



Supporting Information

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Mechanically Resistant Poly(*N*-vinylcaprolactam) Microgels with Sacrificial Supramolecular Catechin Hydrogen Bonds

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Supporting Information for

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1. Results and Discussion

1.1. BIS- and +C-Bonded μ gels

To compare the results with regular PVCL-based μ gels crosslinked with 0.5 mol% BIS instead of OFP, μ gels were sonicated for the same duration. μ gels crosslinked only with BIS showed a core corona structure with a more crosslinked core and a less crosslinked corona. For those μ gels a fast decrease of the size was observed, because the loosely crosslinked corona was degraded by sonication. This was followed by a strong aggregation of the μ gels after 2.5 min of sonication time.^[1] The observed trends for the μ gels crosslinked with BIS and +C were comparable to those obtained for only +C-crosslinked μ gels (Figure S1). In general, the μ gels appeared to be slightly more resistant to shear force than those crosslinked *via* +C only, but not as stable as the μ gels crosslinked with OFP and +C. The μ gels crosslinked with 0.5 mol% BIS and 15 mol% +C showed no changes in their size within a sonication time of 20 min. However, the μ gels composed of 0.5 mol% BIS and 5 mol% +C as well as 10 mol% of +C were less stable than those with 0.5 mol% OFP instead of BIS. This indicated that the OFP molecules additionally increased the mechanical stability of the μ gels.

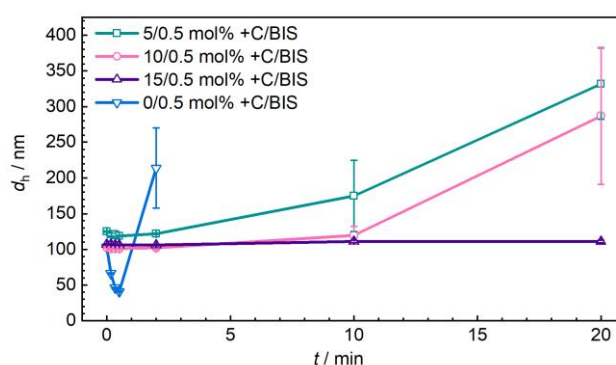


Figure S1. Hydrodynamic diameters d_h gathered from DLS intensity-weighted distributions at $T = 25\text{ }^\circ\text{C}$ of PVCL μ gels bonded with +C (0, 5, 10, and 15 mol%) and BIS crosslinker (0.5 mol%) over the course of sonication time. Mean values \pm SD from the mean. $N = 3$ independent measurements for each data point.

