

Supporting Information for

Strategies to Increase the Thermal Stability of Truly Biomimetic Hydrogels: Combining Hydrophobicity and Directed Hydrogen Bonding

Hongbo Yuan^{†,§}, Jialiang Xu^{*,‡,§}, Eliane P. van Dam[&], Giulia Giubertoni[&], Yves L. A. Rezus[&], Roel Hammink[§], Huib J. Bakker[&], Yong Zhan[†], Alan E. Rowan^{*,§,||}, Chengfen Xing^{*,†} and Paul H. J. Kouwer^{*,§}

[†]School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300401, P.R. China

[‡]School of Chemical Engineering and Technology, Tianjin University, Yaguan Road 135, 300350, Tianjin, P.R. China

[§]Institute for Molecules and Materials (IMM), Radboud University, Heyendaalseweg 135, 6525AJ Nijmegen, The Netherlands

[&]AMOLF, Science Park 104, 1098 XG Amsterdam, The Netherlands

^{||}Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, QLD 4072, Australia

*Email: jialiang.xu@tju.edu.cn; xingc@hebut.edu.cn; alan.rowan@uq.edu.au; p.kouwer@science.ru.nl

Table of Contents

a.	¹ H, ¹³ C NMR spectra of 3EG-L-Ala-D-Ala-L-Ala-Boc.....	S2
b.	¹ H, ¹³ C NMR spectra of 3EG-L-Ala-D-Ala-L-Ala-For.....	S3
c.	¹ H, ¹³ C NMR spectra of monomer	S4
d.	AFM images of polymer.....	S5
e.	Frequency sweeps of TriPIC gel	S5
f.	Reversibility of TriPIC gel.....	S5
g.	Mechanical properties of TriPIC gels with polymer length.....	S6
h.	Mechanical properties of TriPIC gels with salt.....	S6
i.	Deconvoluted components of FTIR at each temperature	S7
j.	FTIR spectra of the TriPIC polymer at 20 °C	S8
k.	FTIR spectra of the TriPIC monomer with temperature	S8
l.	UV-vis spectra of TriPIC polymer with temperature.....	S8

