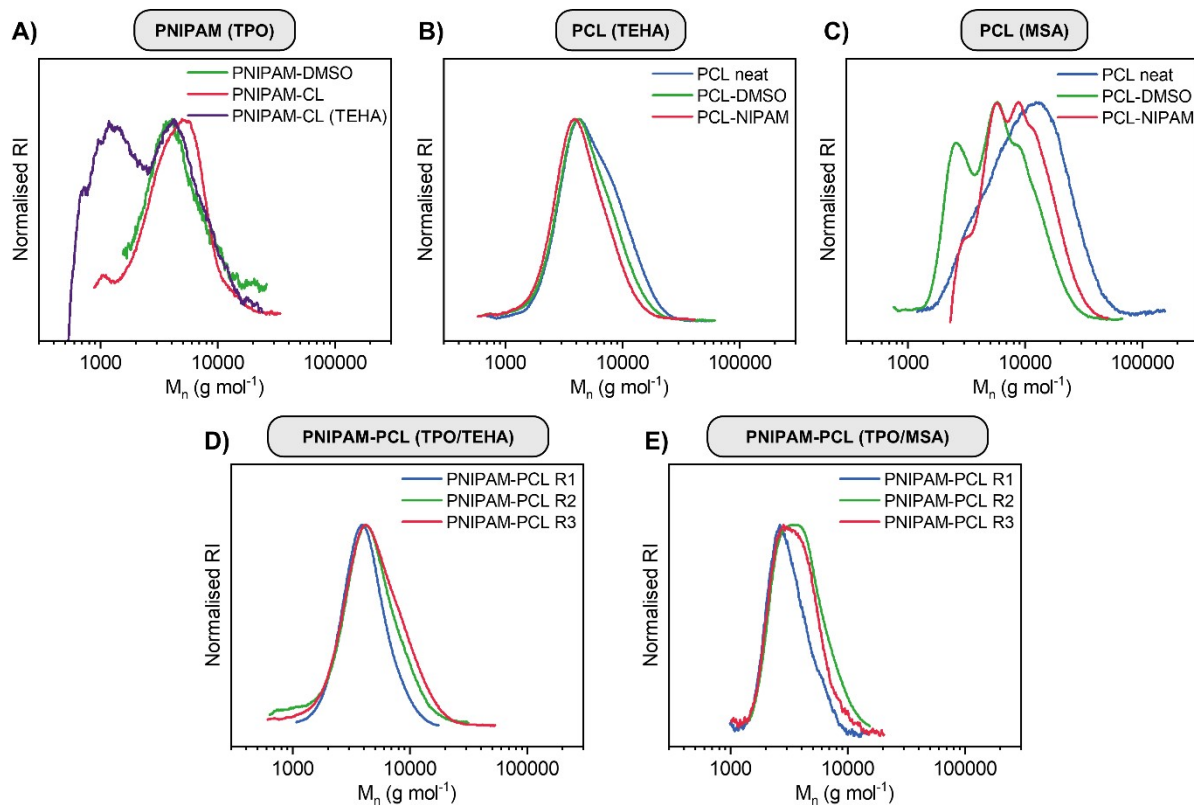


Figure S8. GPC chromatograms for all homopolymer and PNIPAM-PCL blend samples. A) PNIPAM initiated by TPO, B) PCL catalysed by TEHA, C) PCL catalysed by MSA, D) PNIPAM-PCL catalysed by TPO/TEHA, E) PNIPAM-PCL catalysed by TPO/MSA.