2. Supporting Measurements and Data

2.1. Fourier-Transform Infrared (FTIR) Spectroscopy

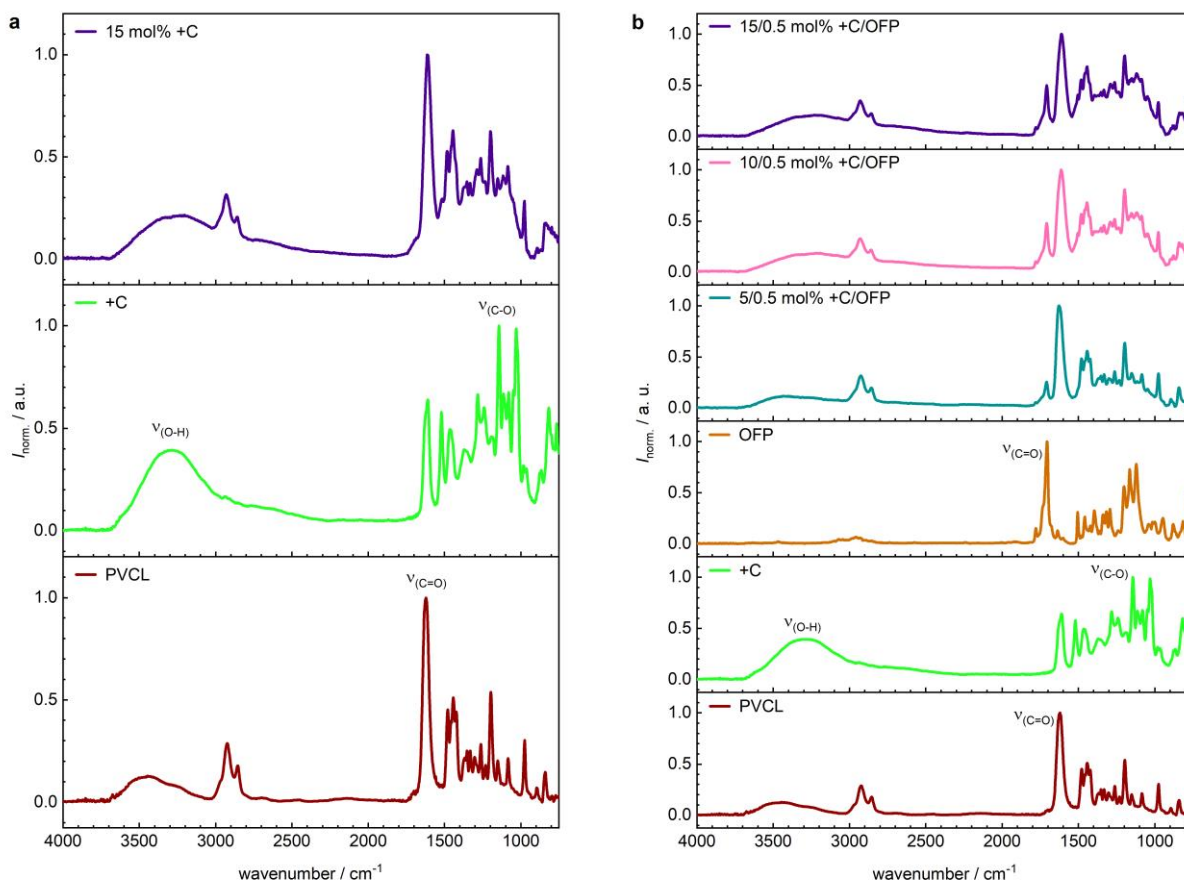


Figure S2. Stacks of FTIR spectra of μ gels bonded with (a) +C and associated starting material references and (b) +C and OFP crosslinker including associated starting material references.

2.2. Dynamic Light Scattering (DLS)

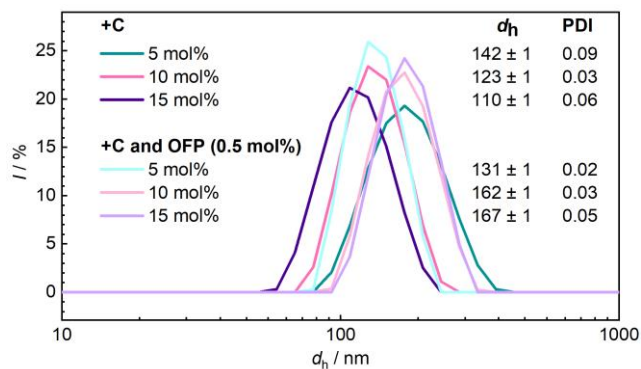


Figure S3. DLS intensity-weighted distributions at $T = 25$ °C of PVCL μ gels bonded only with +C and those with +C together with OFP crosslinker. Mean values \pm SD from the mean. $N = 3$ independent measurements for each data point.

2.3. Quantitative Raman Spectroscopy

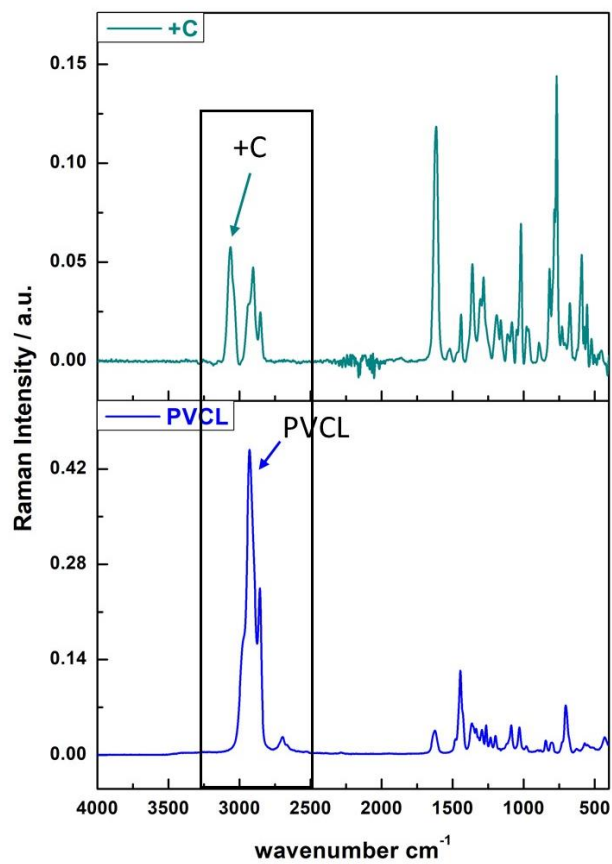


Figure S4. Raman spectra of pure calibration samples (linear PVCL chains and +C).

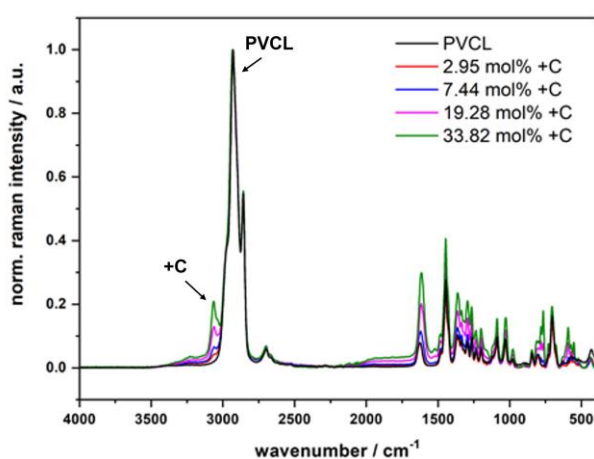


Figure S5. Raman spectra of sample mixtures of linear PVCL and defined amounts of +C to obtain a calibration curve to calculate the +C content in the μgels .

