Supplementary material

Structure–property relations in linear viscoelasticity of supramolecular hydrogels

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S-1 Nomenclature of symbols

a – coefficient in Eq. (23)

f – probability density

f_0 – pre-factor in Eq. (9)

G', G'' – storage and loss moduli

G_r – relaxation modulus

k_B – the Boltzmann constant

K – coefficient in Eq. (22)

n – number of active chains (per unit volume)

N – total number of active chains

P – number of chains merging with a network (per unit volume and unit time)

t – time

T_0 – initial temperature

u – activation energy

v – dimensionless activation energy

w – strain energy of an active chain

W – strain energy density of a network

γ – coefficient in Eq. (22)

Γ – rate of dissociation of bonds

Γ_0 – attempt rate

ϵ – shear strain

ϵ^* – relative shear strain

μ – elastic modulus of a network

$\bar{\mu}$ – rigidity of a chain

σ – shear stress

Σ – standard deviation of the quasi-Gaussian distribution

τ, τ_0, τ_1, τ_2 – instants of time

ω – angular frequency of oscillations.

S-2 Protein hydrogels (Section 3.1)

The protein gels (Sun et al. [1]) consist of two proteins, CCE-$(GB_1)_4$-CCE and CCK-$(GB_1)_5$-CCK-$(GB_1)_5$-CCK, phycally cross-linked by coiled-coil complexes between CCK and CCE blocks (complementary leucine zipper sequences) (Lv et al. [2]). Recombinant protein GB_1 comprises 56 residues of Immunoglobulin G Streptococcus (Gronenborn et al. [3]). Synthetic polypeptides CCK and CCE are formed by heptide repeated units $(abcdefg)_5$ with hydrophobic residuals in a and d positions, charged residuals in e and g positions, and hydrophilic residuals in b, c and f positions. The sequence of amino acids in polypeptides CCK and CCE reads (Sun et al. [1])

Peptide		g	abcdefg	abcdefg	abcdefg	absdefg	abcdef	
CCK	LG	K	VSALKEK	VSALKEE	VSANKEK	VSALKEK	VSALKE	LG
CCE	LG	E	VSALEKE	VSALEKK	VSANEKE	VSALEKE	VSALEK	LG

Here A = alanine, E = glutamic acid, G = glycine, K = lysine, L = leucine, N = asparagine, S = serine, V = valine.

Table S-1: Material parameters for protein gel at various temperatures T.

T °C	μ kPa	γ s^{-1}	Σ	K
20	0.788	1.1	1.05	0.036
37	0.785	9.5	1.18	0.017

References

[1] W. Sun, T. Duan, Y. Cao and H. Li, *Biomacromolecules*, 2019, **20**, 4199–4207.

[2] S. Lv, Y. Cao and H. Li, *Langmuir*, 2012, **28**, 2269–2274.

[3] A.M. Gronenborn, D.R. Filpula, N.Z. Essig, A. Achari, M. Whitlow, P.T. Wingfield and G.M. Clore, *Science*, 1991, **253**, 657–661.

S-3 Supplementary figures

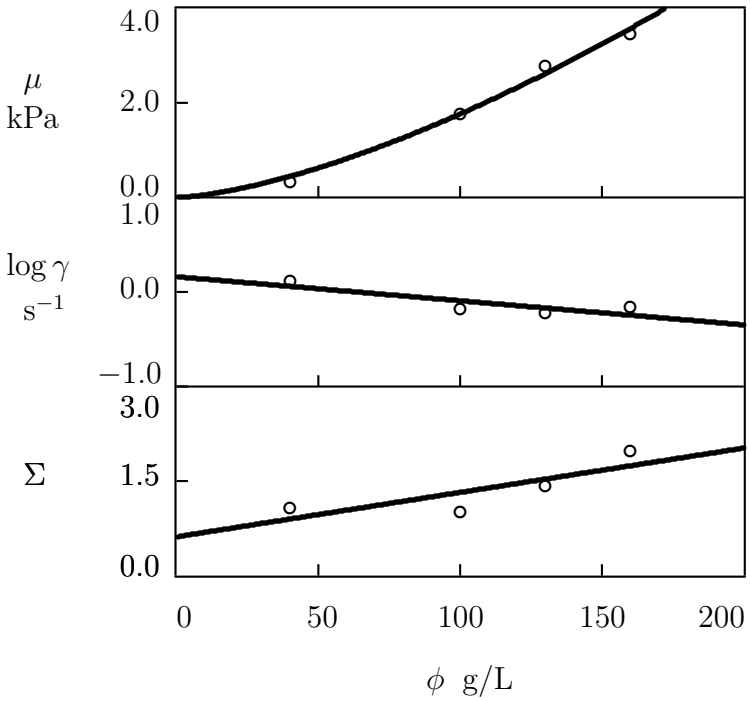

Figure S-1: Parameters μ, γ and Σ versus concentration of proteins ϕ. Circles: treatment of observations (Sun et al., 2019) on protein gels with equal molar fractions of CKK and CCE peptides. Solid lines: results of simulation.

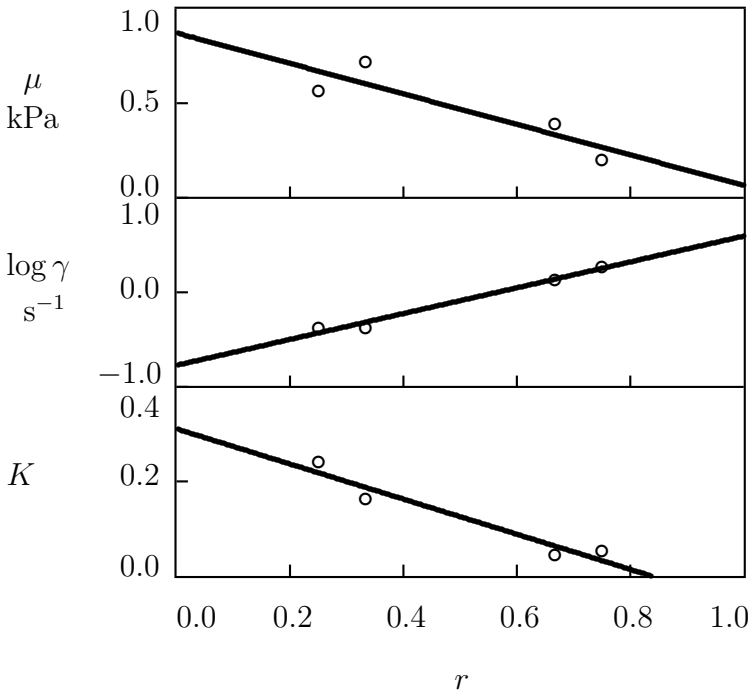

Figure S-2: Parameters μ, γ and K versus molar fraction of CCK peptides r. Circles: treatment of observations (Sun et al., 2019) on protein gels with mass fraction of proteins $\phi = 0.07$. Solid lines: results of simulation.

