Supplementary Information

SAXS study of electric field-induced microstructural evolution in a polyaniline-based conductive hydrogel

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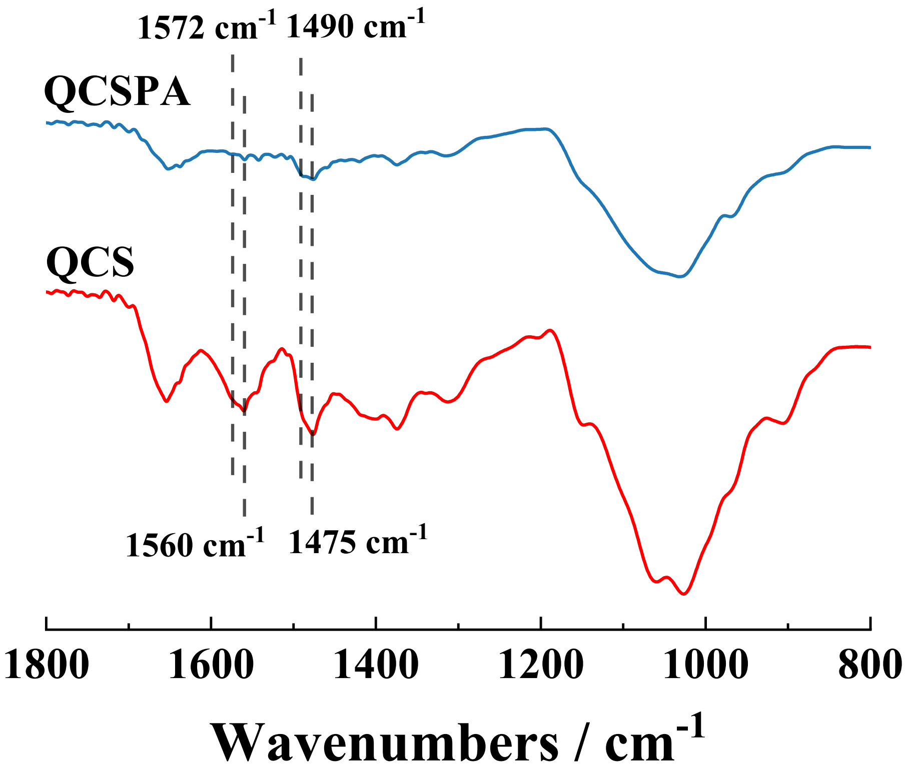

Figure S1. FTIR spectrum of products QCS and QCSPA after lyophilized.

Swelling and Degradation at Different Voltages.

The swelling ratio (SR) of the hydrogels with different voltages applied was measured by swelling tests. Initially, hydrogel samples of identical mass were attached to carbon electrodes and submerged in 10 ml of PBS (0.01 M, pH 7.4) at 25°C, and subjected to the application of 0, 3 and 5 V, respectively. The device is shown in **Figure 2**. At predetermined intervals, all samples were simultaneously removed from the PBS solution and weighed after carefully wiping the surface water with filter paper. The hydrogels were then returned to their original positions in the PBS with the applied voltages maintained. The SR was calculated as follows:

$$SR = \frac{W_t - W_i}{W_i} \times 100\% \#(S1)$$

where W_i is the weight of initial hydrogel, and W_t represent the weight of swollen hydrogel at time t. Each sample was repeated for 3 times for averaged value.

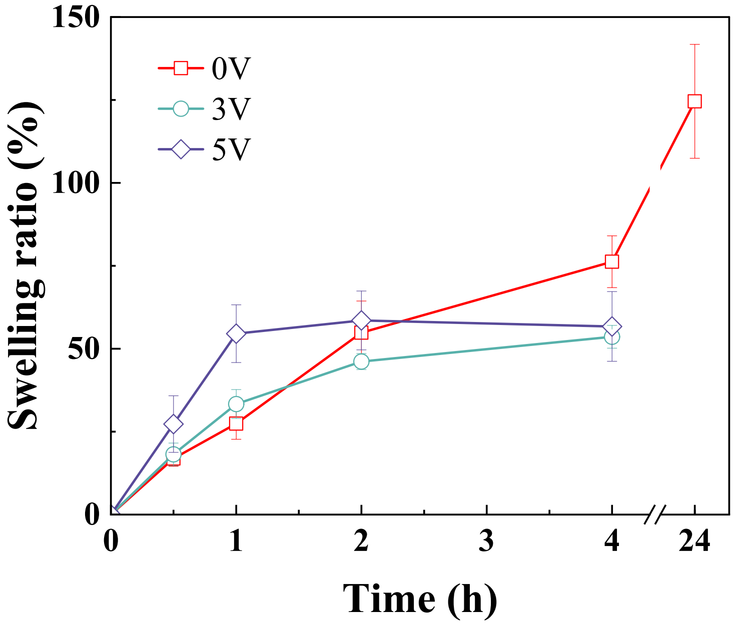

Figure S2. Swelling ratio of the PVA-BA-QCSPA hydrogel in PBS (0.01M, pH 7.4) at 25 °C over time with the application of a voltage of 0, 3 and 5 V.