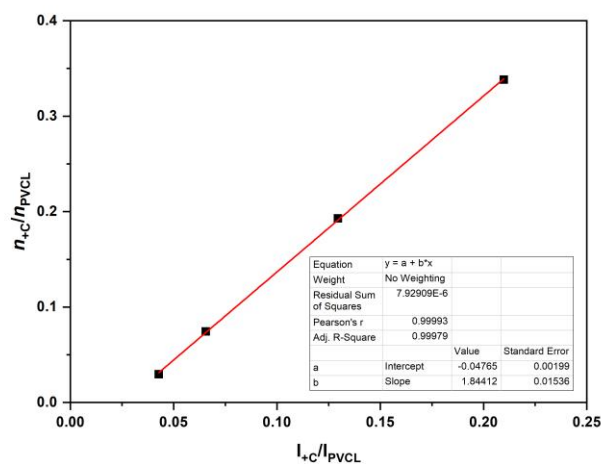


Figure S6. Calibration curve obtained by Raman spectroscopy to calculate the +C content in the μ gels.

Table S1. Incorporated fraction of +C within PVCL/BIS/+C- μ gels with a BIS content of 0.5 mol% determined by Raman spectroscopy.

μ gel sample	+C / mol%
5/0.5 mol% +C/BIS	14.12
10/0.5 mol% +C/BIS	19.32
15/0.5 mol% +C/BIS	25.11

2.4. Quantitative ^1H -Nuclear Magnetic Resonance (NMR) Spectroscopy

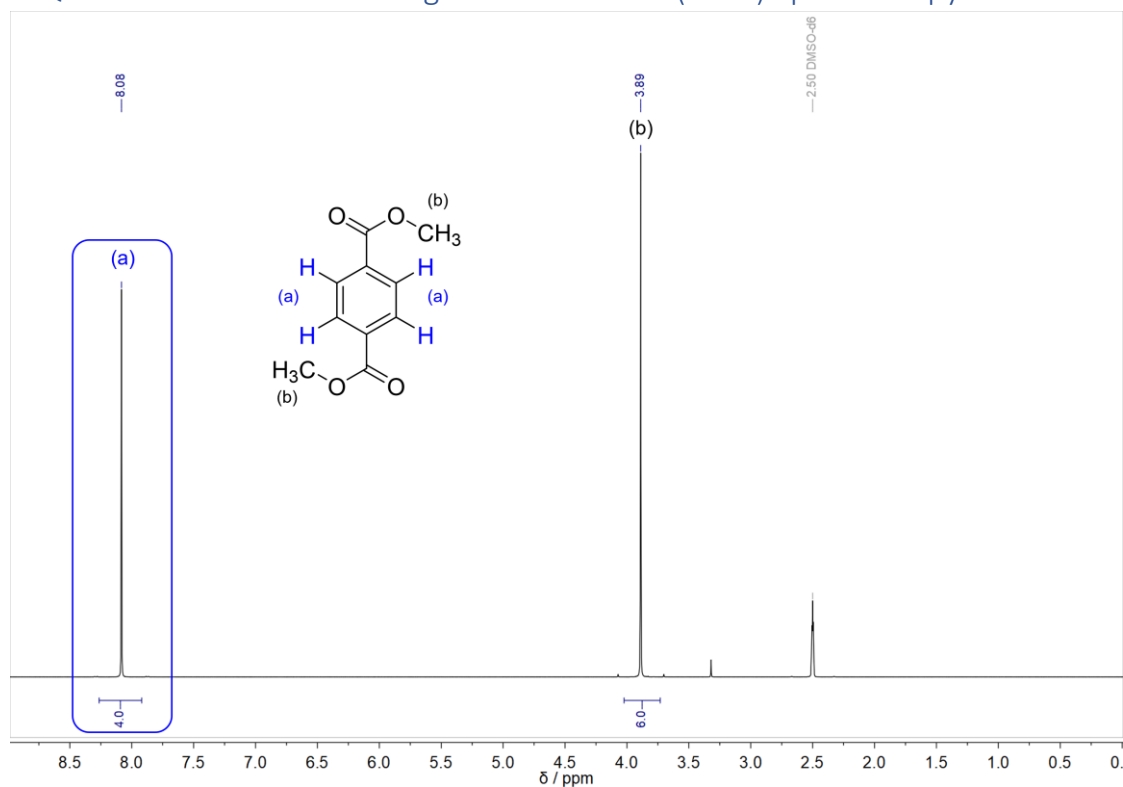


Figure S7. ^1H -NMR spectrum of the internal standard DMT measured in DMSO-d_6 . Highlighted is the signal of the aromatic protons used for the calculation of the +C content.