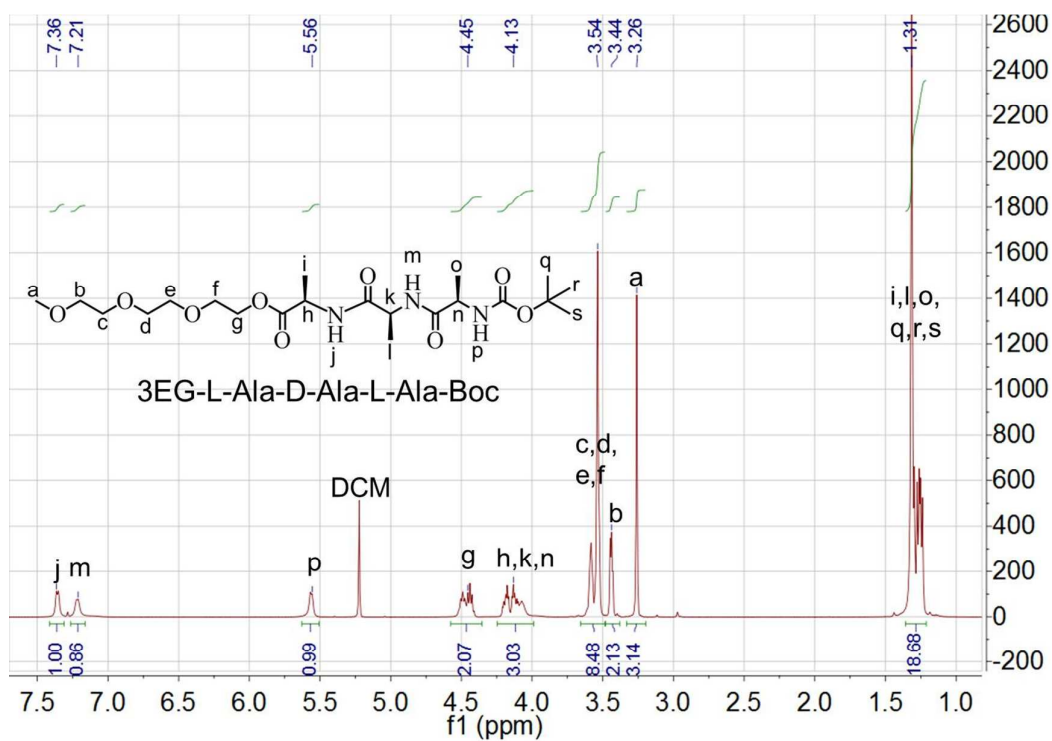


Figure S1. ^1H NMR spectra of 3EG-L-Ala-D-Ala-L-Ala-Boc.

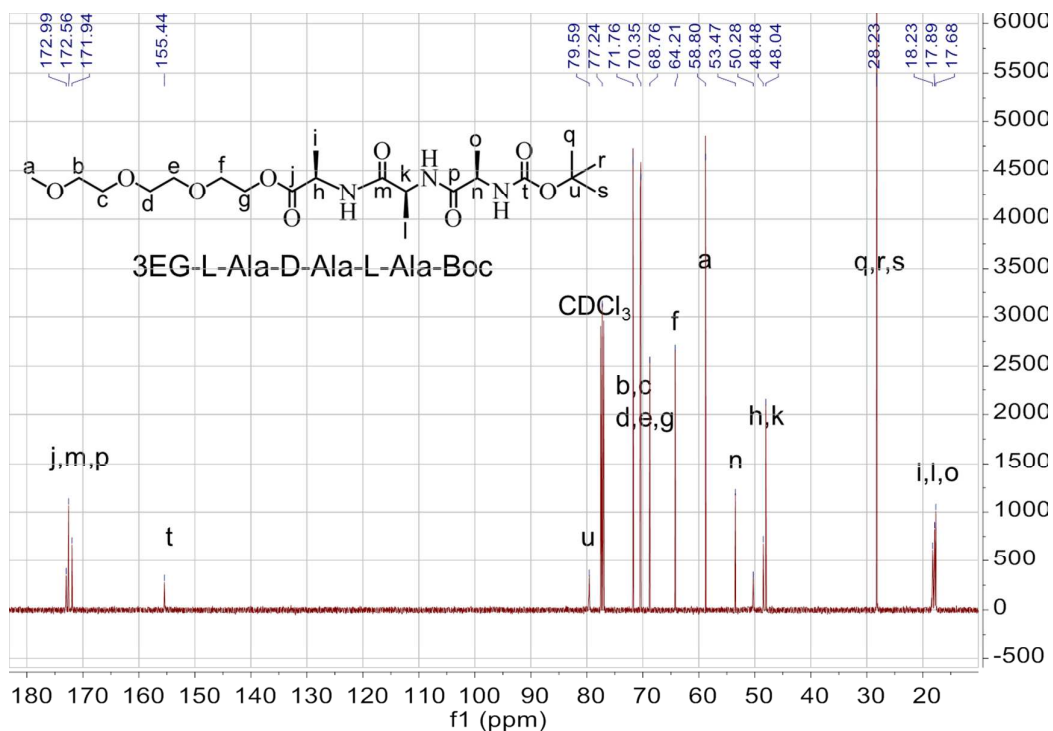


Figure S2. ^{13}C NMR spectra of 3EG-L-Ala-D-Ala-L-Ala-Boc.

