

Electronic Supporting Information

Physical gels of poly(vinylamine) by thermal curing

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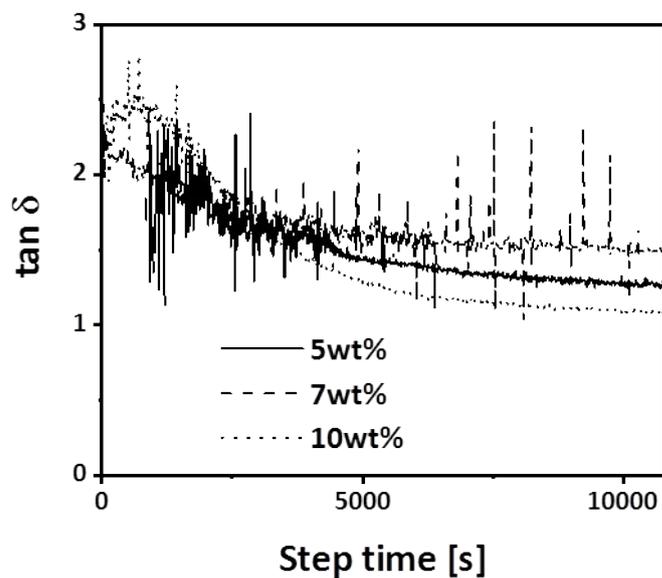


Fig. S1. The dissipation factor $\tan \delta$ for 5, 7, and 10 wt% of p(VAm-co-VAA) in methanol in dependence on the time with a frequency of 1 Hz and an amplitude of 1 %. The lower the dissipation factor the more elastic is the response. At 10 wt% of p(VAm-co-VAA) the dissipation factor is close to 1, which indicates that the behavior is more solide-like than viscous.