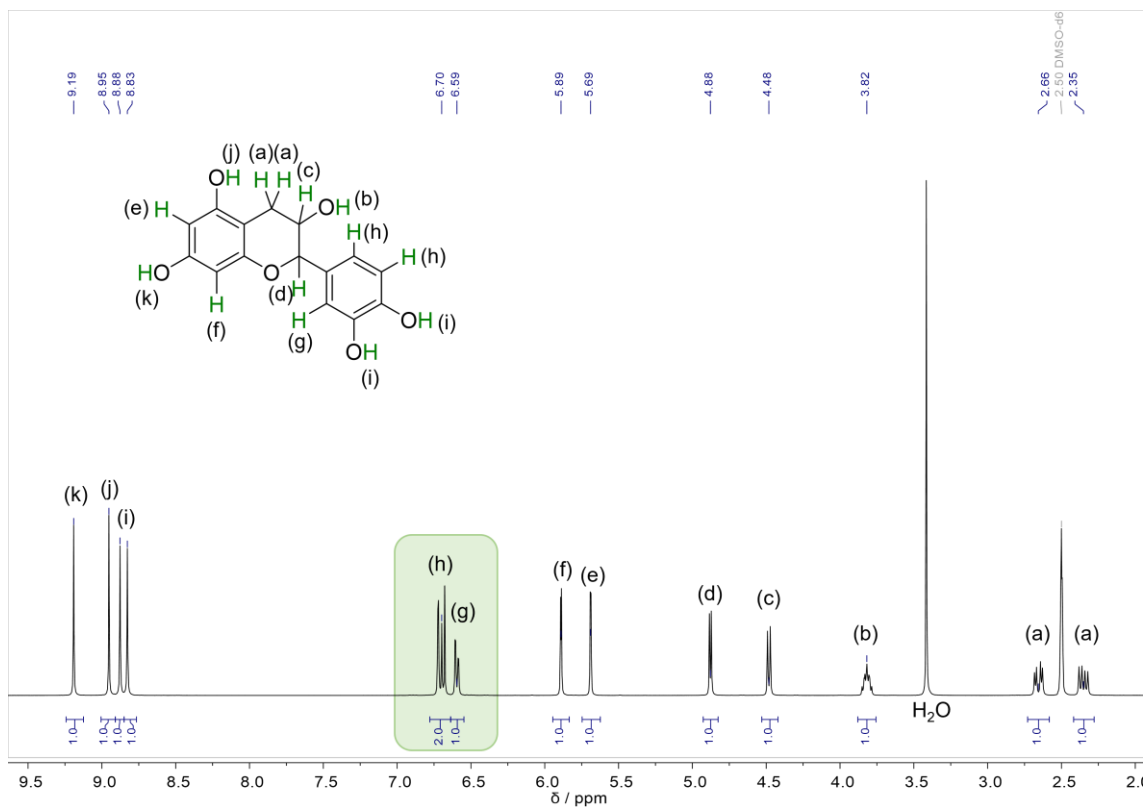


Figure S8. ¹H-NMR spectrum of +C measured in DMSO-d₆. Highlighted are the signals of the aromatic protons used for the calculation of the +C content.