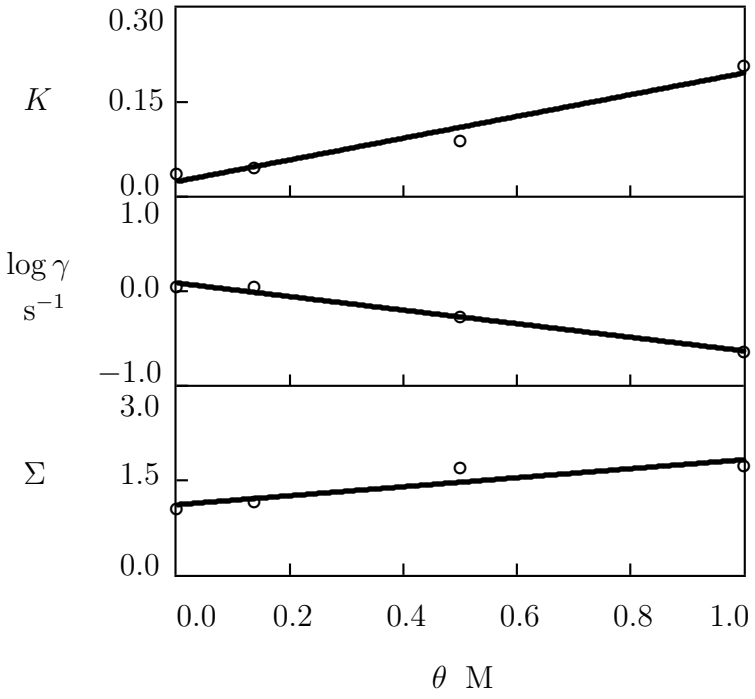

Figure S-3: Parameters K, γ and Σ versus molar fraction θ of NaCl in PBS solution. Circles: treatment of observations (Sun et al., 2019) on protein gels with mass fraction of proteins $\phi = 0.07$ and equal molar fractions of CCK and CCE. Solid lines: results of simulation.

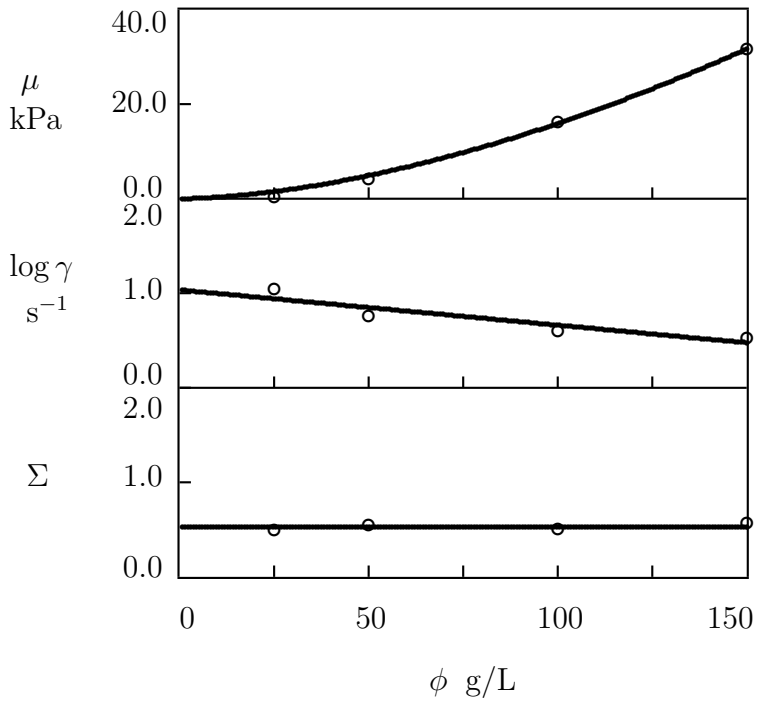

Figure S-4: Parameters μ, γ and Σ versus concentration ϕ of histidine-functionalized PEG chains in buffered solutions. Circles: treatment of observations (Fullenkamp et al., 2013) on histidine-functionalized PEG gels cross-linked with Ni^{2+} ions. Solid lines: results of simulation.

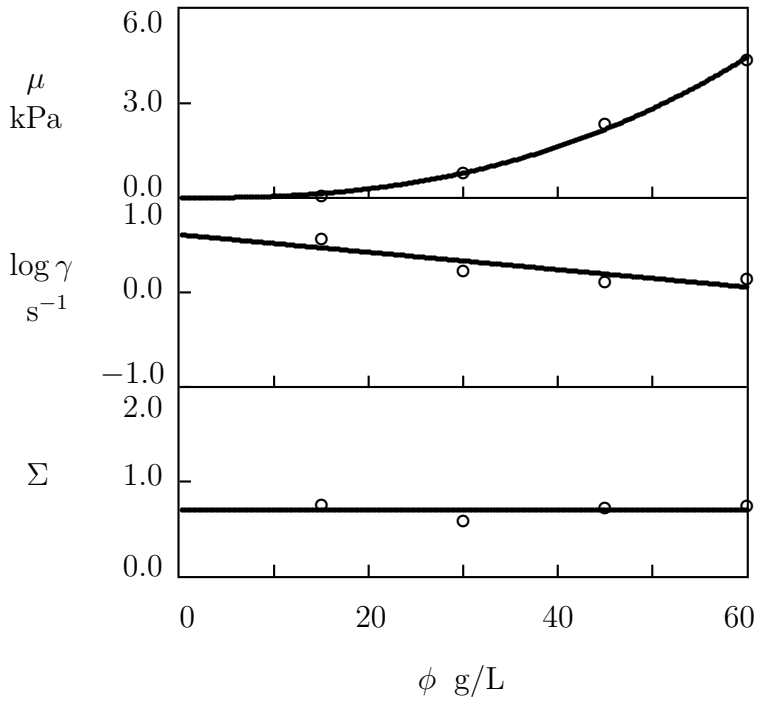

Figure S-5: Parameters μ, γ and Σ versus concentration ϕ of phenanthroline-functionalized PEG chains in buffered solutions. Circles: treatment of observations (Ahmadi and Seiffert, 2021) on phenanthroline-functionalized PEG gels cross-linked with Co^{2+} ions. Solid lines: results of simulation.