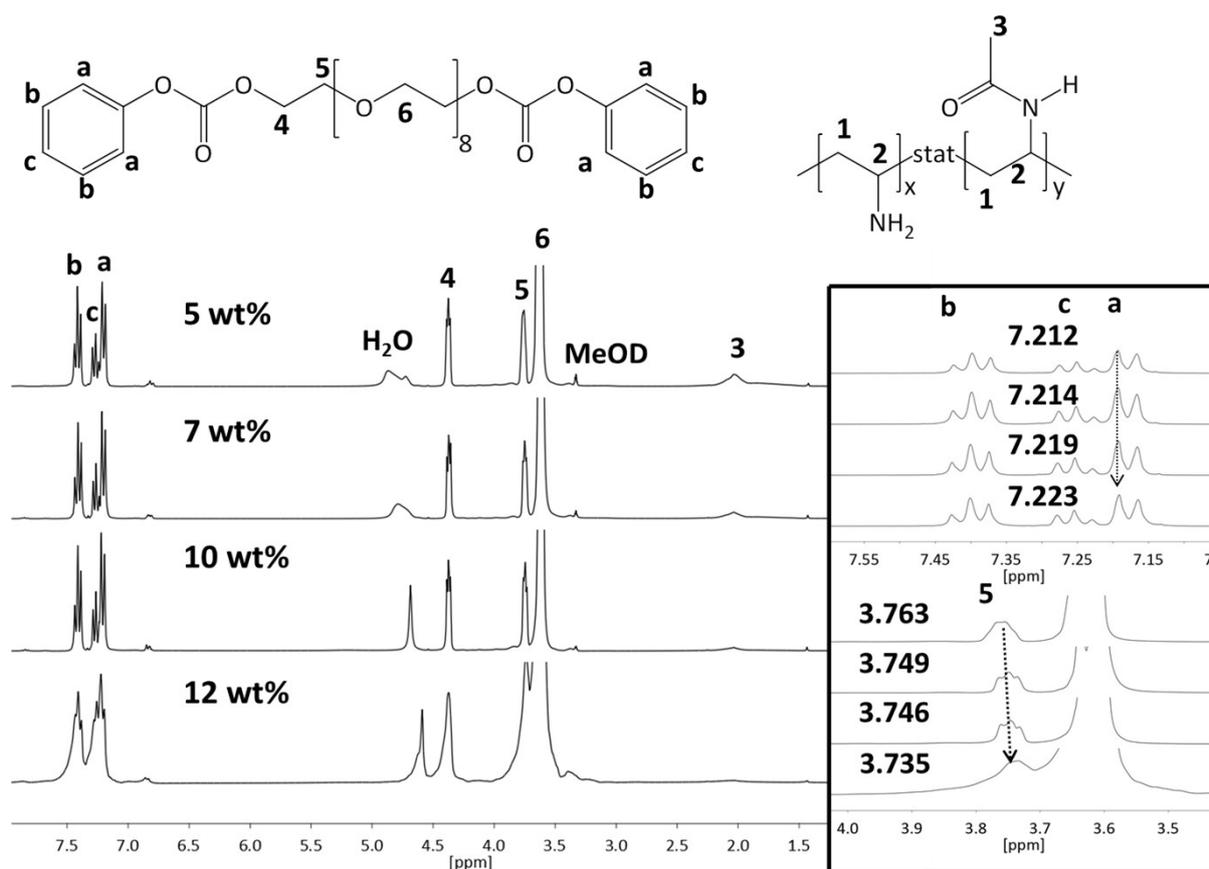


Fig. S2. ^1H NMR of 5 wt%, 7 wt%, 10 wt%, and 12 wt% p(VAm-coVAA) with the respective PEG-PC amount (amine-to-carbonate ratio 1:1). With increasing concentrations the peaks are broadened. The insets show the downfield shift of peak 'a' with the respective chemical shift in ppm (top) and the upfield shift of peak 5 (bottom). Peak 1 and 2 are not visible because of their too low intensity.