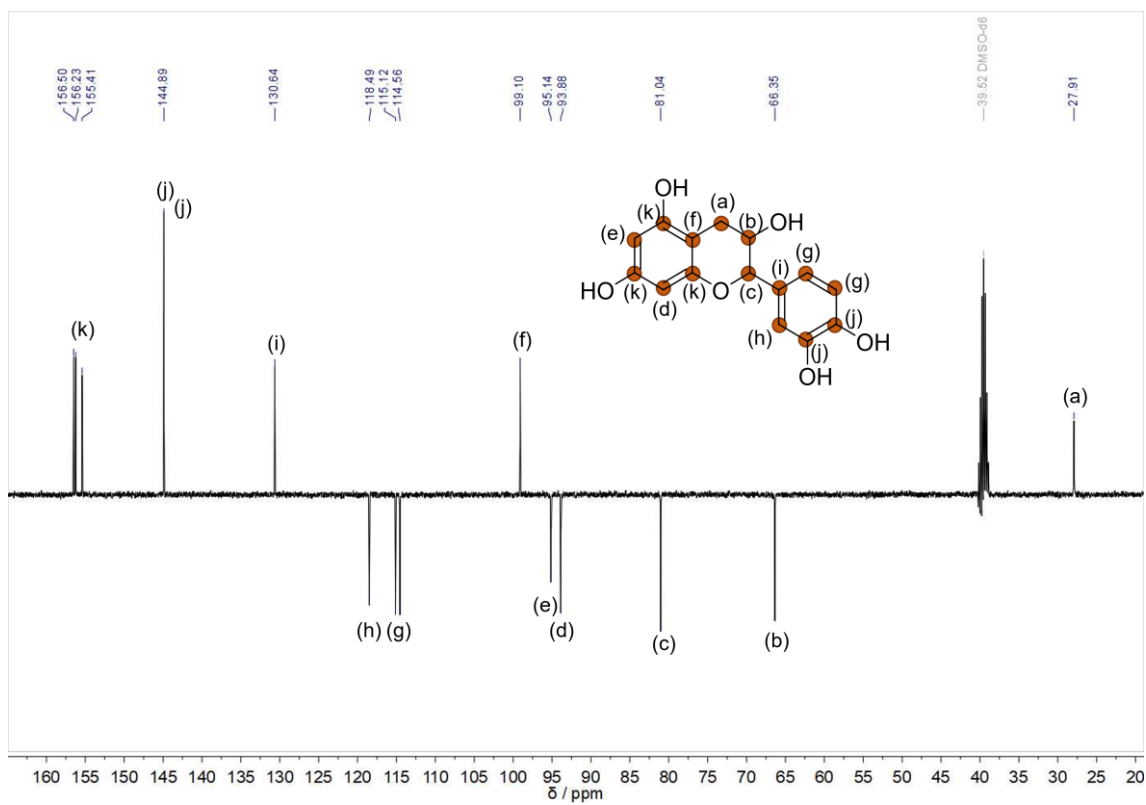


Figure S9. ¹³C-NMR spectrum of +C measured in DMSO-d₆.

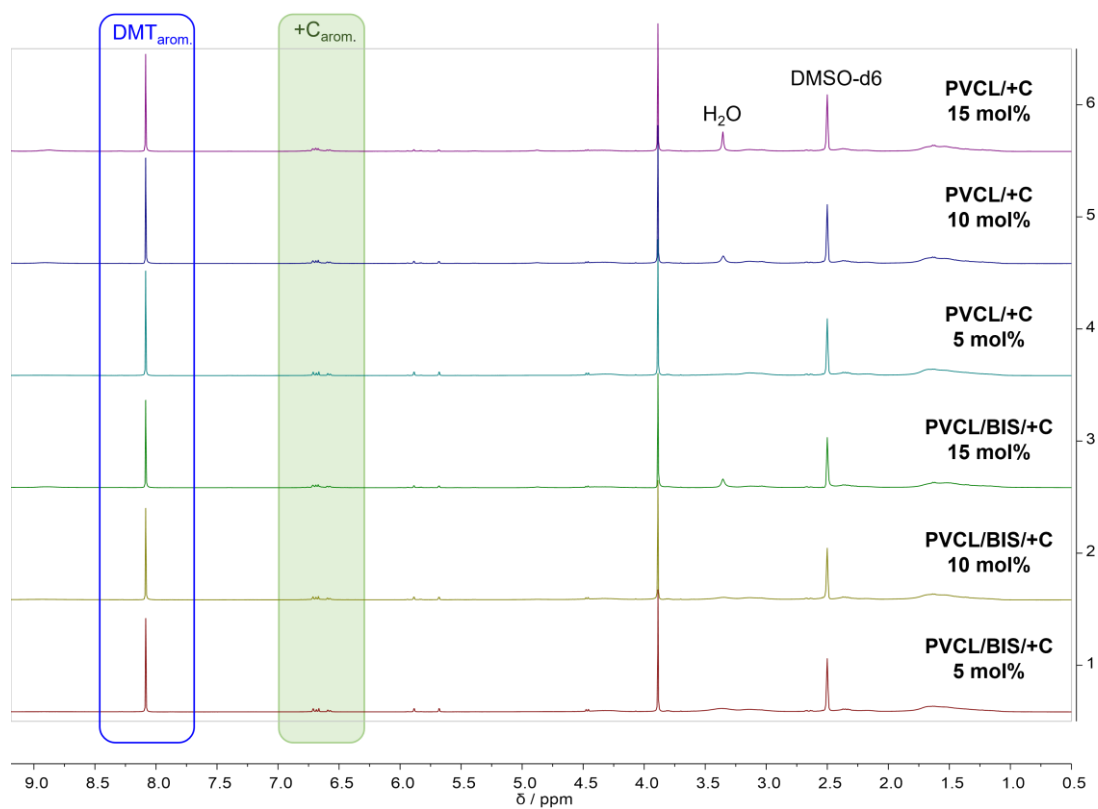


Figure S10. Stacked ^1H -NMR spectra of μ gels bonded with supramolecular +C and μ gels crosslinked with BIS and +C measured in DMSO-d_6 containing the internal standard DMT. Highlighted are the signals of the aromatic protons of the DMT and the +C used for the calculation of the crosslinker content.

Table S2. Incorporated fraction of +C within PVCL/BIS/+C μ gels with a BIS content of 0.5 mol% determined by quantitative ^1H -NMR spectroscopy.