Characterization of crosslinked homopolymer networks, IPNs and semi-IPNs

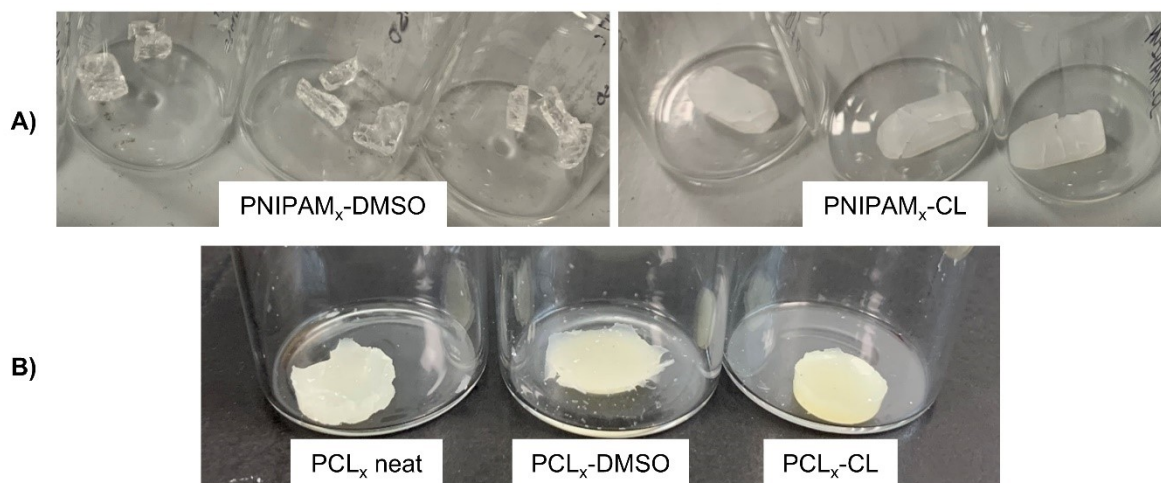


Figure S9. A) Photos of PNIPAM_x gels in triplicate after swelling with water and drying. B) Photos of individual PCL_x gels after washing with both water and chloroform then drying.

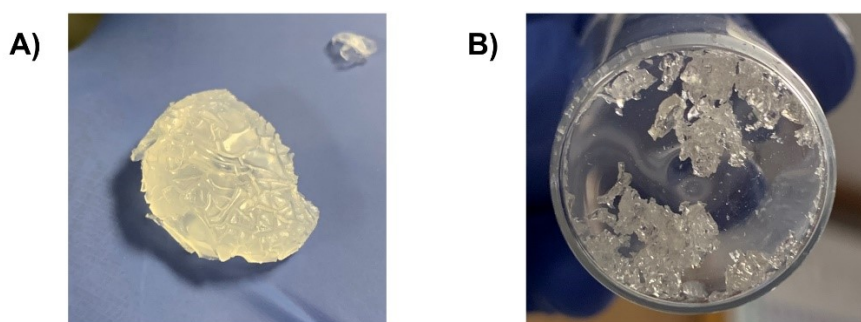


Figure S10. Photos of PCL_x-PNIPAM_x IPN gel A) after washing with water and chloroform and B) after drying and attempting to swell in water.

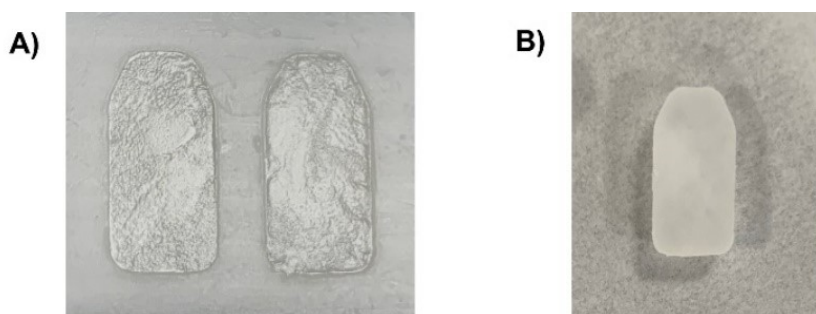


Figure S11. A) Photo of semi-IPN mixture in PTFE moulds with CL polymerised by MSA prior to UV exposure. B) Photo of PCL-PNIPAM_x semi-IPN after UV exposure.

Table S1. PCL_x mass fractions of IPNs based on TGA thermograms presented in Figure 6B.

Sample	T _{max} (°C)	Mass change (%)	PCL _x mass fraction
PNIPAM _x -PCL _x IPN R1	286.0 394.8	9.63 56.06	0.15
PCL _x -PNIPAM _x IPN R2	288.4 398.8	29.72 27.08	0.52

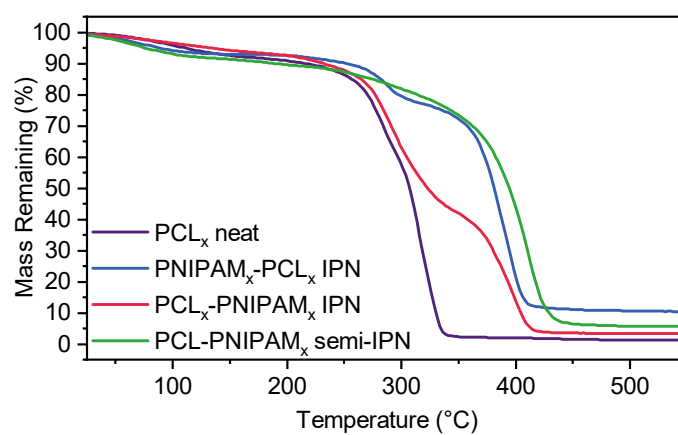


Figure S12. TGA thermogram comparison of IPNs, semi-IPN and homopolymer networks.