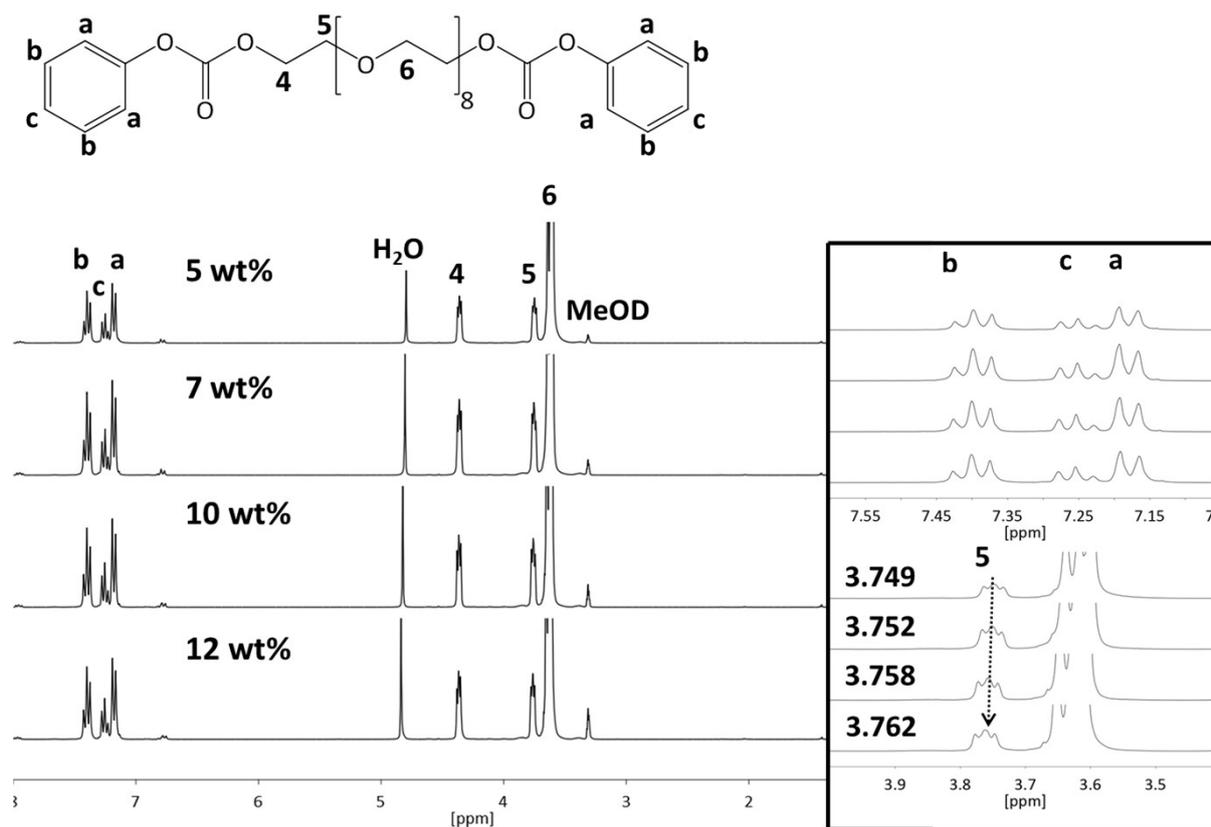
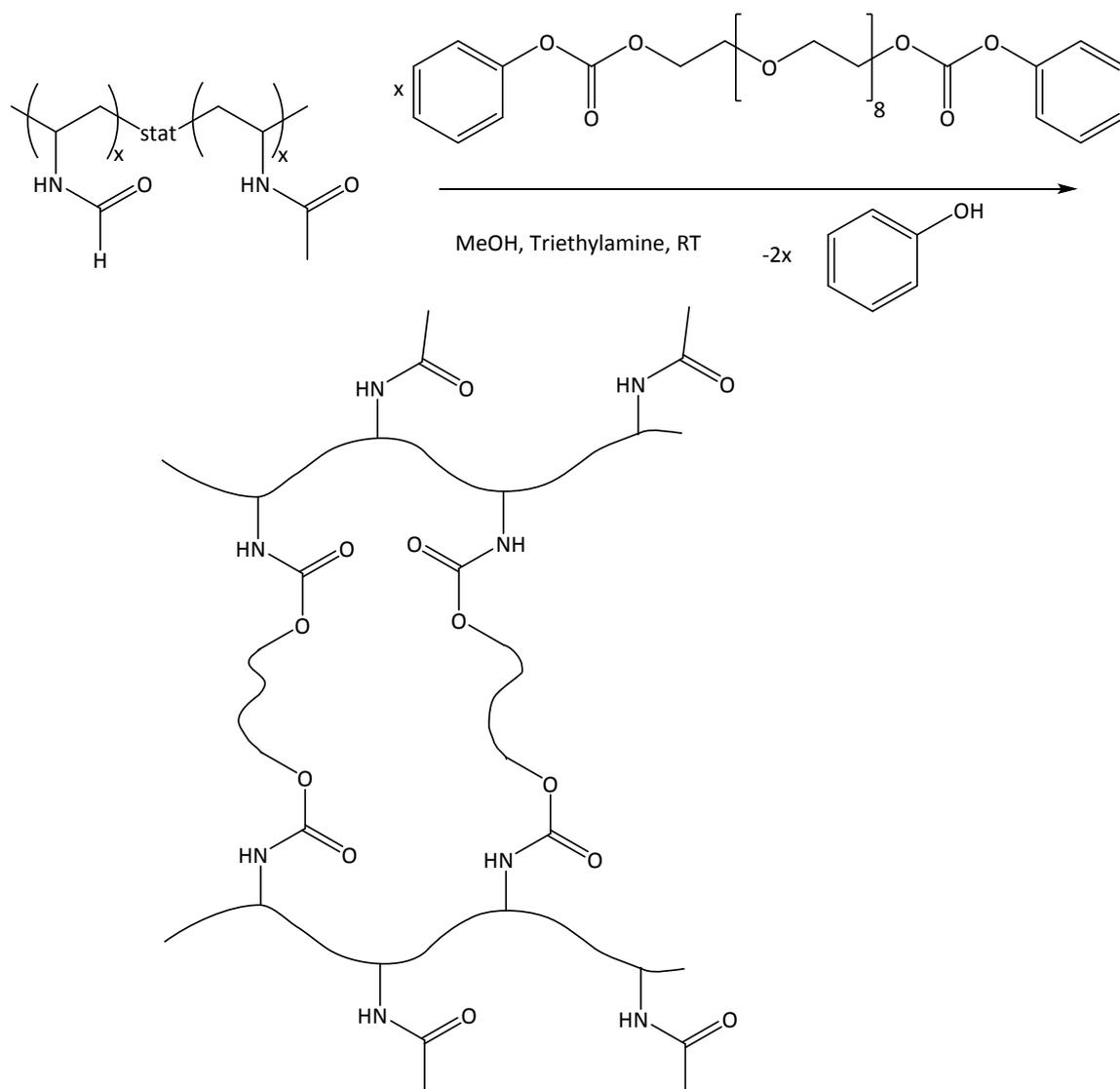


Fig. S3. ^1H NMR of 5 wt%, 7 wt%, 10 wt%, and 12 wt% of only the respective PEG-PC. No peak broadening could be observed. The insets show that there is no shift for peak 'a' and, contrary to the physical gel, a downfield shift of peak 5.



Scheme S1. A chemical crosslinking in presence of a base (triethylamine, TEA) would release phenol.