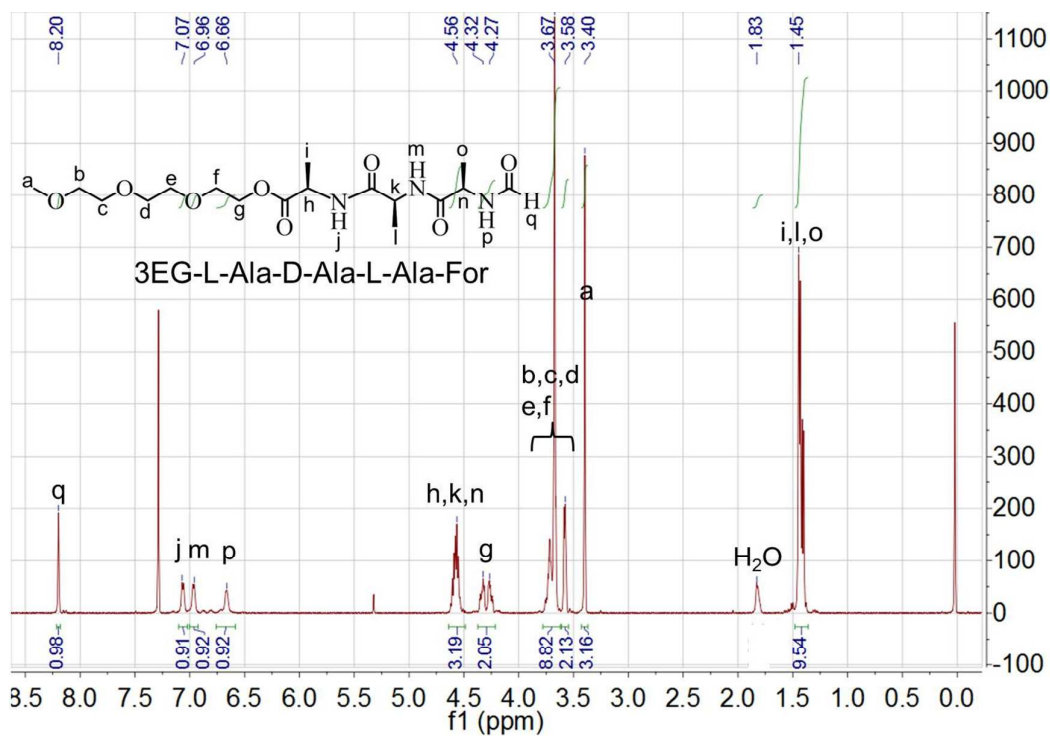


Figure S3. ¹H NMR spectra of 3EG-L-Ala-D-Ala-L-Ala-For.

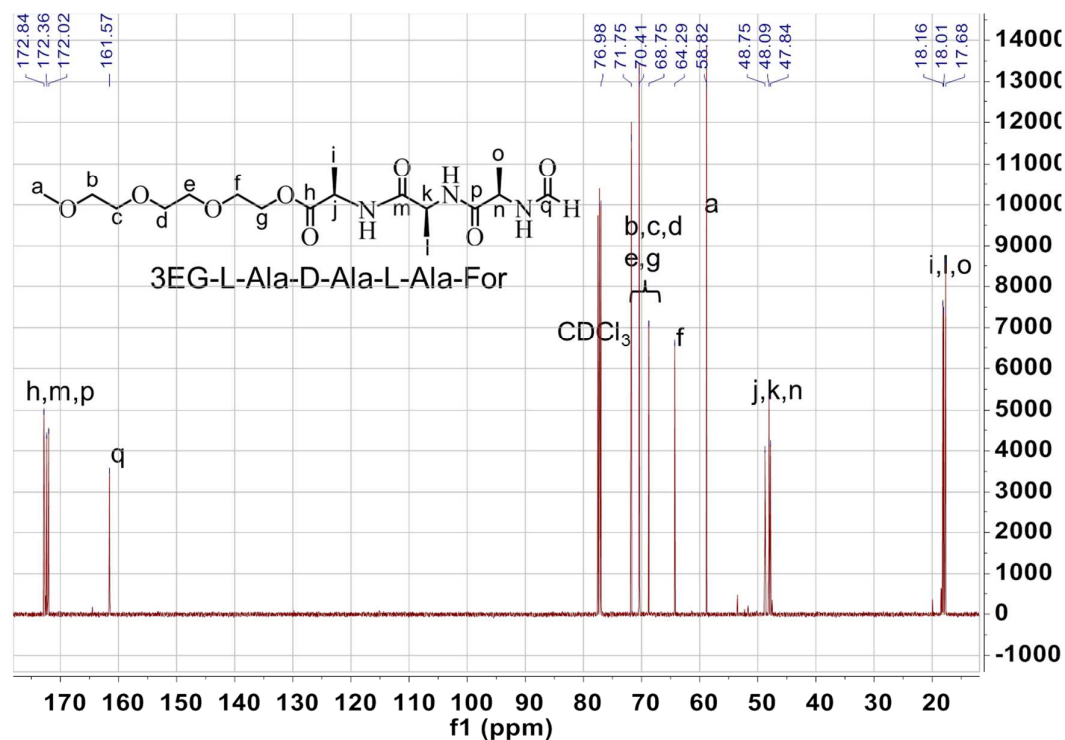


Figure S4. ¹³C NMR spectra of 3EG-L-Ala-D-Ala-L-Ala-For.

