

Supporting Information

Poly(vinylamine-co-*N*-isopropylacrylamide) Linear Polymer and Hydrogels with Tuned Thermoresponsivity

Thorsten Fischer^a, Dan E. Demco^{a,b*}, Radu Fechete^b, Martin Möller^{a*}, Smriti Singh^{a*}

^a*DWI-Leibniz-Institute for Interactive Materials, e.V., RWTH-Aachen University, Forckenbeckstraße 50, D-52074 Aachen, Germany*

^b*Technical University of Cluj-Napoca, Department of Physics and Chemistry, 25 G. Baritiu Str., RO-400027, Cluj-Napoca, Romania*

*Corresponding authors: Fax: +49-241-233-01

E-Mail: singh@dwirwth-aachen.de
demco@dwirwth-aachen.de
moeller@dwirwth-aachen.de

Table of Content

| | |
|---|----|
| 1. Determination of the average molecular weight between two crosslinking points M_c | 3 |
| 2. Determination of the copolymerization parameters | 3 |
| 3. Figure S1. Copolymerization parameters | 4 |
| 4. Figure S2. Proton spectra of p(NVF-co-NIPAm) before and after hydrolysis | 5 |
| 5. Table S1. Theoretical and experimental integral ratios | 5 |
| 6. Figure S3 Proton NMR spectra of phenylcarbonate telechelic ethylene glycol | 6 |
| 7. Figure S4. Hydrolysis kinetics | 6 |
| 8. Table S2. Degree of hydrolysis | 7 |
| 9. Figure S5. Frequency dependence of the copolymers on G' and G'' | 7 |
| 10. Figure S6. Proton spectrum of the hydrogels | 8 |
| 11. Figure S7. Proton NMR spectra of the washed hydrogels | 8 |
| 12. Figure S8. Proton NMR spectrum of the washing solution | 9 |
| 13. Figure S9. Time dependence of G' and G'' during the gelation | 9 |
| 14. Figure S10. UV-Vis spectrum of the swollen gel | 10 |
| 15. Scheme S1. Gelation of p(VAm-co-NIPAm) with EG-PC | 11 |
| 16. Figure S11. Rheology of the swollen gels | 12 |
| 17. Figure S12. G' and G'' dependence on the frequency of the swollen gels | 12 |
| 18. Figure S13. Boltzmann fits of the temperature induced phase transition of the hydrogels | 13 |
| 19. Figure S14. SEM image of the hydrogel | 13 |

Determination of the average molecular weight between two crosslinking points M_c

The ratio of the phenylcarbonate to amine moieties was kept 1:1, which means that the average molecular weight between two crosslinking points M_c equals the molecular weight of the average number of NIPAm units between two crosslinking points assuming a statistical distribution of the monomers within the copolymer and a crosslinking efficiency of 100%. The values are given in Table S1.

Table S1. Theoretical M_c values of the hydrogels

| VAm:NIPAm ratio | M_c [g·mol ⁻¹] |
|-----------------|------------------------------|
| 1:5 | 565 |
| 1:4 | 452 |
| 1:3 | 339 |

Determination of the copolymerization parameters

The copolymerization parameters were determined by the methods of Fineman-Ross and Mayo- Lewis. The Fineman-Ross method uses a linearization of the copolymerization equation (S1)^{S1}.

$$\frac{d[A]}{d[B]} = \frac{1 + r_A \frac{[A]}{[B]}}{1 + r_A \frac{[B]}{[A]}} = \frac{[A]}{[B]} * \frac{r_A[A] + [B]}{[A] + r_B[B]} \quad (S1)$$

With [A] and [B] being the concentration of the monomers and r_A and r_B the respective copolymerization parameters. The linearization suggested by Fineman and Ross leads to Equation (2)

$$y * \frac{x-1}{x} = \frac{y^2 r_A}{x} - r_B \quad (S2)$$

With $x = n_A n_B^{-1}$ and $y = [A] [B]^{-1}$

Where n_A and n_B is the amount of monomer A and B, respectively. The copolymerization parameters can be determined with the slope (r_A) and the y-intercept (r_B) plotting $y \cdot (x-1) x^{-1}$ against $y^2 x^{-1}$.

Determination of the copolymerization parameters by Mayo-Lewis

Another linearization was suggested by Mayo and Lewis (Equation S3)^{S2}

$$r_A = \frac{[B]}{[A]} \left[\frac{n_A}{n_B} \left(1 + \frac{[B]}{[A]} r_B \right) - 1 \right] \quad (S3)$$

Every monomer ratio will result in a straight line. The intersections of these lines will give the copolymerization parameters.