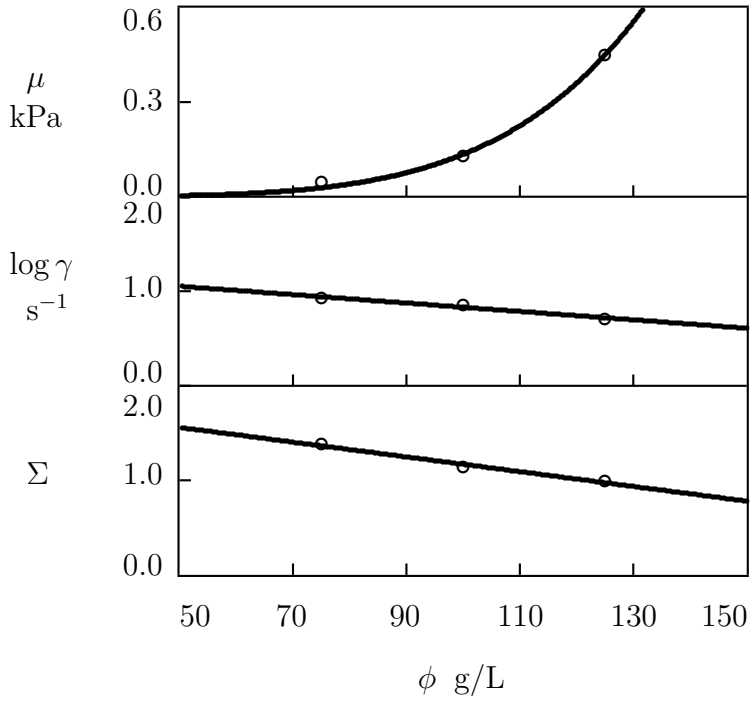

Figure S-6: Parameters μ, γ and Σ versus concentration ϕ of MPC chains functionalized with MAABO and DMA monomers. Circles: treatment of observations (Chen et al., 2018) on MPC gels cross-linked by benzoxaborole-catechol complexes. Solid lines: results of simulation.

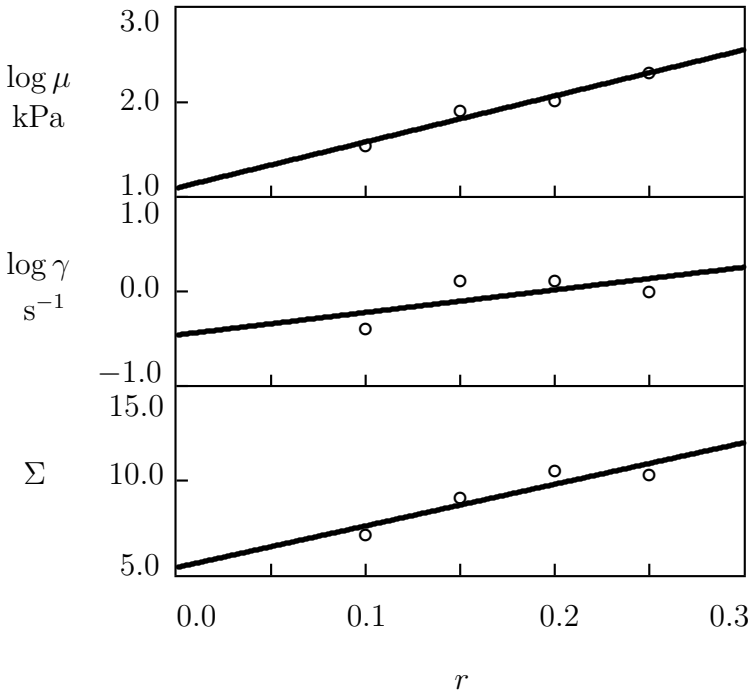

Figure S-7: Parameters μ, γ and Σ versus ratio r of molar fractions of AAc and AAm monomers. Circles: treatment of observations (Zou et al., 2017) on P(AAm-AAc) gels cross-linked with Fe^{3+} ions. Solid lines: results of simulation.

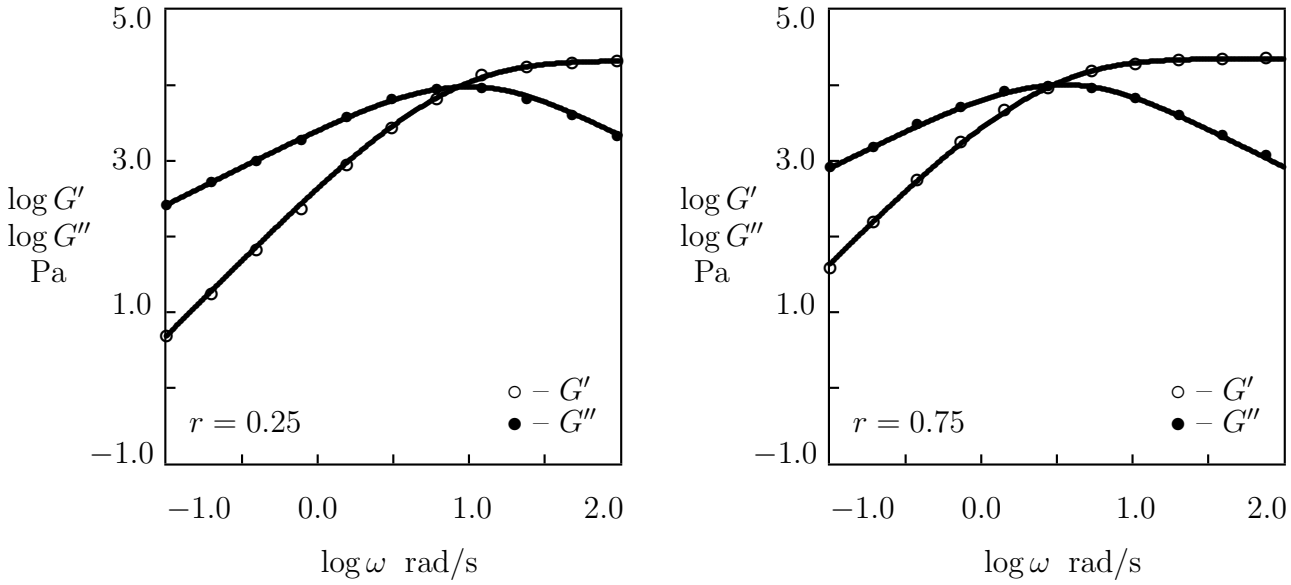

Figure S-8: Storage modulus G' and loss modulus G'' versus frequency ω. Symbols: experimental data (Yesilyurt et al., 2017) on PEG gels cross-linked by phenylboronic acid-diol (PBA-GL and APBA-GL) complexation with mass fractions of PEG-APBA macromers $r = 0.25$ and 0.75. Solid lines: results of simulation.