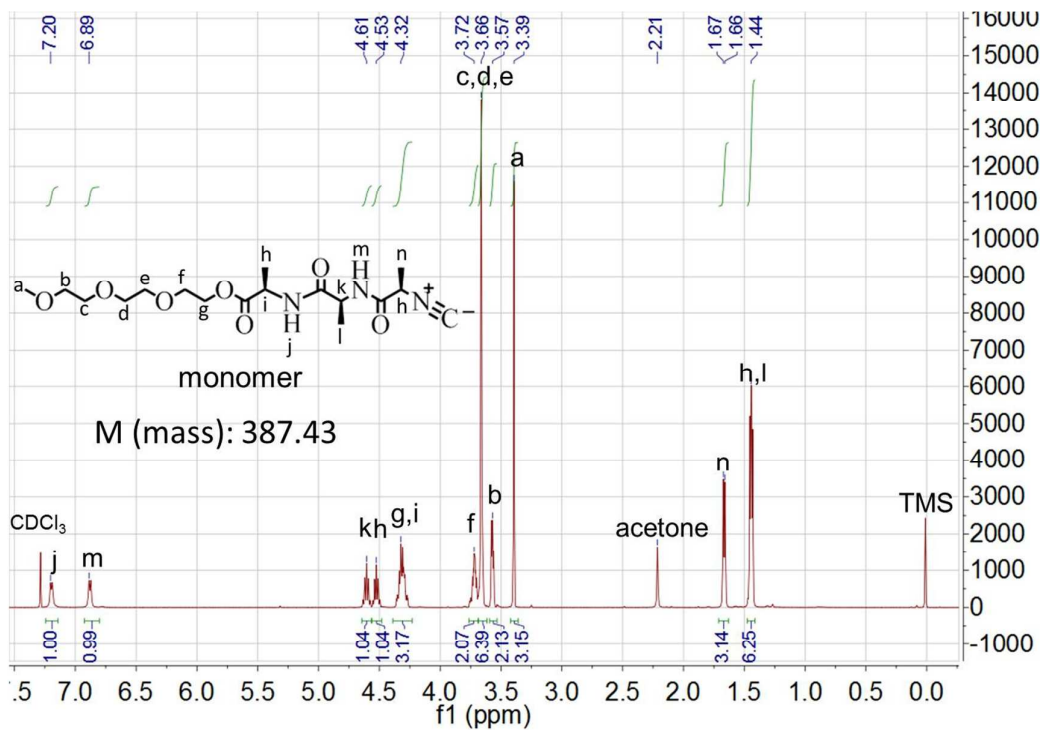


Figure S5. ¹H NMR spectra of the monomer.