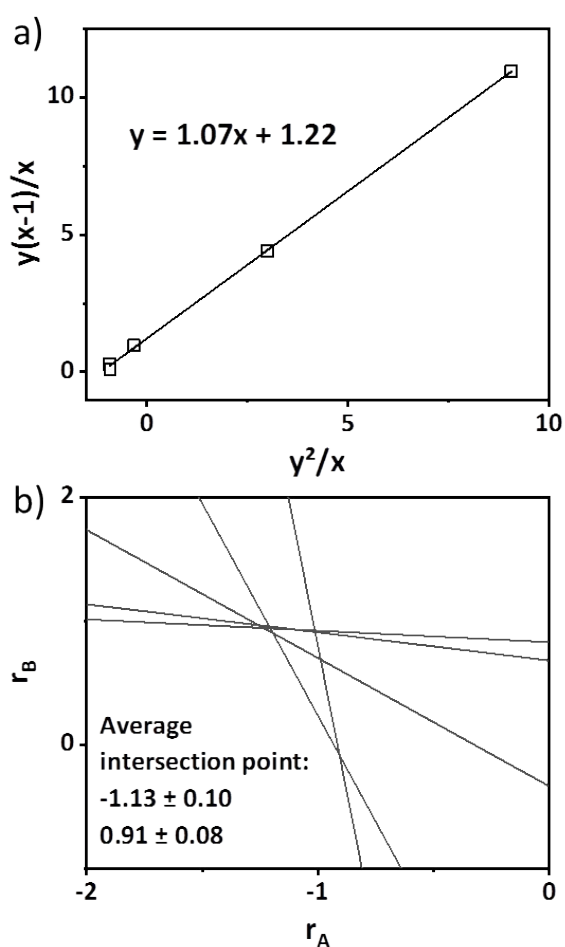


Figure S1. Copolymerization parameters determined with the methods of a) Fineman-Ross and b) Mayo-Lewis