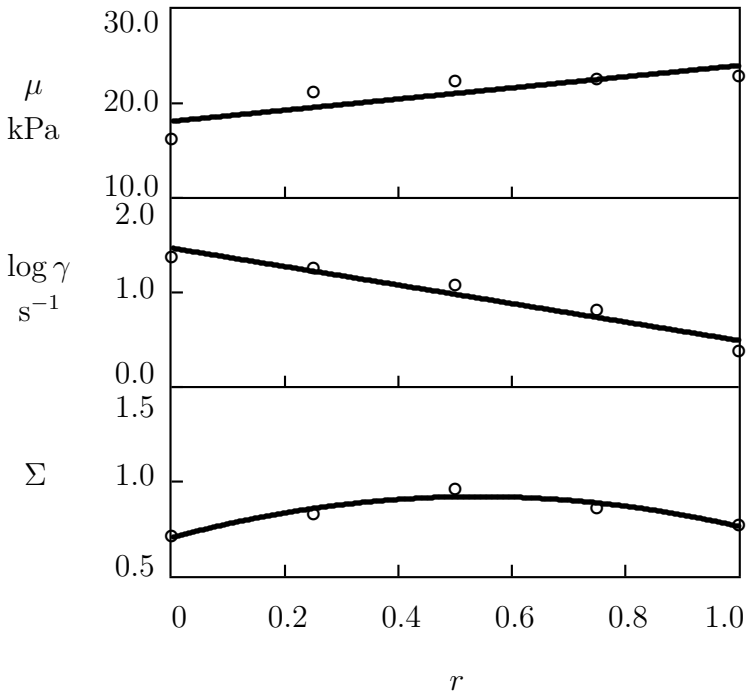

Figure S-9: Parameters μ, γ and Σ versus mass fraction r of PEG-APBA macromers. Circles: treatment of observations (Yesilyurt et al., 2017) on PEG gels cross-linked by phenylboronic acid-diol (PBA-GL and APBA-GL) complexation. Solid lines: results of simulation.

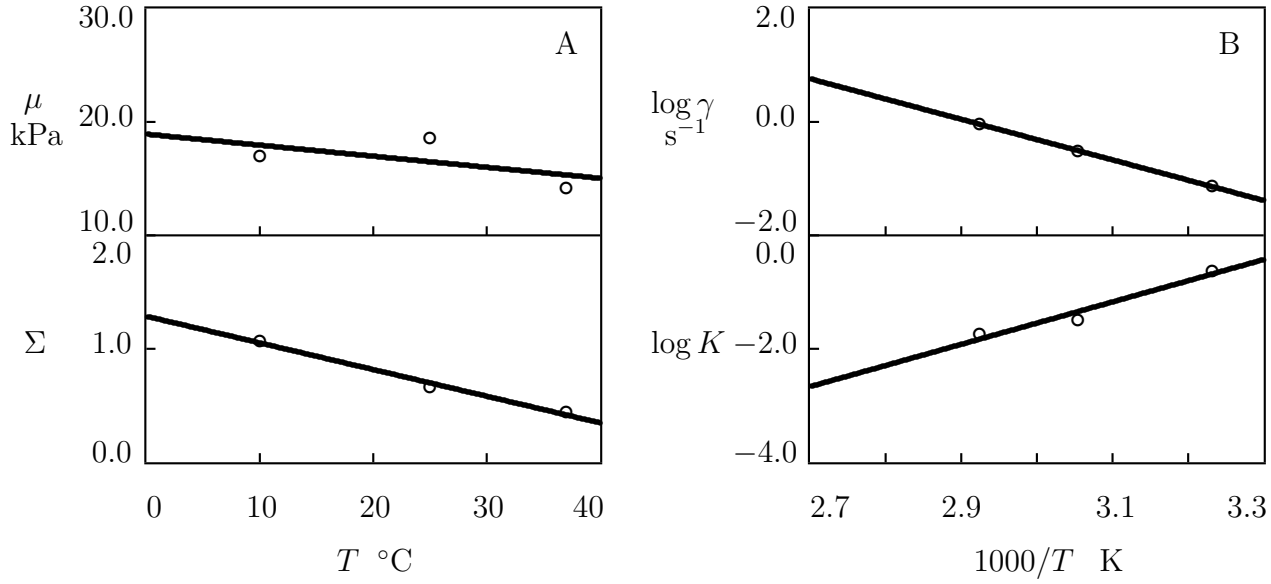

Figure S-10: Parameters μ, Σ (A) and γ, K (B) versus temperature T. Circles: treatment of observations (Fullenkamp et al., 2013) on histidine-modified PEG gels cross-linked with Ni^{2+} ions. Solid lines: results of simulation.