μ gel sample	+C / wt%	+C / mol%
5/0.5 mol% +C/BIS	24.6	13.53
10/0.5 mol% +C/BIS	32.5	18.74
15/0.5 mol% +C/BIS	35.4	20.84

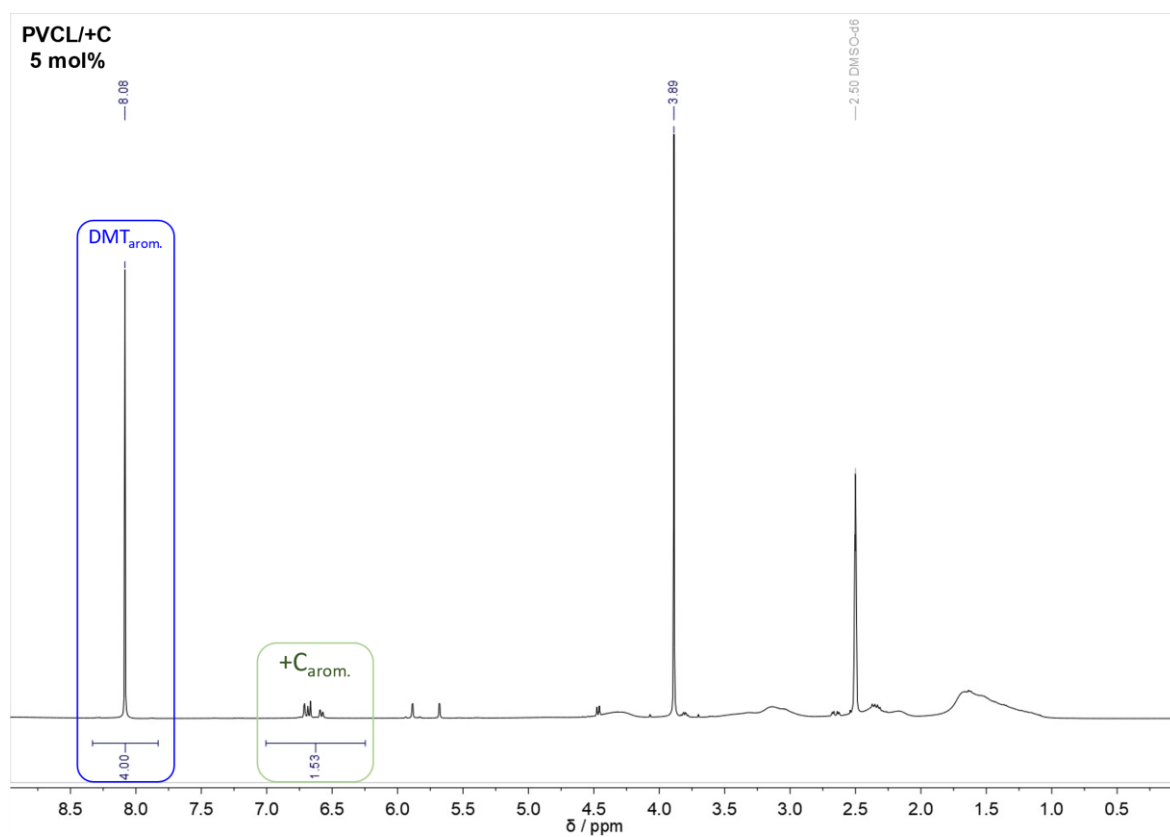


Figure S11. Exemplary ^1H -NMR spectrum of PVCL/+C μgels measured in DMSO-d_6 containing the internal standard DMT. Highlighted are the signals of the aromatic protons of DMT and +C used for the calculation of the +C content.