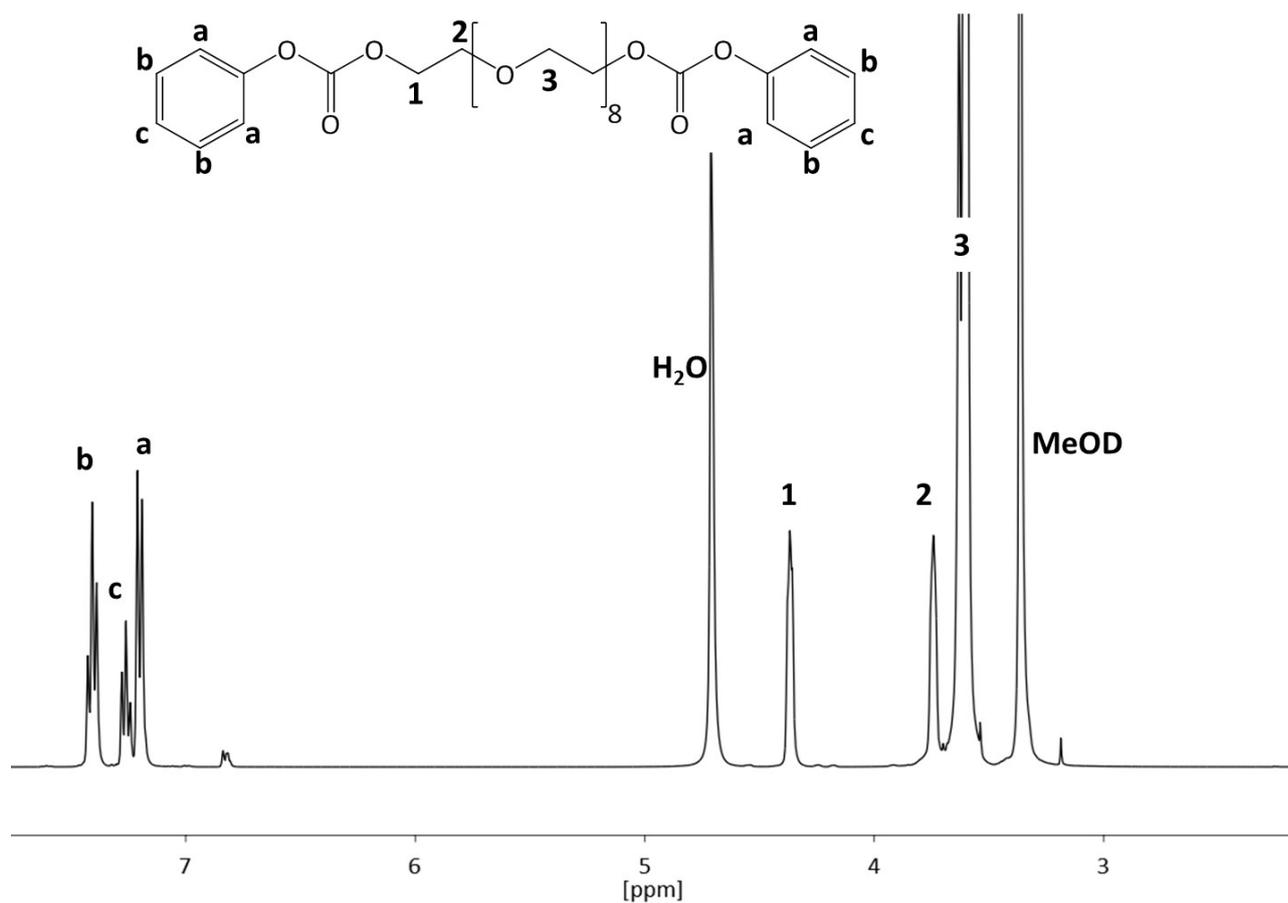


Fig. S4. ^1H NMR of the supernatant. Only PEG-PC is visible.