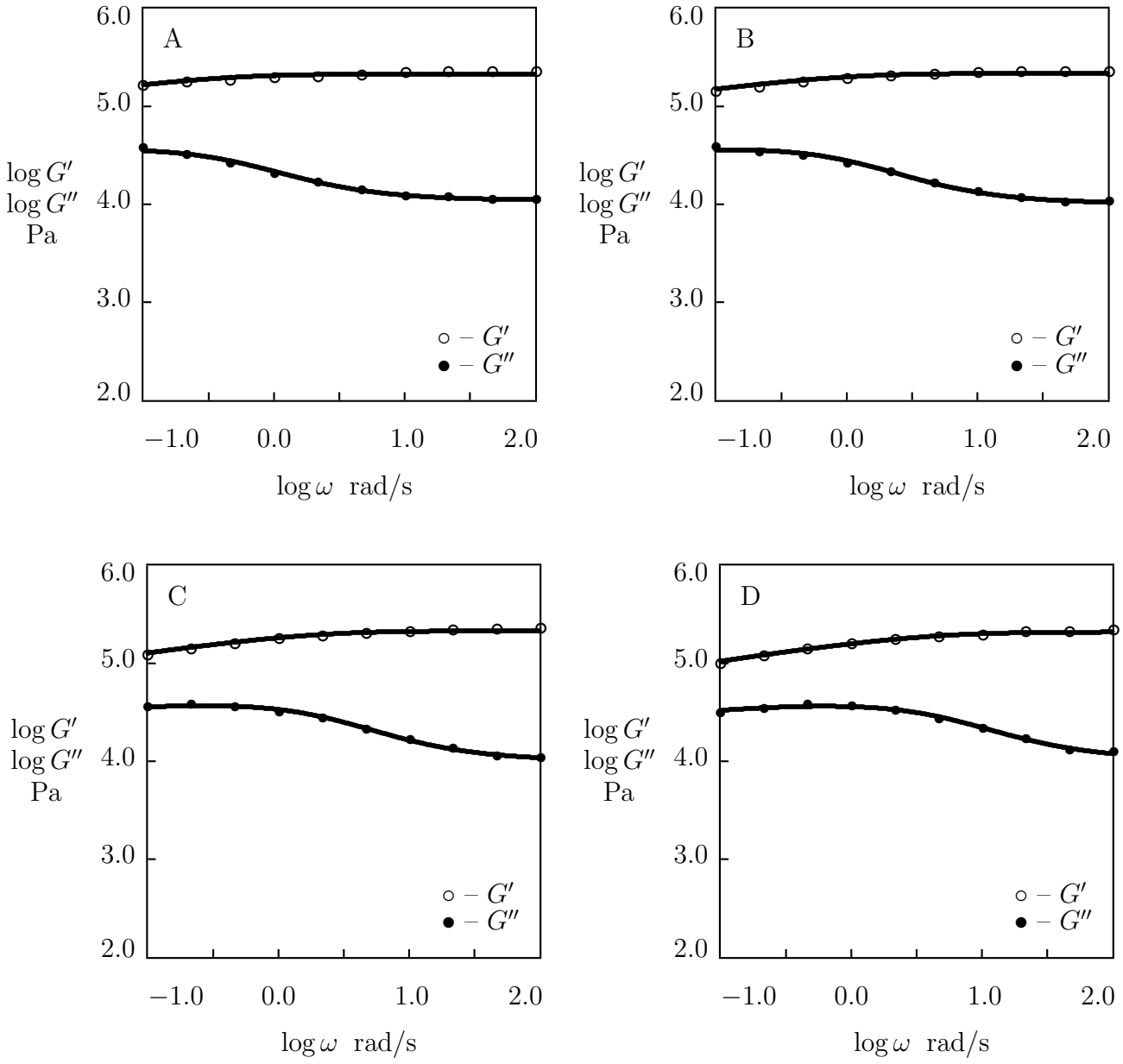

Figure S-11: Storage modulus G' and loss modulus G'' versus frequency ω. Symbols: experimental data (Zou et al., 2017) on P(AAm-AAc) gel cross-linked with Fe^{3+} ions at various temperatures T (A – $T = 40$, B – $T = 50$, C – $T = 60$, D – $T = 70$ °C). Solid lines: results of simulation.

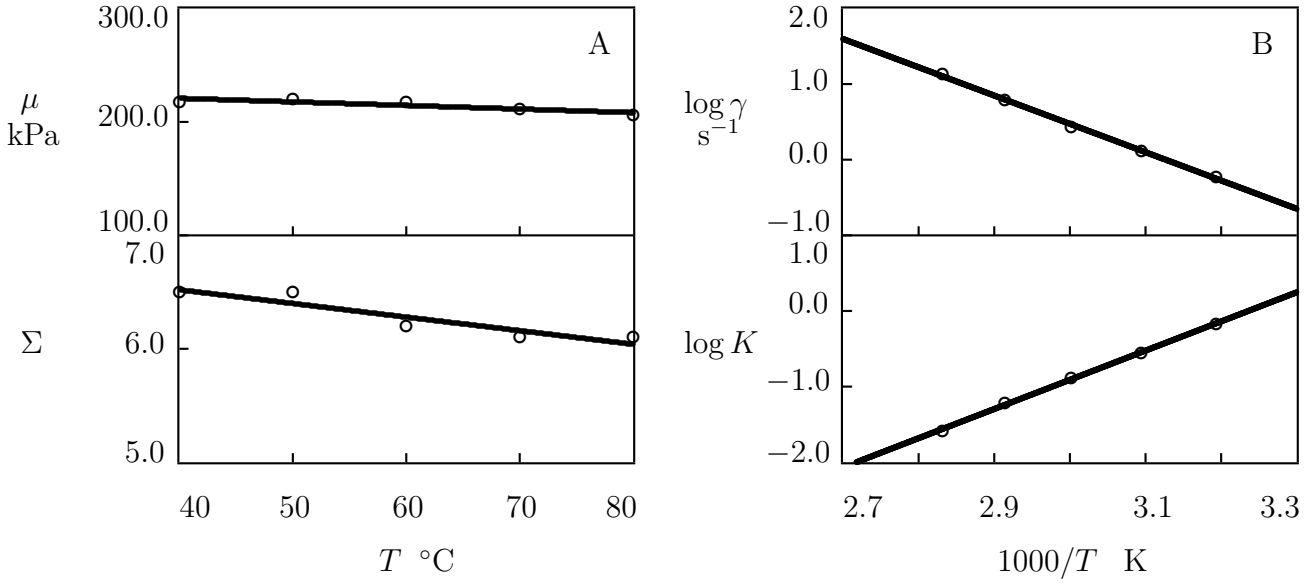

Figure S-12: Parameters μ, Σ (A) and γ, K (B) versus temperature T. Circles: treatment of observations (Zou et al., 2017) on P(AAm-AAc) gel cross-linked with Fe^{3+} ions. Solid lines: results of simulation.