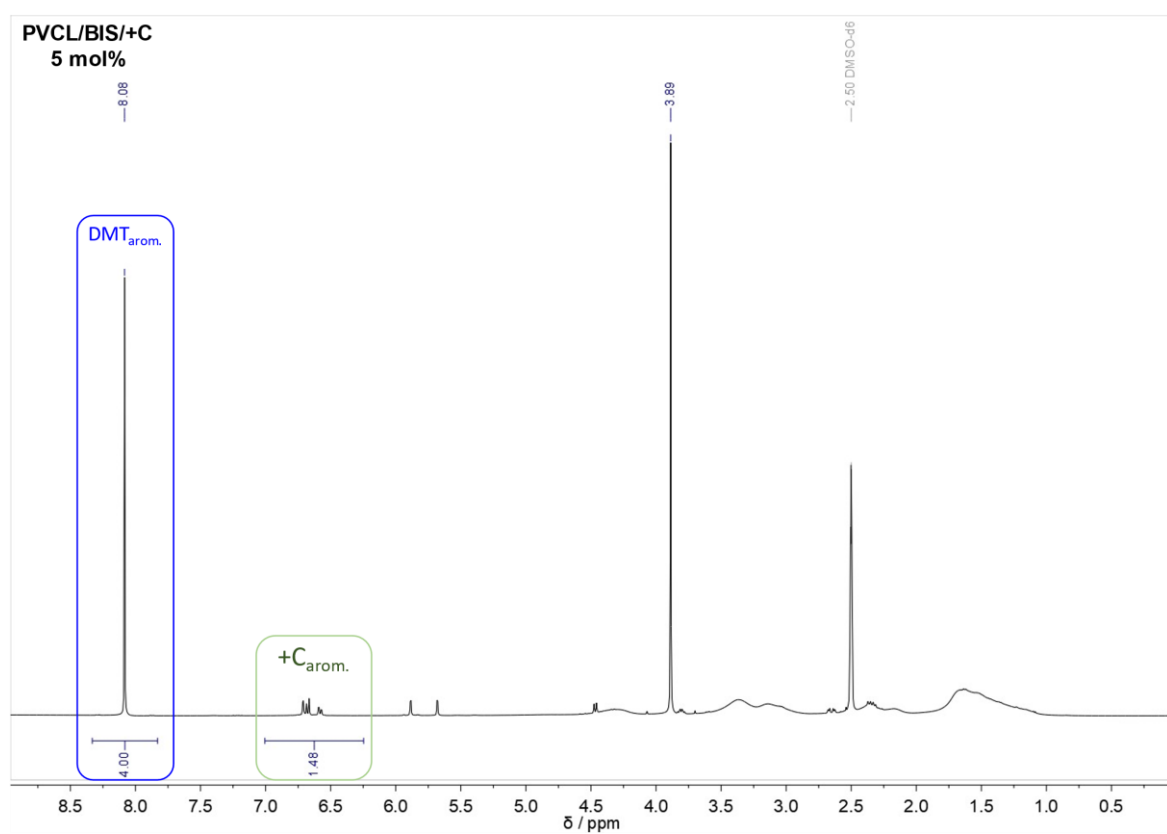


Figure S12. Exemplary ^1H -NMR spectrum of PVCL/BIS/+C μgels measured in DMSO-d_6 containing the internal standard DMT. Highlighted are the signals of the aromatic protons of DMT and +C used for the calculation of the physical crosslinker content.

2.5. Fluorescence Spectroscopy (FS)

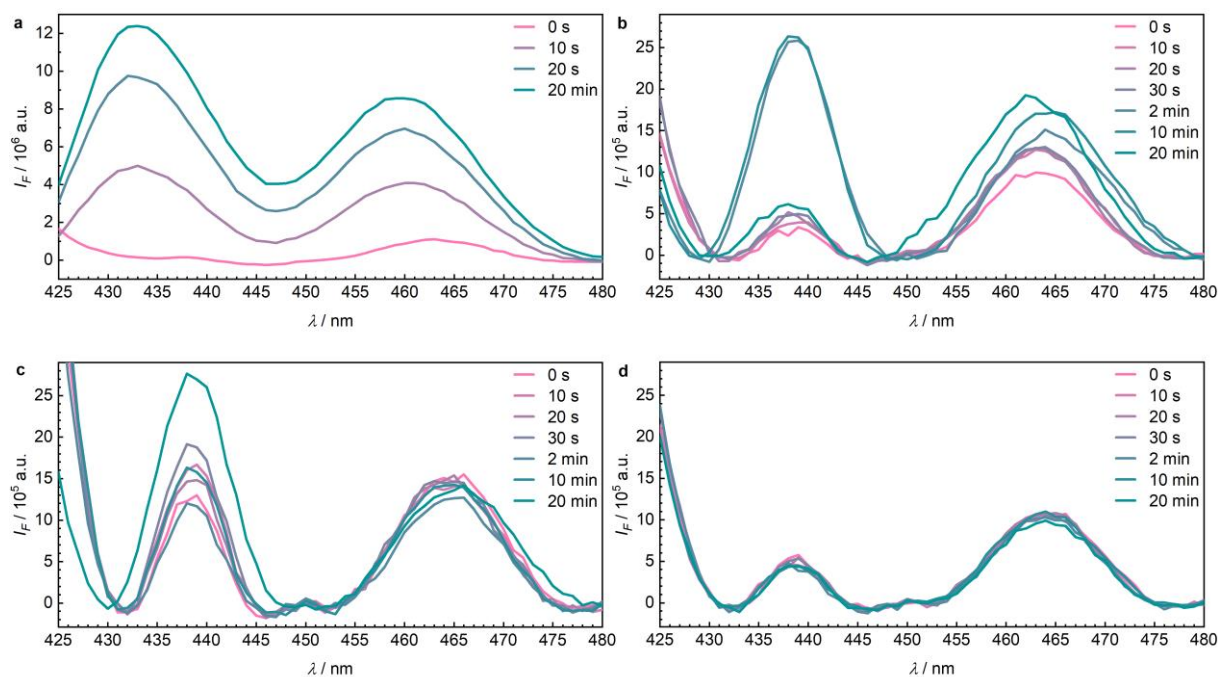


Figure S13. Fluorescence intensity I_F for μ gels bonded with +C and OFP crosslinker (0.5 mol%) over the course of the sonication. (a) +C (0 mol%), (b) +C (5 mol%), (c) +C (10 mol%), and (d) +C (15 mol%).