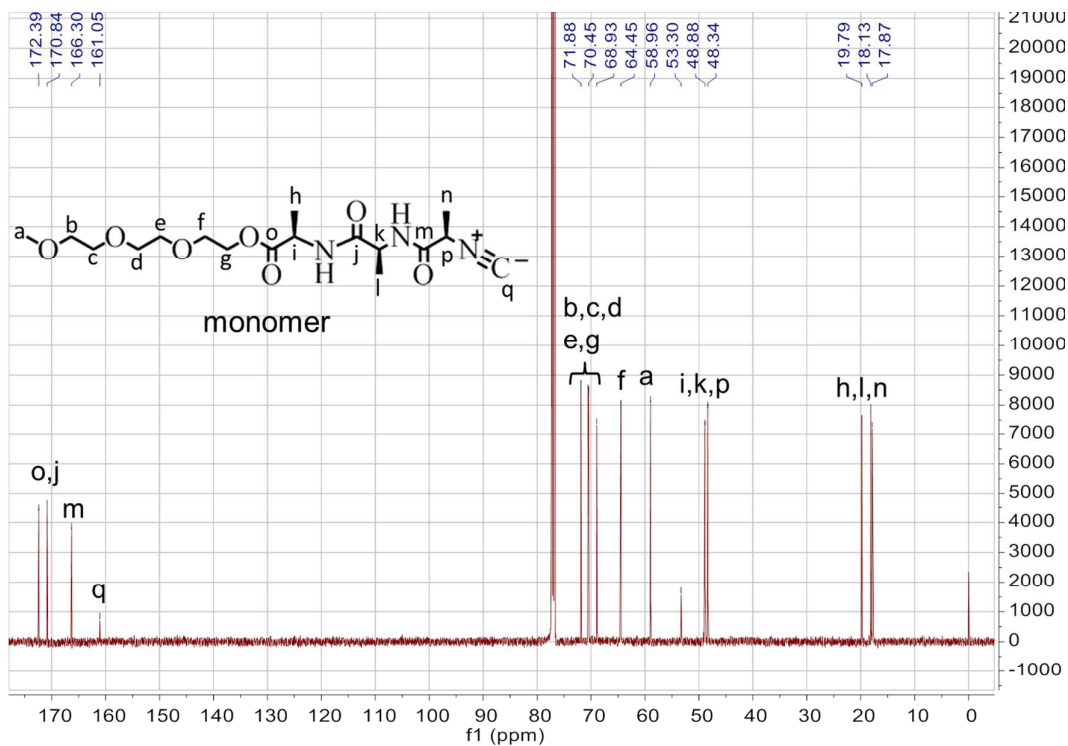


Figure S6. ¹³C NMR spectra of the monomer.

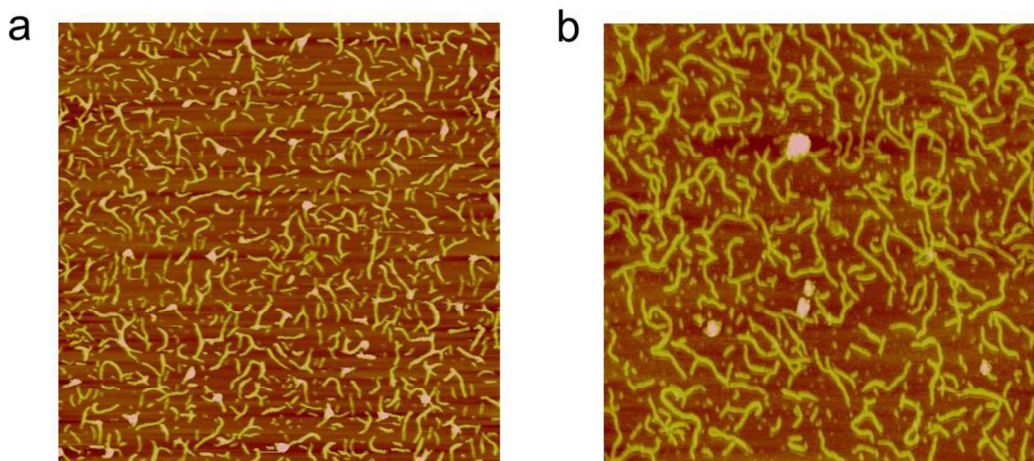


Figure S7. The representative AFM images of polymer TriPIC-a (a) and TriPIC-f (b).

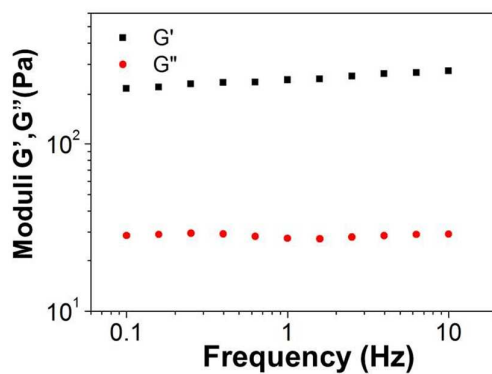


Figure S8. Frequency sweeps of TriPIC-f gel (2.0 g L^{-1}) in the linear viscoelastic regime at $80 \text{ }^\circ\text{C}$.