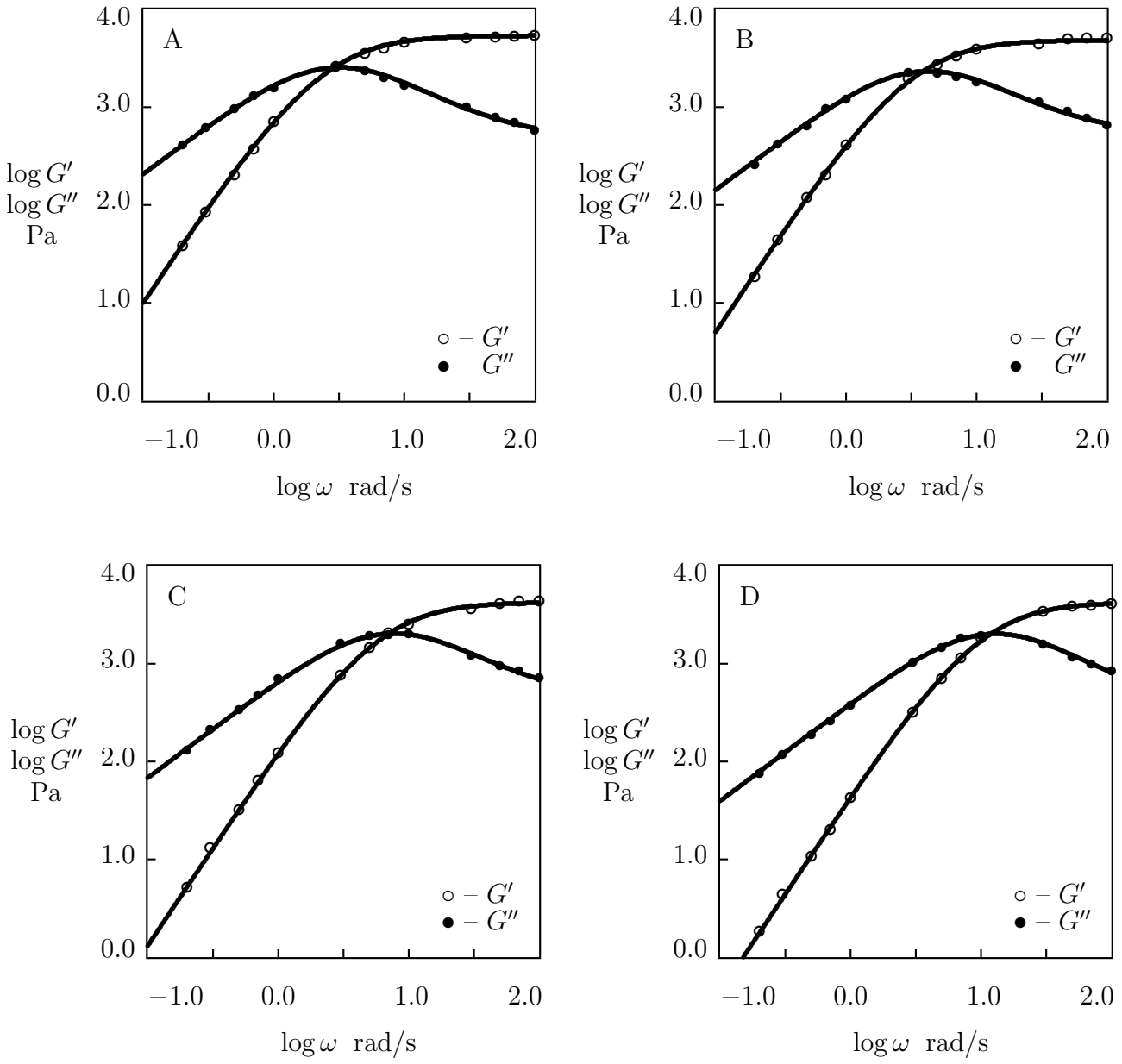

Figure S-13: Storage modulus G' and loss modulus G'' versus frequency ω. Symbols: experimental data (Parada and Zhao, 2018) on PEG gel cross-linked by phenylboronic acid–diol (FPBA-GL) complexation at various temperatures T (A – $T = 10$, B – $T = 15$, C – $T = 25$, D – $T = 35$ °C). Solid lines: results of simulation.

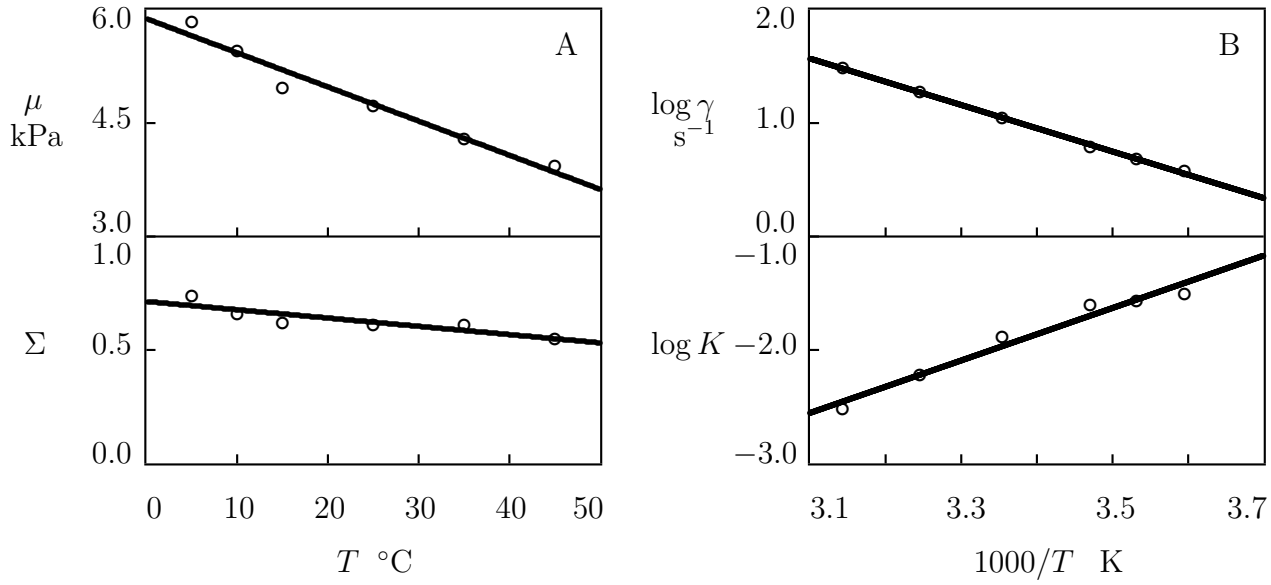

Figure S-14: Parameters μ, Σ (A) and γ, K (B) versus temperature T. Circles: treatment of observations (Parada and Zhao, 2018) on PEG gel cross-linked by phenylboronic acid–diol (FPBA-GL) complexation. Solid lines: results of simulation.

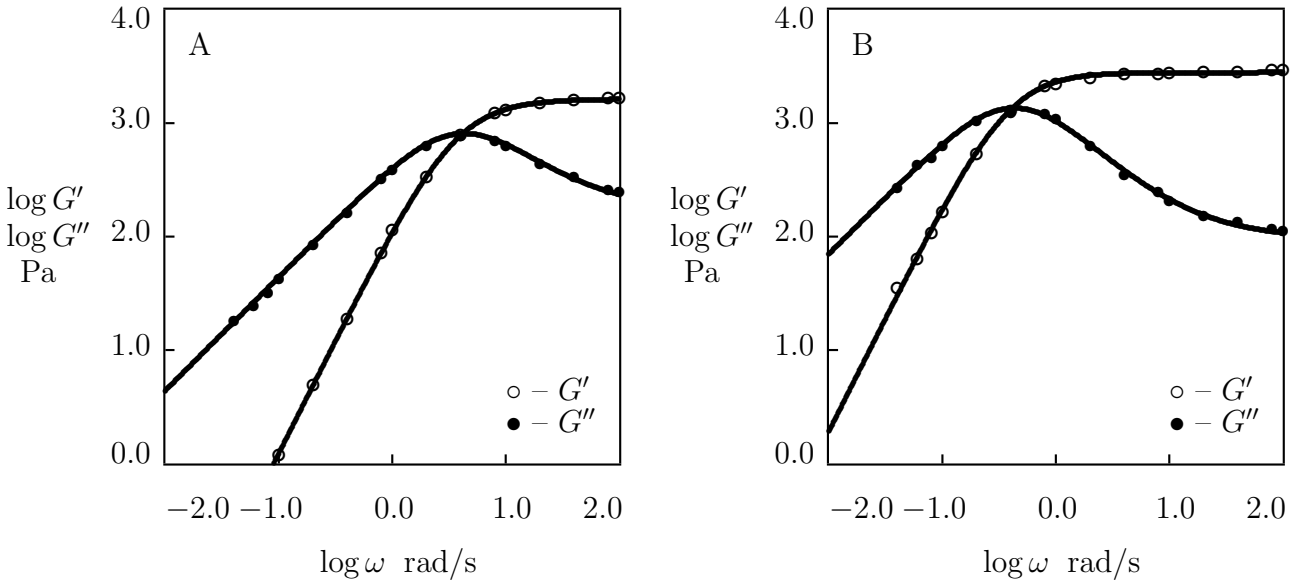

Figure S-15: Storage modulus G' and loss modulus G'' versus frequency ω. Symbols: experimental data (Parada and Zhao, 2018) on PEG gel cross-linked by phenylboronic acid–diol (FPBA-GL) complexation at various pH (A – pH = 7.2, B – pH = 7.7). Solid lines: results of simulation.