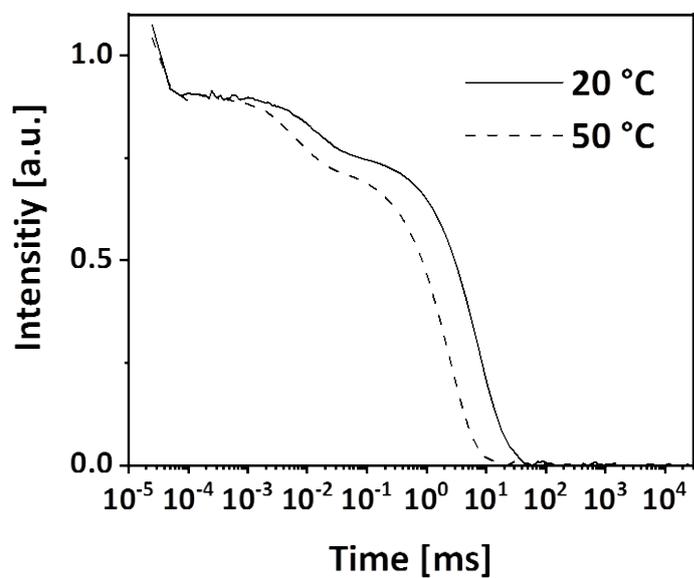


Fig. S5. Autocorrelation function of p(VAm-co-VAA) in methanol ($10\text{ mg}\cdot\text{mL}^{-1}$) at $20\text{ }^\circ\text{C}$ and $50\text{ }^\circ\text{C}$. In both cases there are a slow and a fast mode visible reflecting the aggregations and neat polymer, respectively. With increasing temperature the aggregates became smaller.

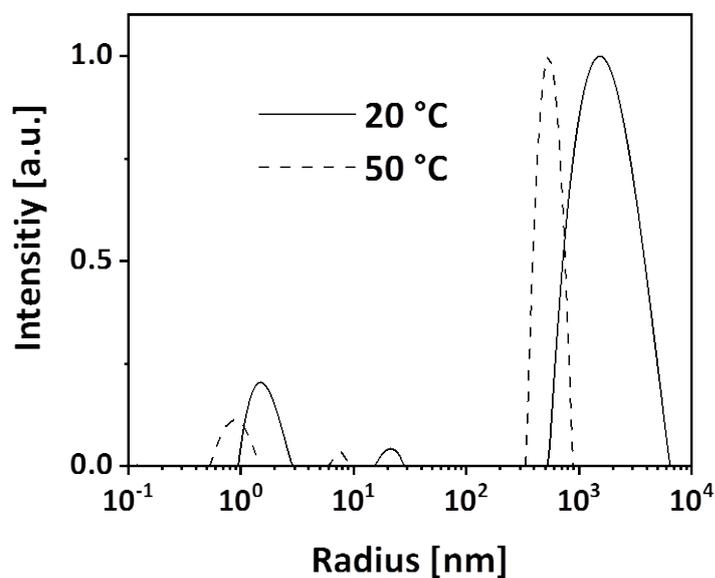


Fig. S6. Radius distribution function of p(VAm-co-VAA) in methanol ($10 \text{ mg}\cdot\text{mL}^{-1}$) at $20 \text{ }^\circ\text{C}$ and $50 \text{ }^\circ\text{C}$ based on Fig. S6. At higher temperature the aggregates became smaller.

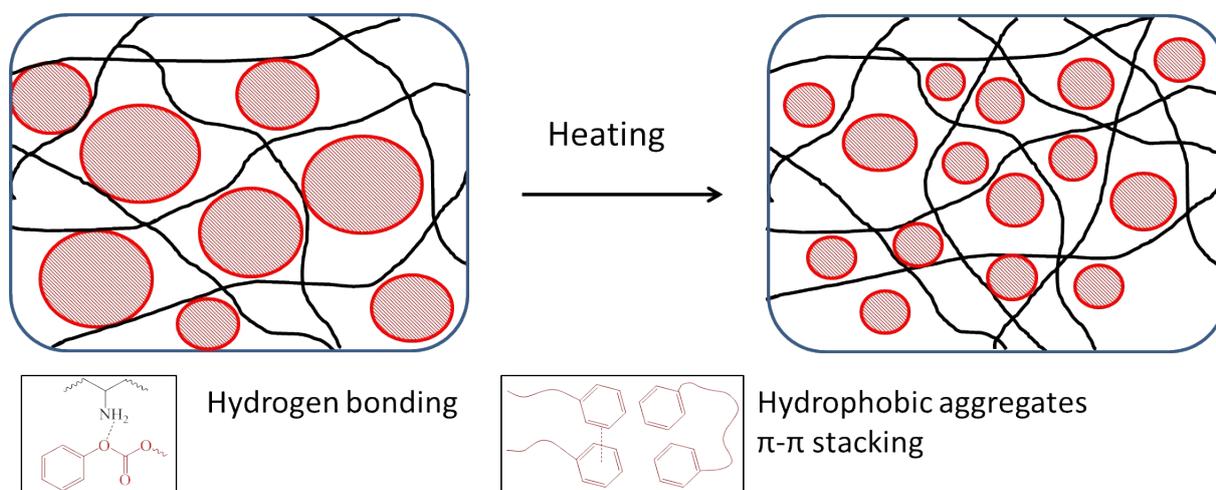


Fig. S7. Schematic illustration of the physical gel. The hydrophobic aggregates are stabilized by hydrogen bonding at the periphery and by π - π stacking in the core. Upon heating the stabilizing effect of the hydrogen bonds is decreased and the physical gel becomes more homogeneous