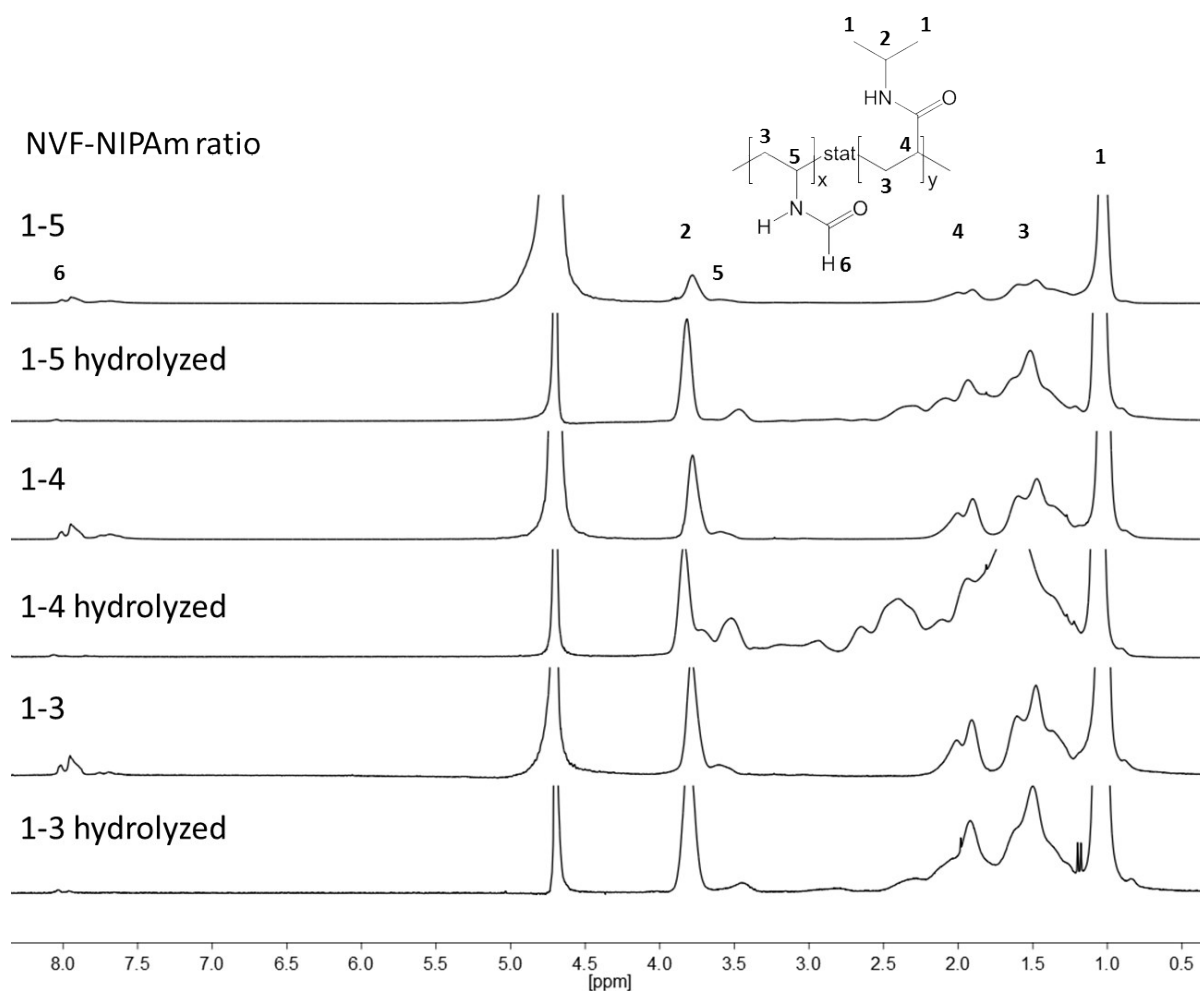


Figure S2. Proton NMR spectra of p(NVF-co-NIPAm) before and after hydrolysis. It is visible that the signal of the formamide proton nearly disappears after hydrolysis.

Table S2. Theoretical and experimental integral ratios 1:5, 1:4, and 1:3. The integral of the iso-propylgroup was taken as reference.

| VAm:NIPAm ratio | Integral iso-propyl group I1/6 | Integral formamide group I6 |
|-----------------|--------------------------------|-----------------------------|
| 1:5 | 5 | 0.99 |
| 1:4 | 4 | 1.29 |
| 1:3 | 3 | 1.01 |



Figure S3. Proton NMR spectra of phenylcarbonate telechelic ethylene glycol in CDCl₃.

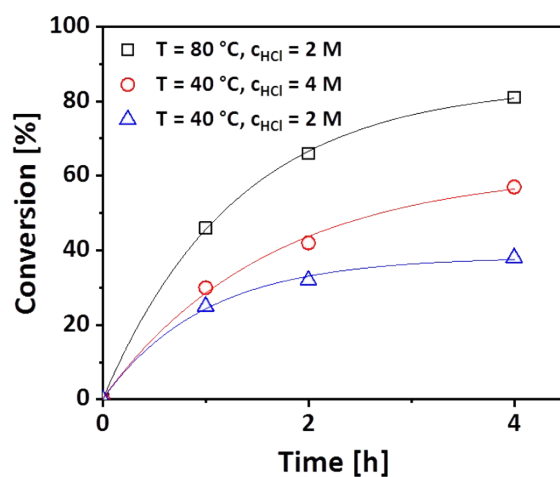


Figure S4. Degree of hydrolysis after 1, 2 and 4 h. The continuous line represents an exponential fit.

Table S3. Degree of hydrolysis for the VAm:NIPAm ratios 1:5, 1:4, and 1:3.

| VAm:NIPAm ratio | Degree of hydrolysis [%] |
|-----------------|--------------------------|
| 1:5 | 91.5 |
| 1:4 | 90.2 |
| 1:3 | 93.3 |