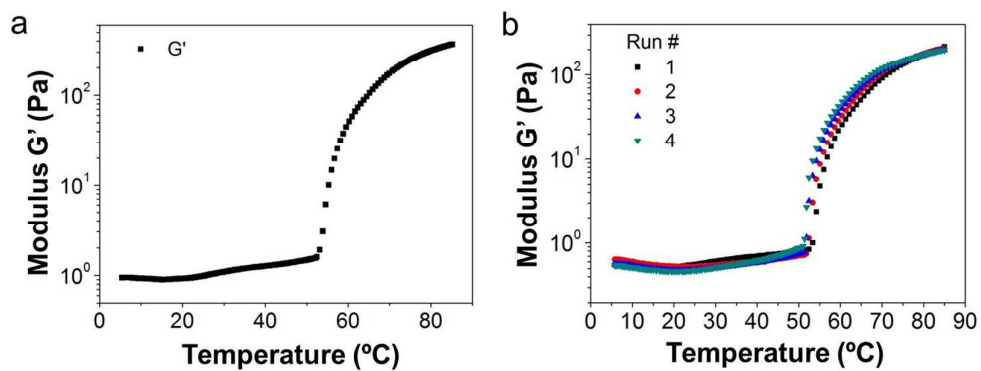


Figure S9. (a) Modulus G' of TriPIC-f as a function of temperature after the 10 h time sweep performed at $80 \text{ }^\circ\text{C}$. (b) Storage modulus G' of TriPIC-f as a function of temperature for 4 sequential heating and cooling runs, $c = 2.0 \text{ g L}^{-1}$.

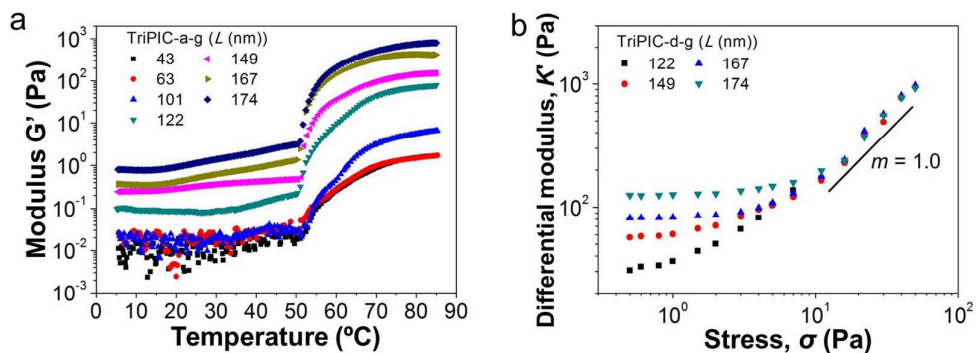


Figure S10. (a) Temperature ramps of the storage modulus G' for different length (L) polymers. (b) Differential modulus K' against stress for different length (L) polymers at 60 $^{\circ}\text{C}$, $c = 2.0 \text{ g L}^{-1}$.

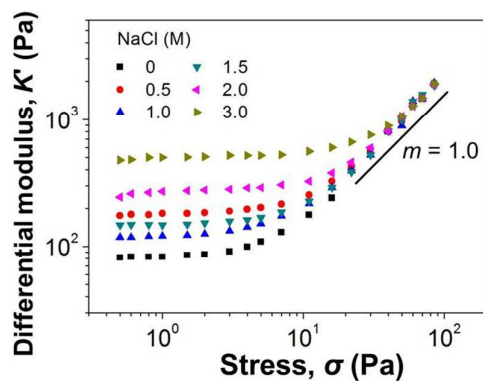


Figure S11. The differential modulus K' as a function of the applied stress for TriPIC-f with different concentrations of NaCl at 60 $^{\circ}\text{C}$.