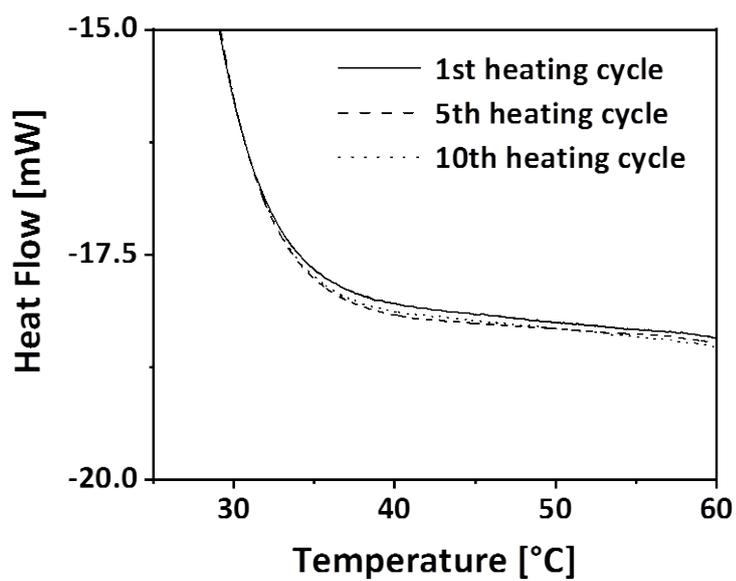


Fig. S8. DSC curve (endo up) of p(VAm-co-VAA) in methanol (10 wt%) with a heating rate of 5 °C·min⁻¹. No signal is visible

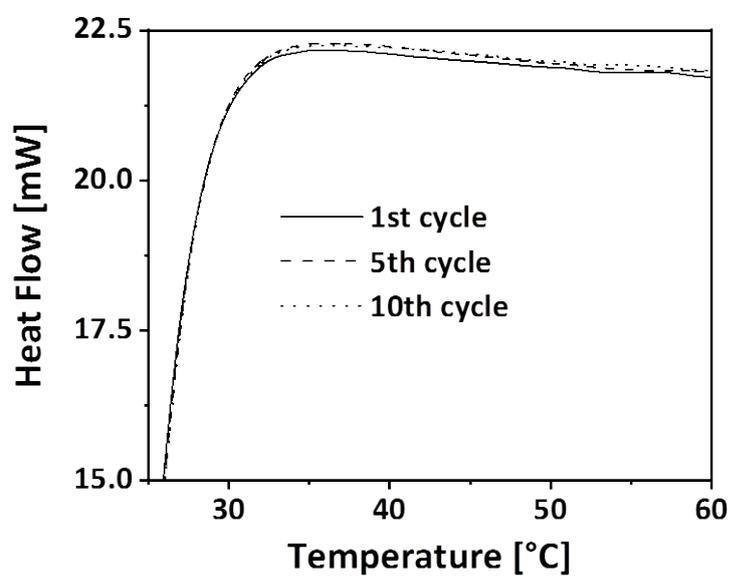


Fig. S9. DSC curve (endo up) of PEG-PC in methanol (34 wt%) with a heating rate of 5 °C·min⁻¹. No signal is visible.

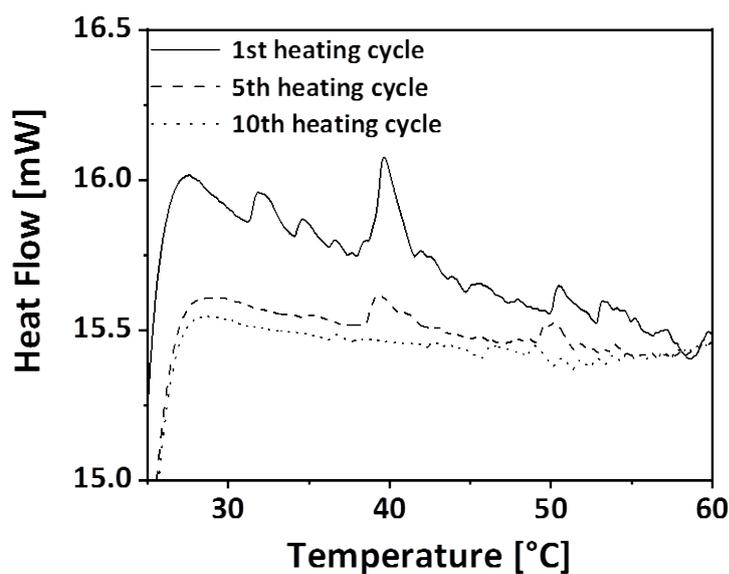


Fig. S10. DSC curve (endo up) of the supernatant of the physical gel with a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The prominent signal around $40\text{ }^{\circ}\text{C}$ is caused by mixing/homogenization.