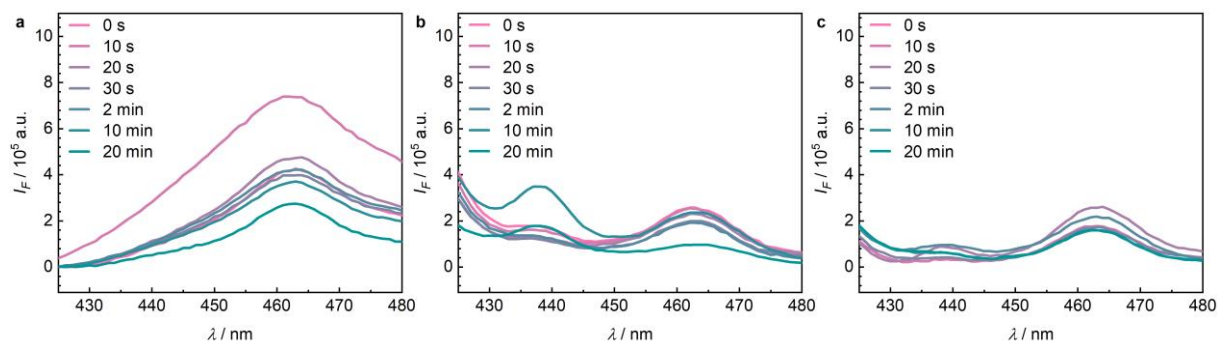


Figure S14. Fluorescence intensity I_F for μ gels bonded with +C over the course of the sonication. (a) 5 mol%, (b) 10 mol%, and (c) 15 mol%.

2.6. Titrations for pH-Sensitivity

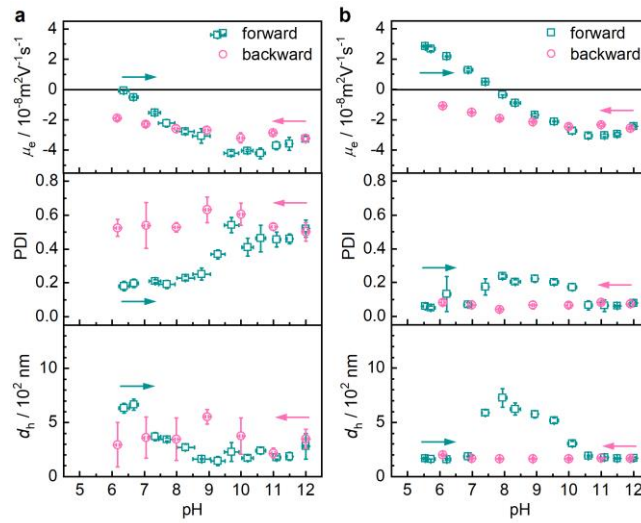


Figure S15. pH-sensitivity of μ gels under alkaline conditions. d_h , PDI, and μ_e for μ gels crosslinked with (a) +C (5 mol%) and (b) +C (5 mol%) and OFP (0.5 mol%).

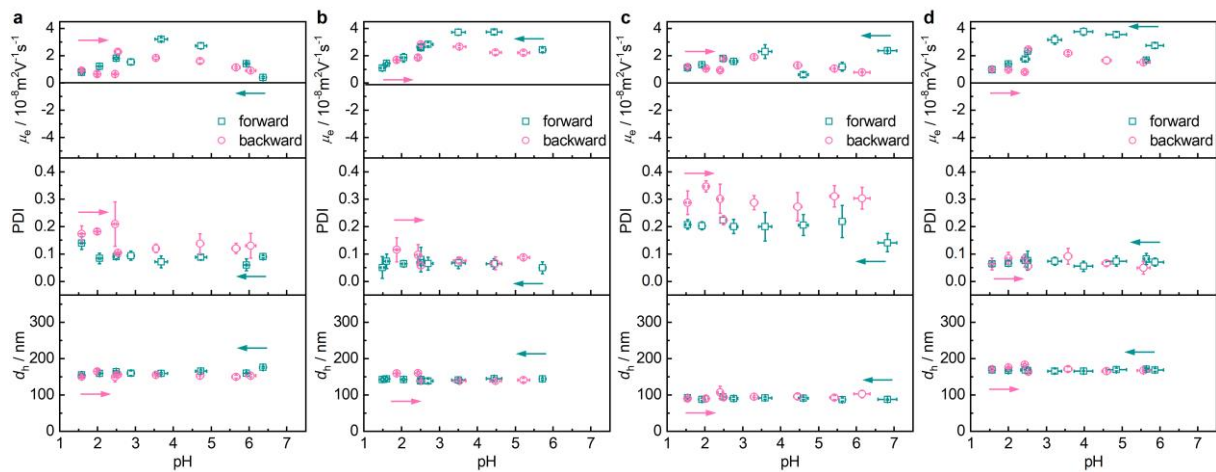


Figure S16. pH-sensitivity of μ gels under acidic conditions. d_h , PDI, and μ_e for μ gels crosslinked with (a) +C (15 mol%), (b) +C (15 mol%) and OFP (0.5 mol%), (c) +C (5 mol%), and (d) +C (5 mol%) and OFP (0.5 mol%).

3. References

- [1] E. Izak-Nau, D. E. Demco, S. Braun, C. Baumann, A. Pich, R. Göstl, *ACS Appl. Polym. Mater.* **2020**, *2*, 1682-1691.