Characterization of 3D Printed PE Materials

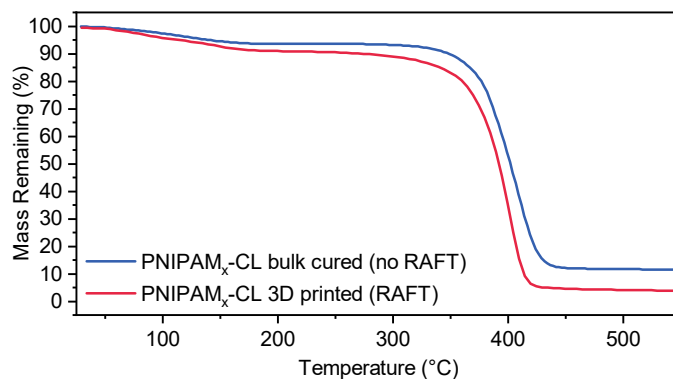


Figure S13. TGA thermograms of bulk-cured and 3D-printed PNIPAM_x-CL networks after washing with water to remove CL and any unreacted NIPAM.

Table S2. Mass and dimensions of PNIPAM_x-CL 3D printed cube structure under different conditions (as printed versus once swollen in water).

PNIPAM _x -CL 3DP	Mass (g)	External Dimensions (l×w×h mm ³)
Digital design	-	10 × 10 × 10
As printed	0.6799	10.5 × 10.5 × 9.7
Swelled H ₂ O RT	2.2539	16.5 × 16.4 × 14.5
Swelled H ₂ O 45 °C	1.4341	14.9 × 15.0 × 13.5

Flory-Rehner Analysis

Flory-Rehner theory was used to determine the average molecular weight between crosslinks (M_c) based on the equilibrium degree of swelling (S_{eq}) of homopolymer networks when immersed in different solvents.

The Flory-Rehner equation for an affine network model can be stated as:

$$\ln(1-\phi) + \phi + \chi\phi^2 = \frac{d_p V_s}{M_c} \left[\left(\frac{\phi}{2\phi_0} \right) - \left(\frac{\phi}{\phi_0} \right)^{1/3} \right]$$

Where ϕ = polymer volume fraction in the gel, χ the Flory-Huggins parameter between the polymer and solvent, d_p the density of polymer, V_s the molar volume of solvent, M_c the average molecular weight between crosslinks, and ϕ_0 the polymer volume fraction of the gel in a reference state.

The volume fraction of polymer ϕ was calculated from equilibrium swelling values via the following relation:

$$\phi = \frac{1}{1 + \frac{d_p}{d_s} S_{eq}}$$

Where d_p and d_s are the densities of polymer and solvent respectively. The values of d_p and d_s used in this work for PNIPAM and water were 1.1 and 1.0 g mL⁻¹ respectively; the equivalent values used for PCL and chloroform were 1.14 and 1.49 g mL⁻¹ respectively.

The value of M_c was then used to calculate the effective cross-linking density q_{eff} , which is defined as M_0/M_c where M_0 is the molar mass of either a NIPAM repeat unit (113 Da) or a CL repeat unit (114 Da).

The following temperature and concentration dependence of χ for the interaction between PNIPAM and water was used:¹

$$\chi = \frac{1}{2} - A \left(1 - \frac{\theta}{T} \right) + C\phi + D\phi^2$$

Where θ is the theta temperature for NIPAM (303.6 K), and A, C and D are coefficients. Values of A = -2, C = 0.32, D = 0.24 were used based on recently published values from Lopez and Richtering.¹

To determine the value of χ for the interaction between PCL and chloroform, estimation via published solubility parameters was used. Solubility parameters of PCL (19.52 MPa^{0.5}) and chloroform (19.0 MPa^{0.5}) were used and χ was estimated through the following relation:²

$$\chi = \sqrt{v_p v_s} \frac{(\delta_p - \delta_s)^2}{RT} + \beta$$

Where β is a constant (0.34), δ the respective Hildebrand solubility parameters for polymer (p) and solvent (s), v the molar volumes of polymer (p) and solvent (s), T the absolute temperature in Kelvin and R the gas constant.

Refs:

1. Lopez, C.G. and Richtering, W. *Soft Matter*, **2017**, 13, 8271.
2. Nistane, A. *et al.*, *MRS Comm.*, **2022**, 12, 1096.