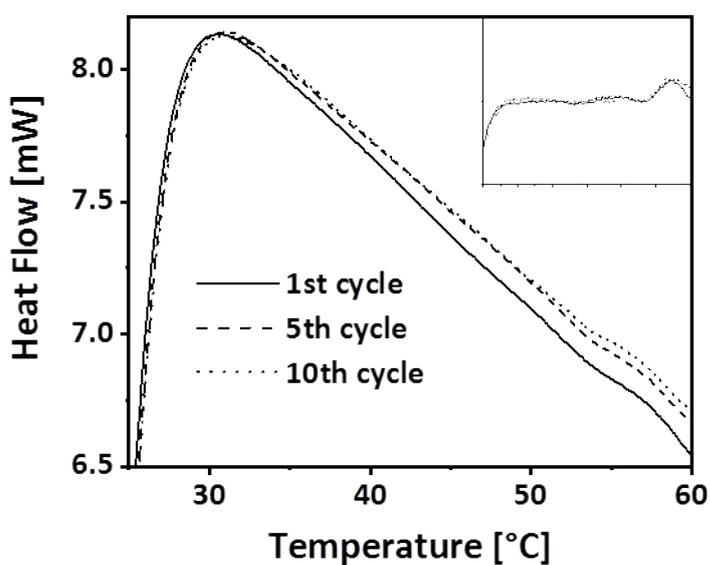


Fig. S11. DSC curve (endo up) for the physical gel with a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The inset shows the baseline corrected graph to make the signal around $55\text{ }^{\circ}\text{C}$ more visible. The signal is caused by the mixing enthalpy and shifted towards higher temperature and weaker compared to the supernatant because the gel is more strongly bound.