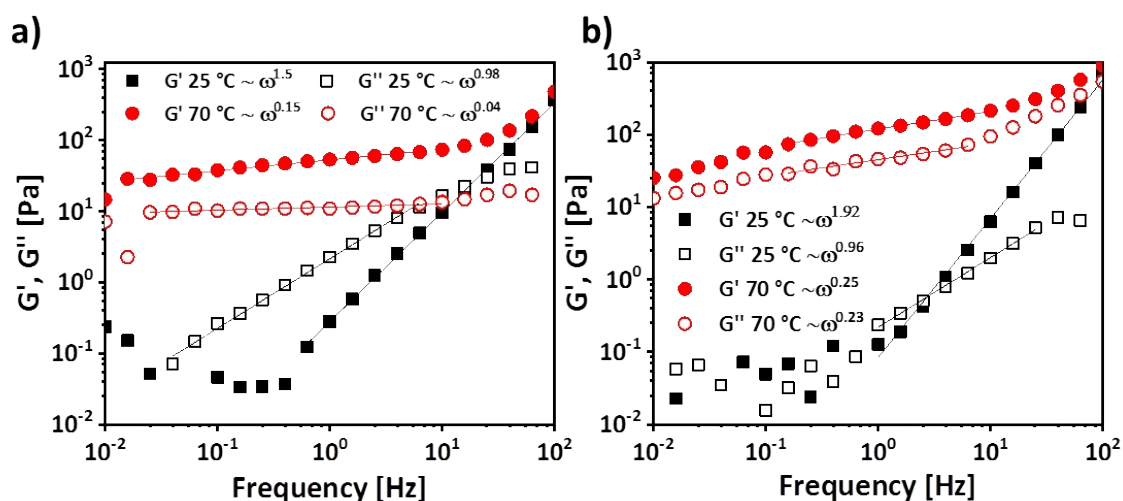


Figure S5. Frequency dependence of storage modulus (G') and loss modulus (G'') for P(VAm-co-NIPAm) linear polymers with VAm:NIPAm monomer ratios of 1:3 (a) and 1:4 (b). The rheometry measurements were made at temperature of 25 °C (squares) and 70 °C (circles). The frequency dependence power law exponents are shown in the figure legend and obtained from the fit with a straight lines.

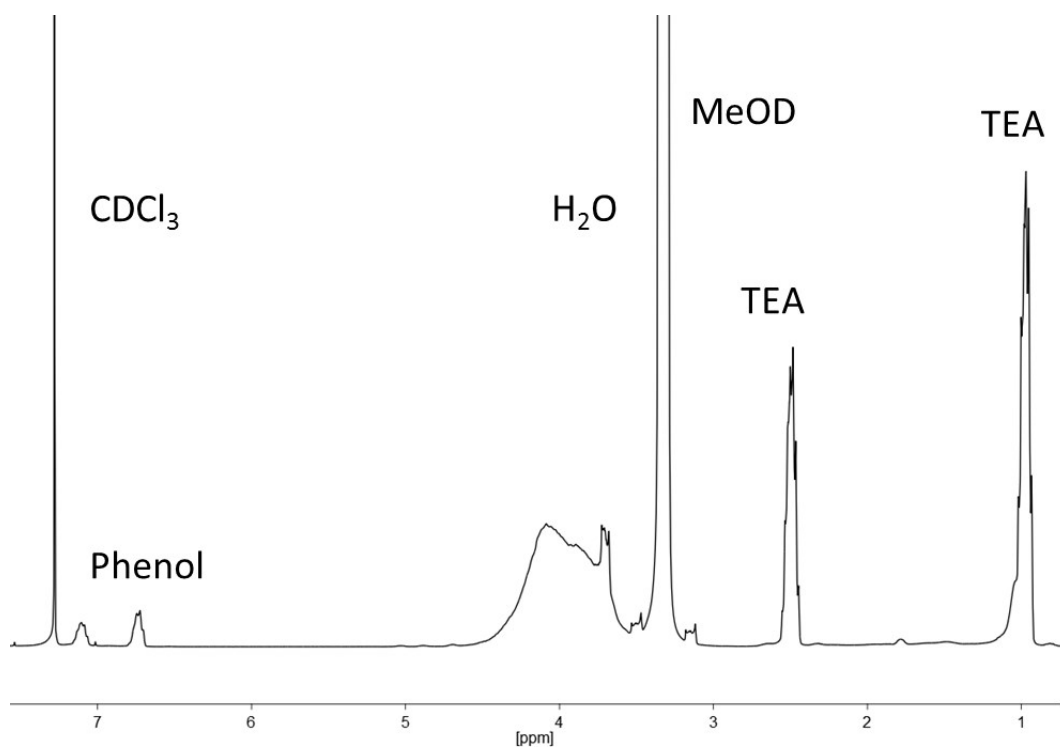


Figure S6. Proton NMR spectrum of the gel prepared inside the NMR tube in CDCl₃ and MeOD in presence of triethyl amine (TEA). The presence of phenol shows the successful conversion of the crosslinker.