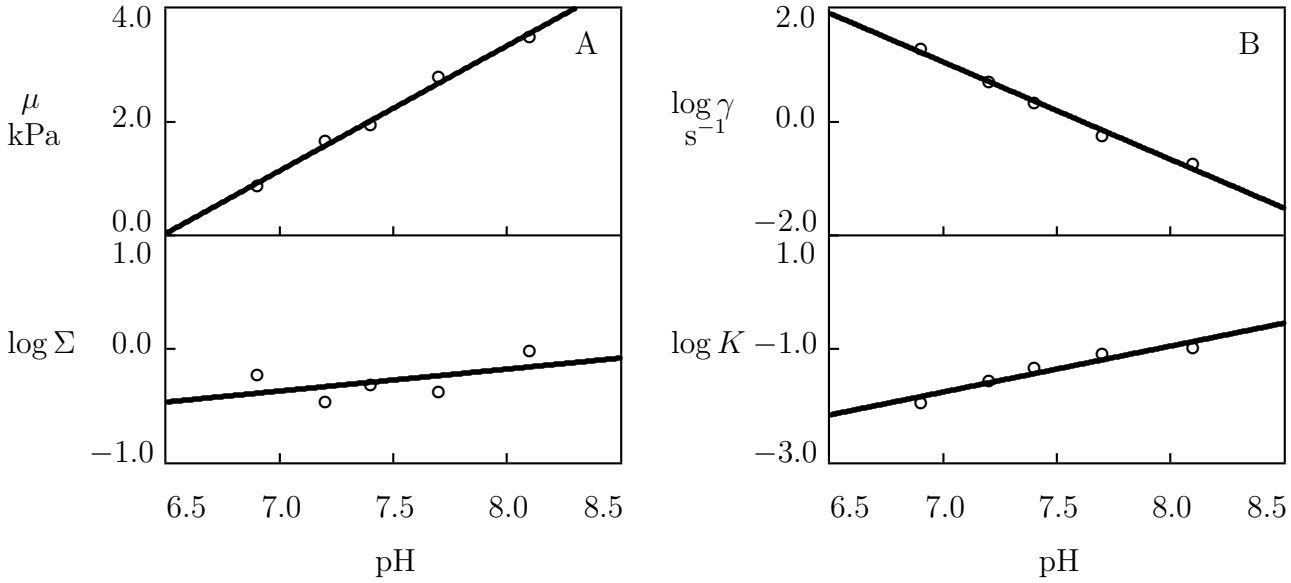

Figure S-16: Parameters μ, Σ (A) and γ, K (B) versus pH. Circles: treatment of observations (Parada and Zhao, 2018) on PEG gel cross-linked by phenylboronic acid–diol (FPBA-GL) complexation. Solid lines: results of simulation.

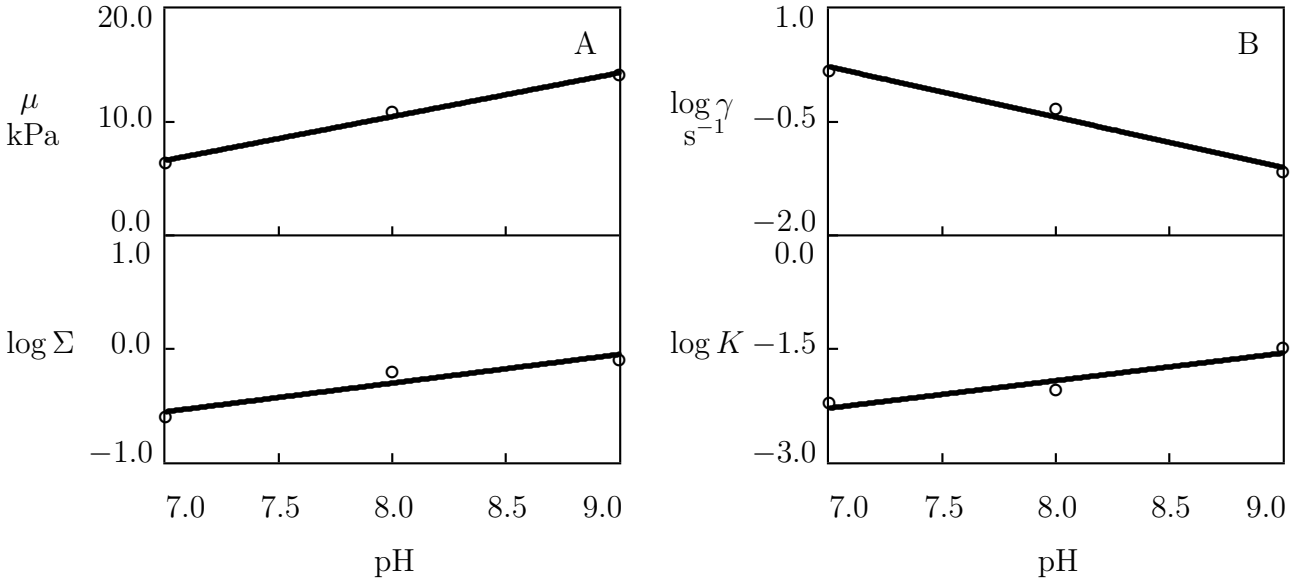

Figure S-17: Parameters μ, Σ (A) and γ, K (B) versus pH. Circles: treatment of observations (Marco-Dufort et al., 2020) on PEG gels cross-linked by phenylboronic acid-diol (PBA-GL) complexation. Solid lines: results of simulation.