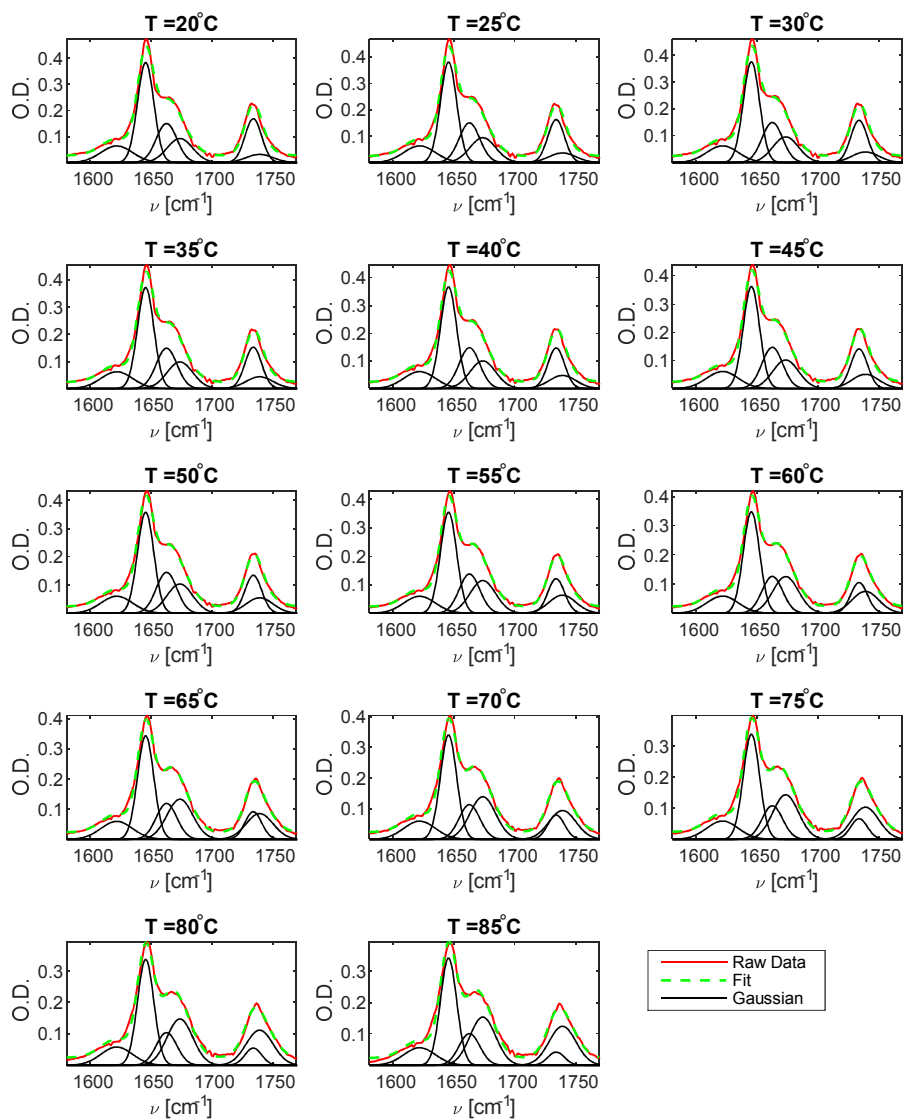


Figure S12. The best-fitted FTIR spectra and the deconvoluted components with 6 Gaussian-curves at 1622, 1646, 1661, 1674, 1734 and 1739 cm^{-1} in the 1550–1780 cm^{-1} region for TriPIC polymers at each temperature.