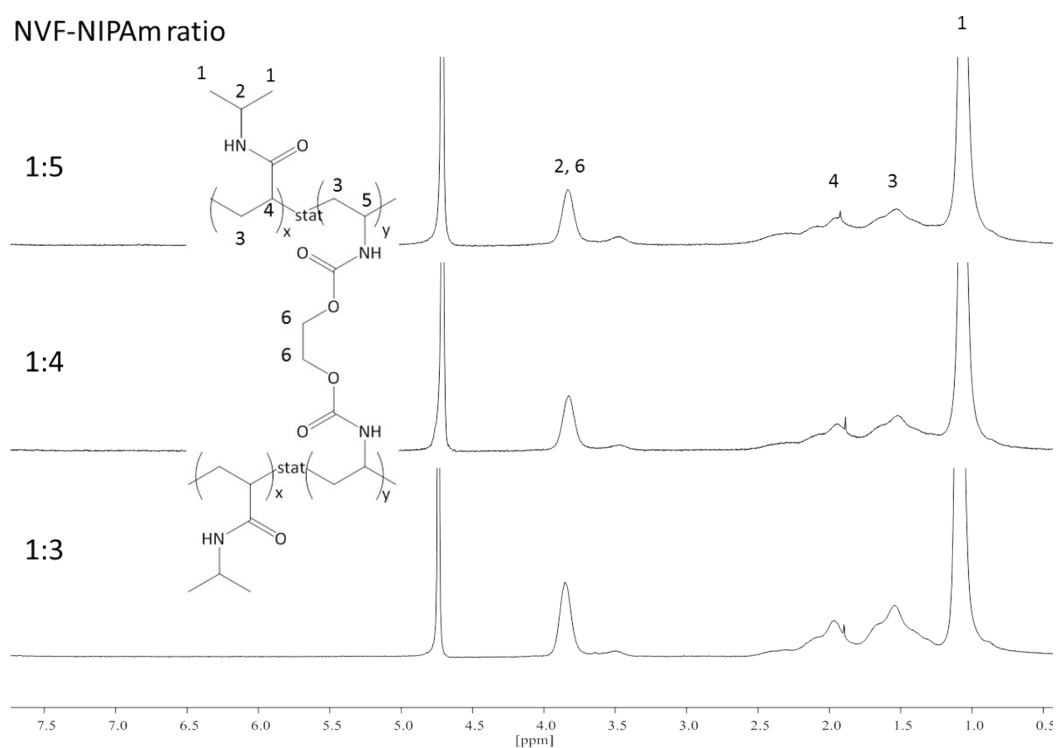


Figure S7. Proton NMR spectra of the washed hydrogels in D₂O. It is visible that there is no phenol present