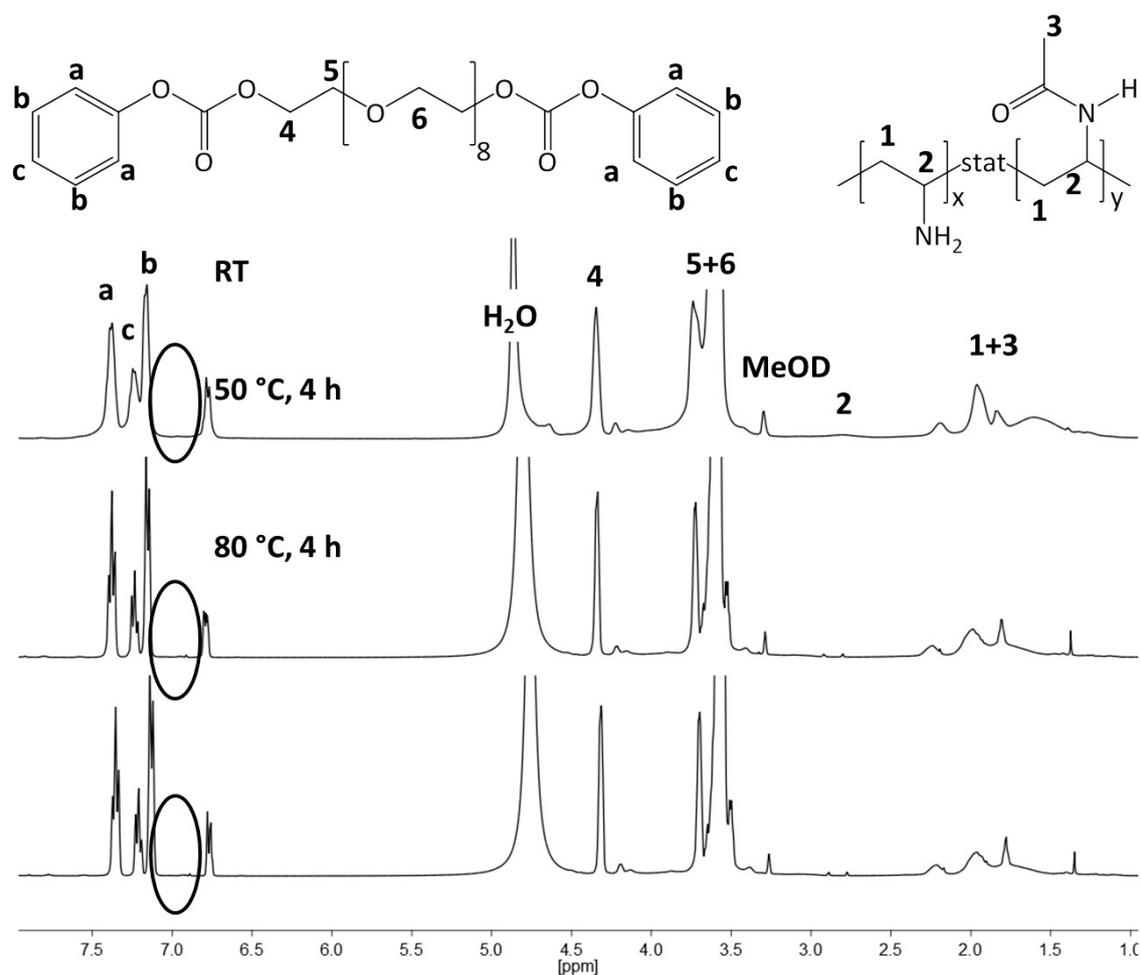


Fig. S12. ^1H NMR of the physical gel. The circle indicates, where the shifts of any phenol would be. Since no phenol is found, there is no chemical reaction/crosslinking, so the physical gel is thermostable.

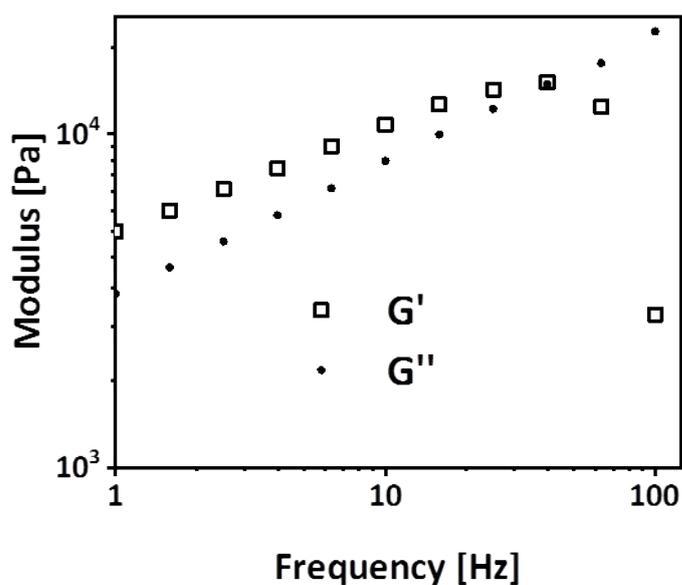


Fig. S13. Frequency sweep after five heating/cooling cycles in a range of 1 – 100 Hz with an amplitude of 1 %. The frequency dependence shows, that the gel is physically crosslinked.

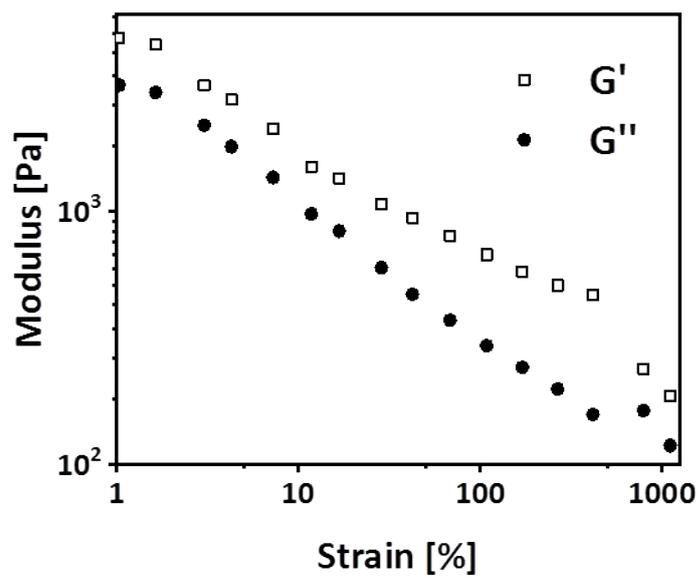


Fig. S14. Amplitude Sweep of the physical gel with a frequency of 1 Hz.