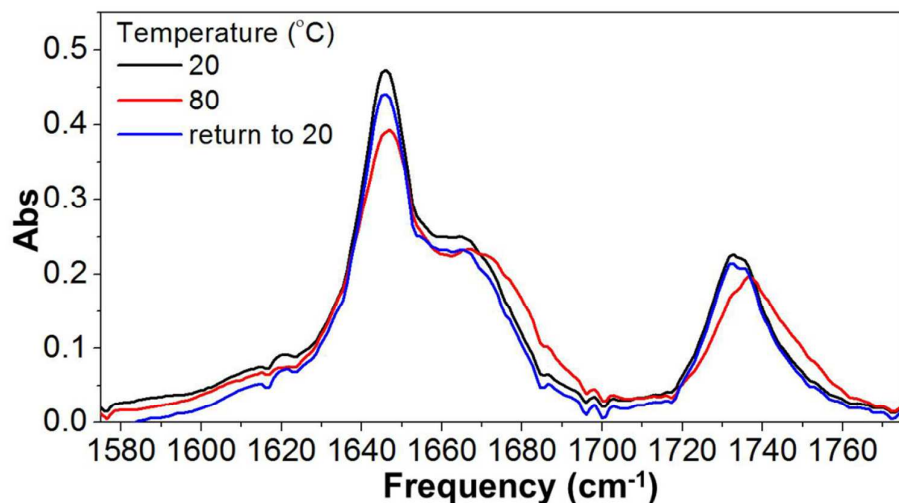


Figure S13. FTIR spectra of the TriPIC polymer (17.0 g L^{-1} in D_2O) in the amide I and ester regions at $20 \text{ }^\circ\text{C}$ cooling down from $80 \text{ }^\circ\text{C}$.

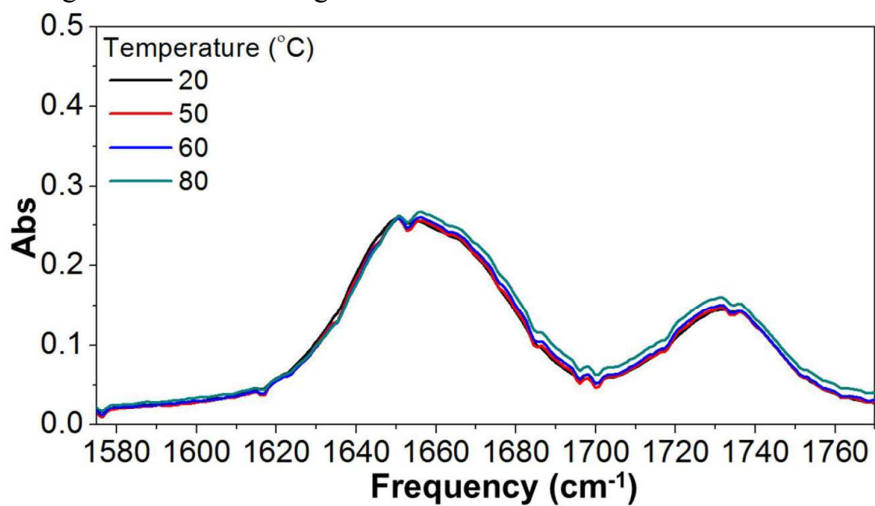


Figure S14. FTIR spectra of the TriPIC monomer (17.0 g L^{-1} in D_2O) in the amide I and ester regions as a function of temperature.

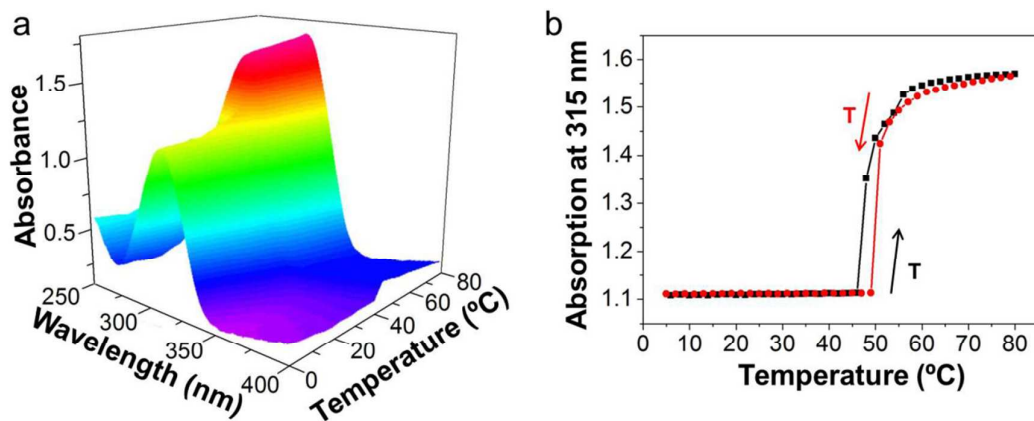


Figure S15. (a) UV-vis spectra of TriPIC as a function of temperature. (d) Evaluation of the absorption signal at $\lambda = 315 \text{ nm}$ of TriPIC with temperature. Measurements were performed in water, $c = 0.5 \text{ g L}^{-1}$.