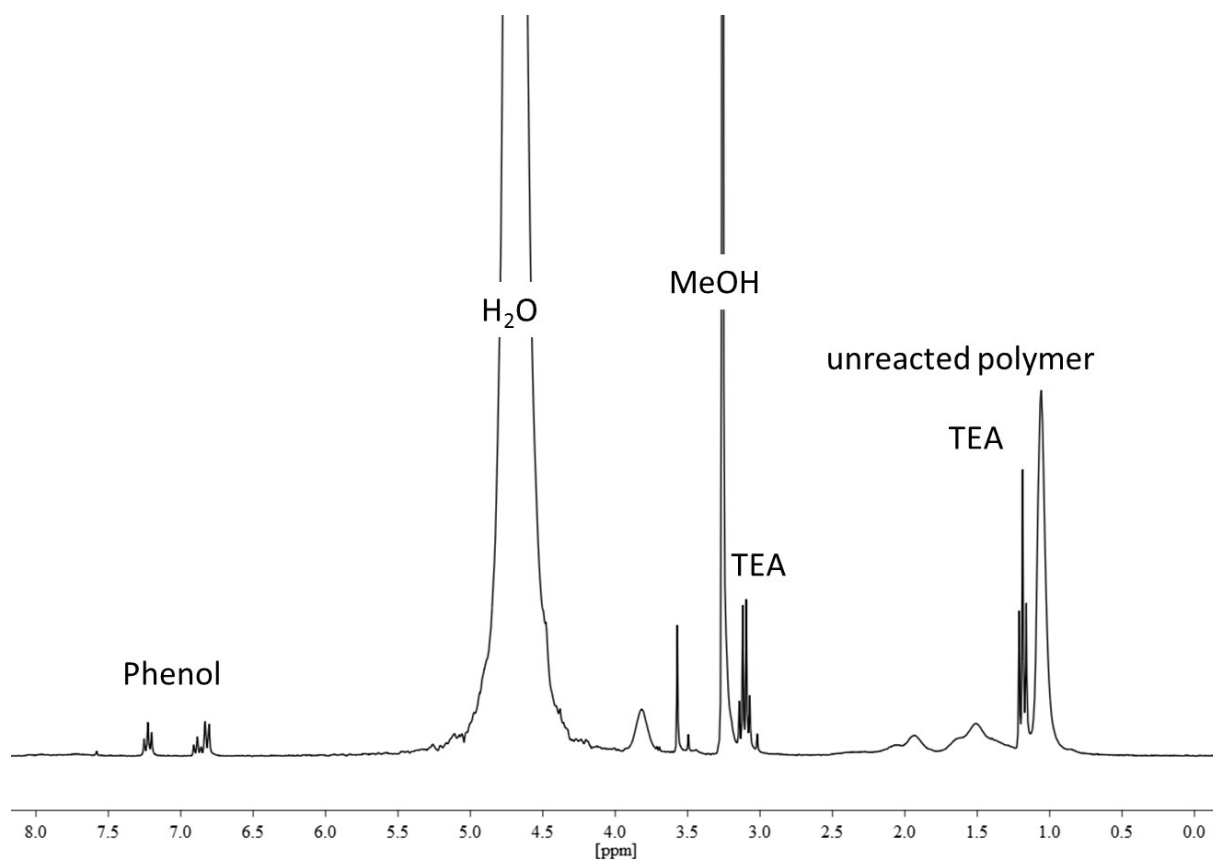


Figure S8. Proton NMR spectrum of the washing solution, where the phenol and (TEA) is present

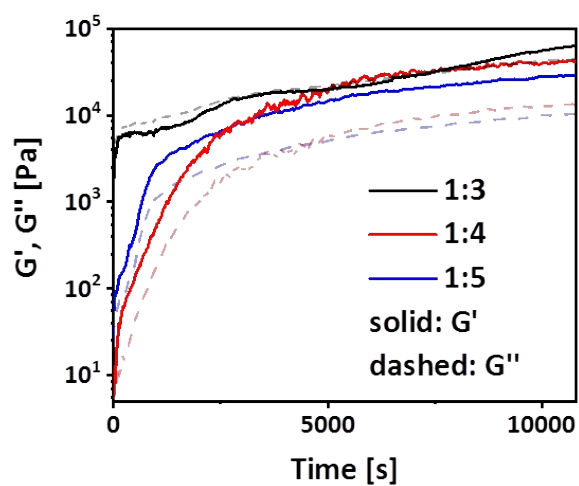


Figure S9. The storage modulus G' and loss modulus G'' in dependence of the time for the gelation of different VAm:NIPAm ratios inside the rheometer.

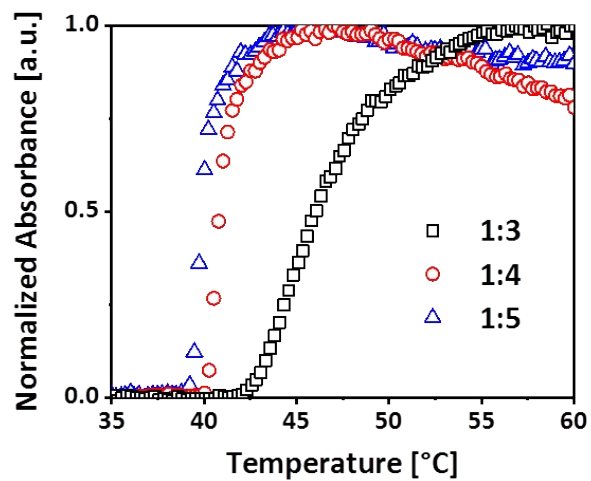
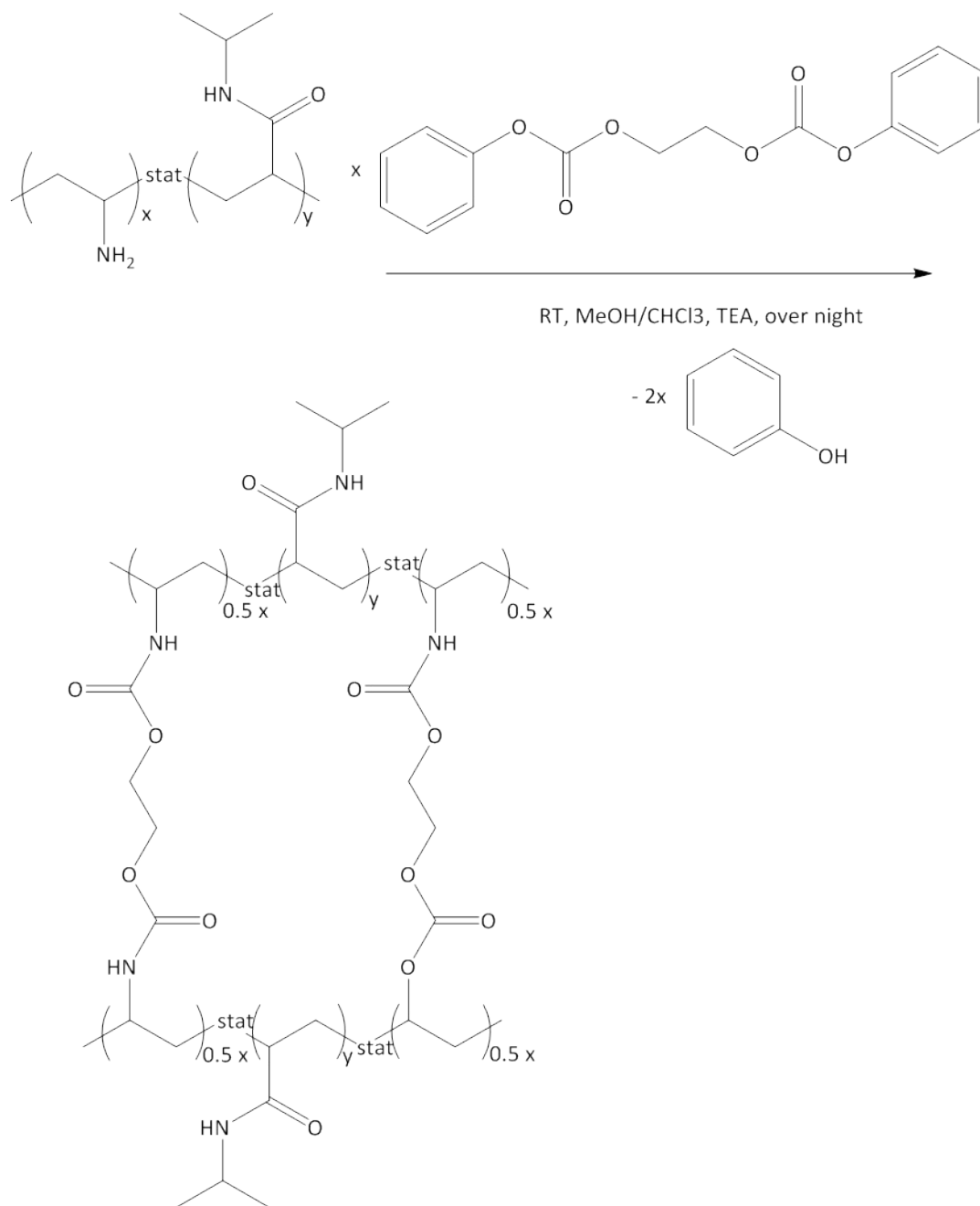