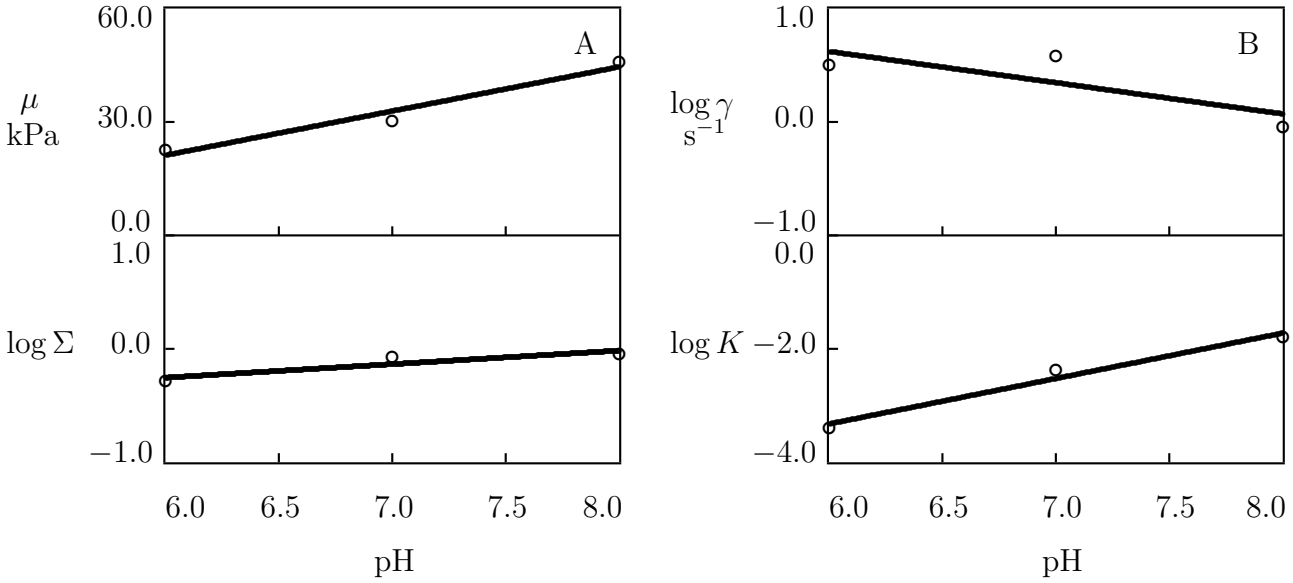

Figure S-18: Parameters μ, Σ (A) and γ, K (B) versus pH. Circles: treatment of observations (Yesilyurt et al., 2016) on PEG gel cross-linked by phenylboronic acid-diol (APBA-GL) complexation at temperature $T = 37$ °C. Solid lines: results of simulation.

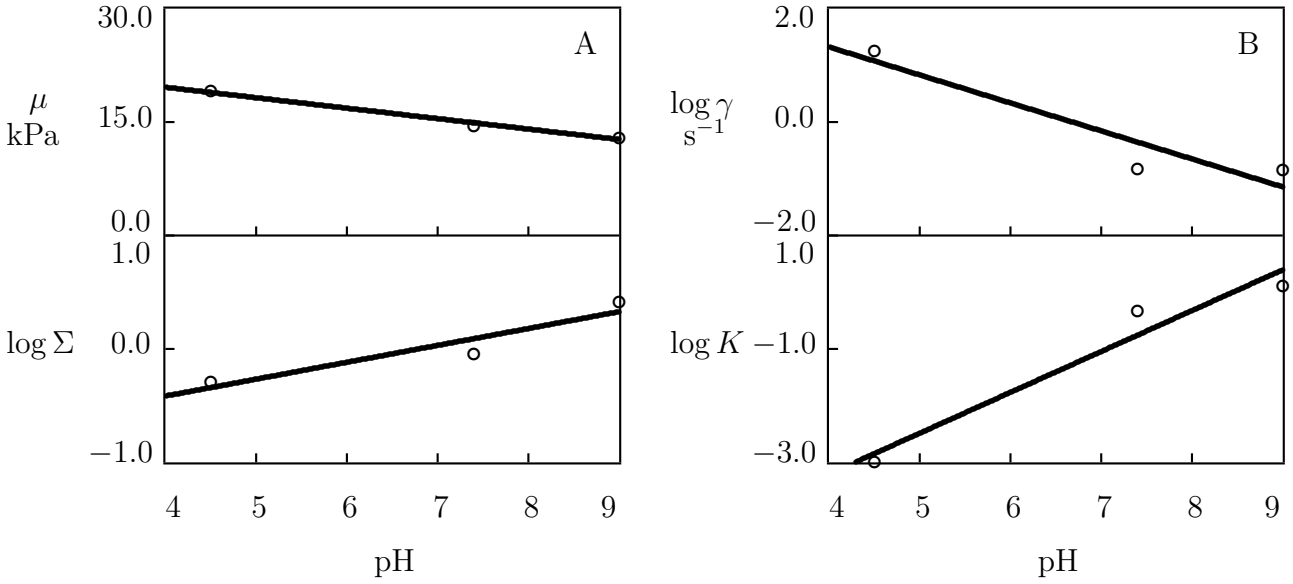

Figure S-19: Parameters μ, Σ (A) and γ, K (B) versus pH. Circles: treatment of observations (Menyo et al., 2013) on HOPO-functionalized PEG gel cross-linked with Fe^{3+} ions. Solid lines: results of simulation.

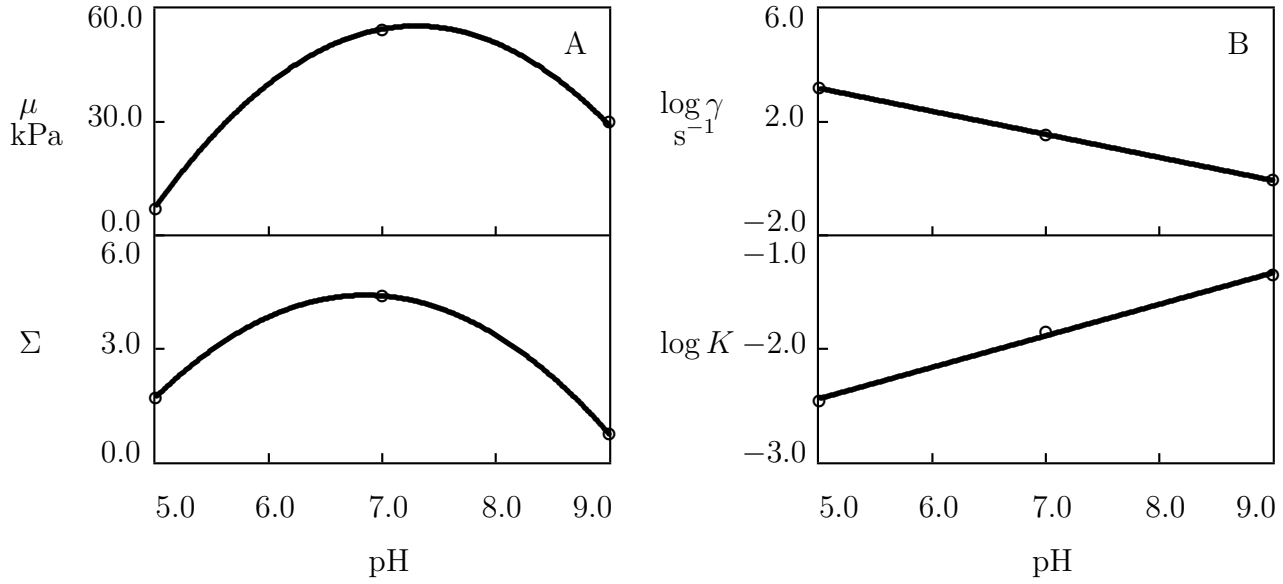

Figure S-20: Parameters μ, Σ (A) and γ, K (B) versus pH. Circles: treatment of observations (Barrett et al., 2013) on on catechol-functionalized PEG gel cross-linked with Fe^{3+} ions. Solid lines: results of simulation.