Figure S10. UV-Vis spectra of the swollen gels with different VAm:NIPAm ratio in dependence of the temperature (260 nm, pH = 7, 0.5 °C·min⁻¹).



Scheme S1. Gelation of P(VAm-co-NIPAm) with phenylcarbonate telechelic ethylene glycol.

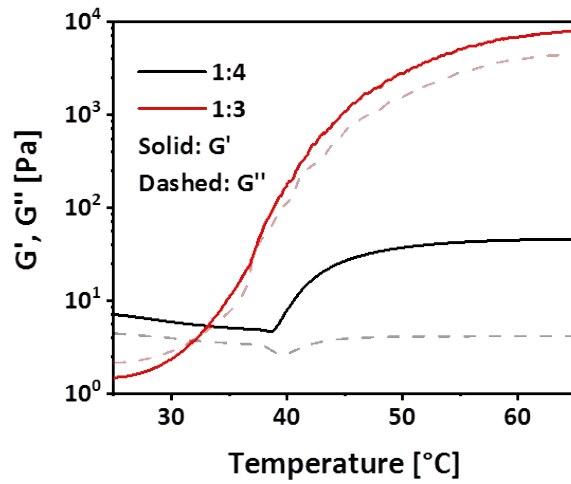


Figure S11. Temperature ramp of the swollen gels for the VAm:NIPAm ratio of 1:4 and 1:3.

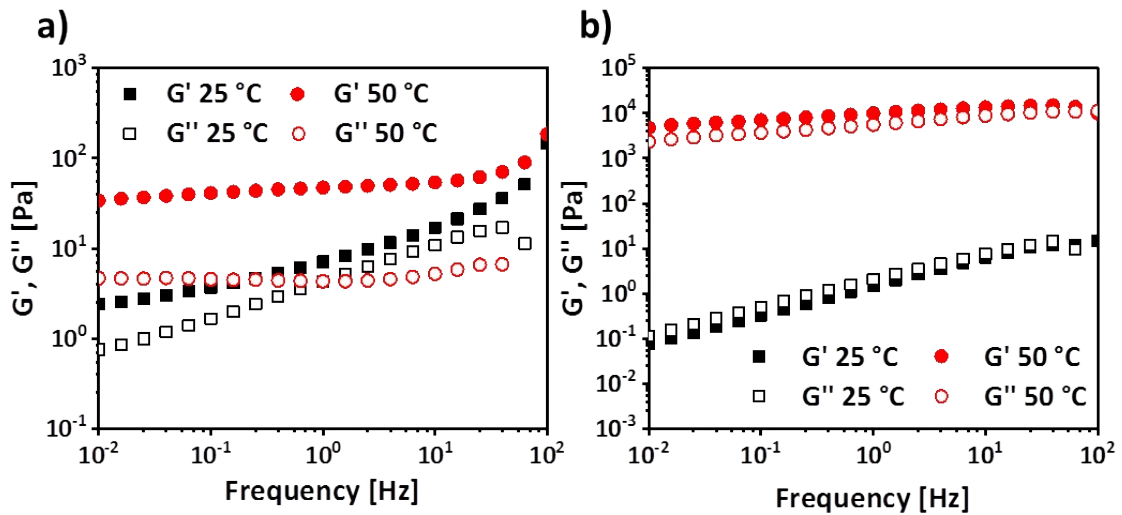


Figure S12. Frequency dependence of the swollen gels with the VAm:NIPAm ratios of 1:4 (a) and 1:3 (b).

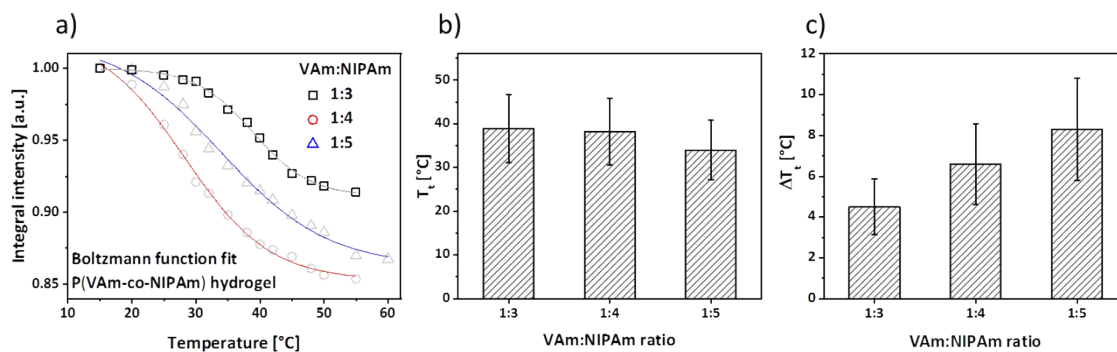


Figure S13 (a) Temperature-induced phase transition curves of poly(VAm-*stat*-NIPAm) hydrogels with different VAm:NIPAm monomer ratios. The data were fitted with Boltzmann functions and shown with continuous lines. (b) Transition temperatures T_t , and (c) width of transition temperatures ΔT_t as a function of monomer ratios obtained from the fits with Boltzmann functions.

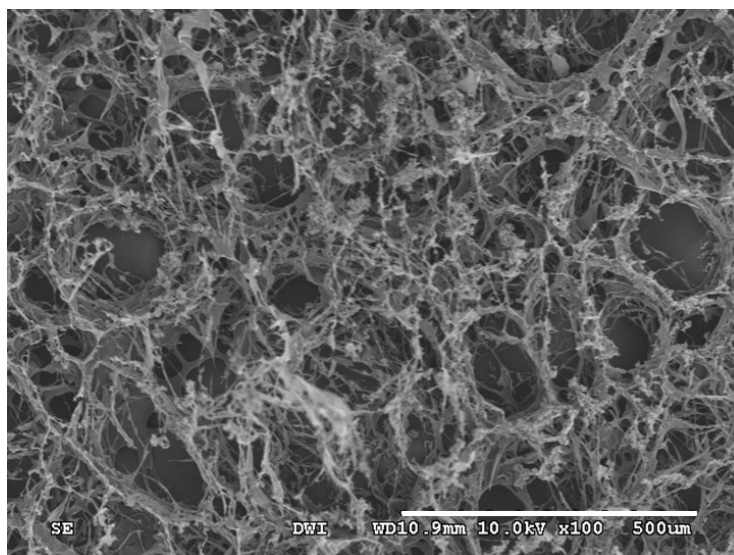


Figure S14. SEM image of the hydrogel with the VAm:NIPAm ratio 1:5. The scale bar represents 500 μm.

References

- S1 M. Fineman and S. D. Ross, *J. Polym. Sci.*, 1950, **5**, 259-265.
 S2 F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, 1944, **66**, 1594-1601.