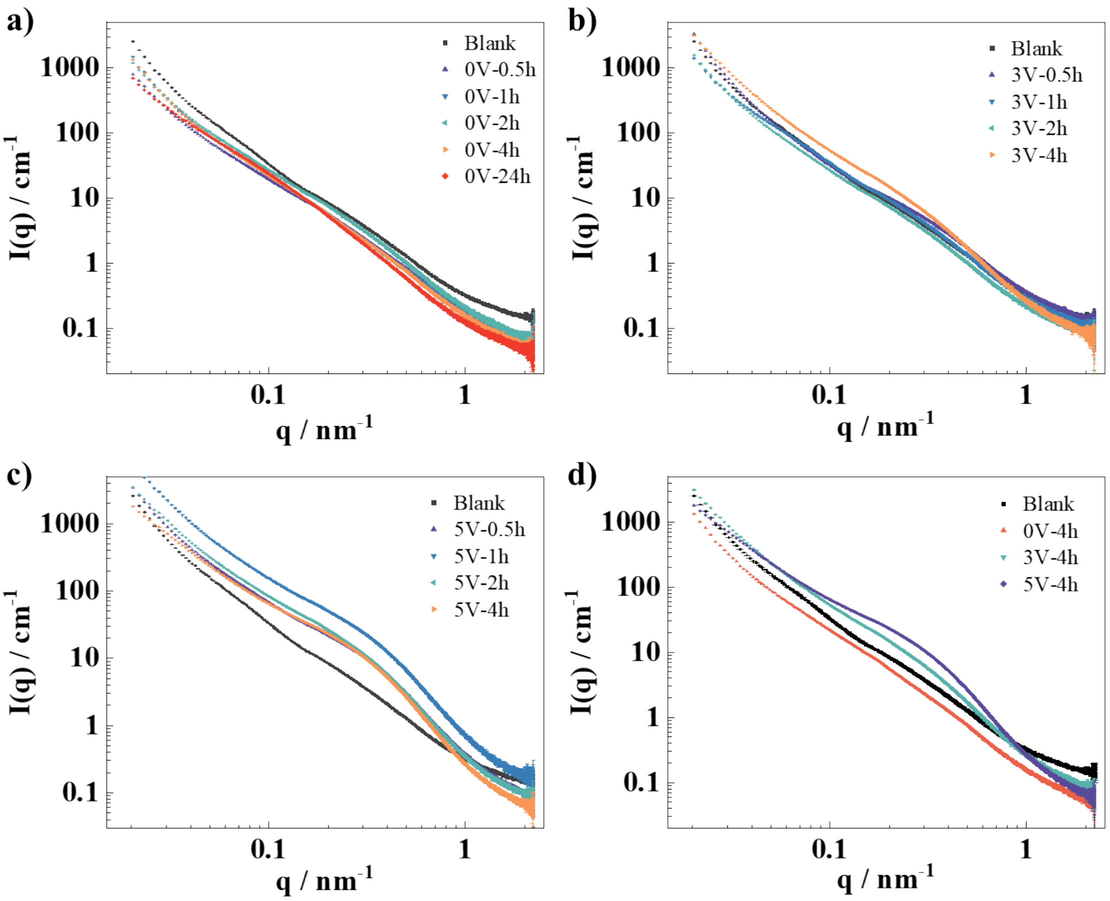

Figure S3. SAXS intensity of the PVA-BA-QCSPA hydrogel with the application of a) 0 V, b) 3 V, and c) 5 V. d) Comparison of the PVA-BA-QCSPA hydrogel at different voltages for 4 h.

Fitting of the correlation length model.

The scattering intensity I(q) of the PVA-BA-QCSPA hydrogels were fitted by the correlation length model (Eq. S2). It is given by:

$$I(q) = \frac{A}{q^n} + \frac{C}{1 + (q\xi)^m} + Bkg\#(S2)$$

Prior to fitting, the background was first approximated by a power-law function and subtracted from each scattering curve. Then by minimizing the weighted least-squares function:

$$X^2 = \sum_i^N \left[\frac{I_{exp}(q_i) - I_{model}(q_i;p)}{\sigma_i}\right]^2 \#(S3)$$

where $I_{exp}(q_i)$ is the experimentally measured scattering intensity, and $I_{model}(q_i;p)$ is the corresponding intensity calculated from the correlation-length model using a set of fitting parameters $P = \{A, C, \xi, n, m\}$. The fitting results for the correlation length model are presented using *SasView* software.

The experimental uncertainty σ_i was taken directly from the third column of the original 1D scattering data files (denoted as *dI* or $E(q_i)$). These values are determined during the 2D to 1D reduction step, represents the estimated standard deviation of measured intensity *I(qi)* after radial averaging and data reduction, i.e. an experimental uncertainty rather than a "fitting error".[1, 2] In the fitting procedure implemented in SasView, σ_i was used for weighted nonlinear least-squares optimisation with inverse-variance weights $w_i = 1/\sigma_i^2$, so that data points with smaller σ_i have a higher influence on the minimised cost function.

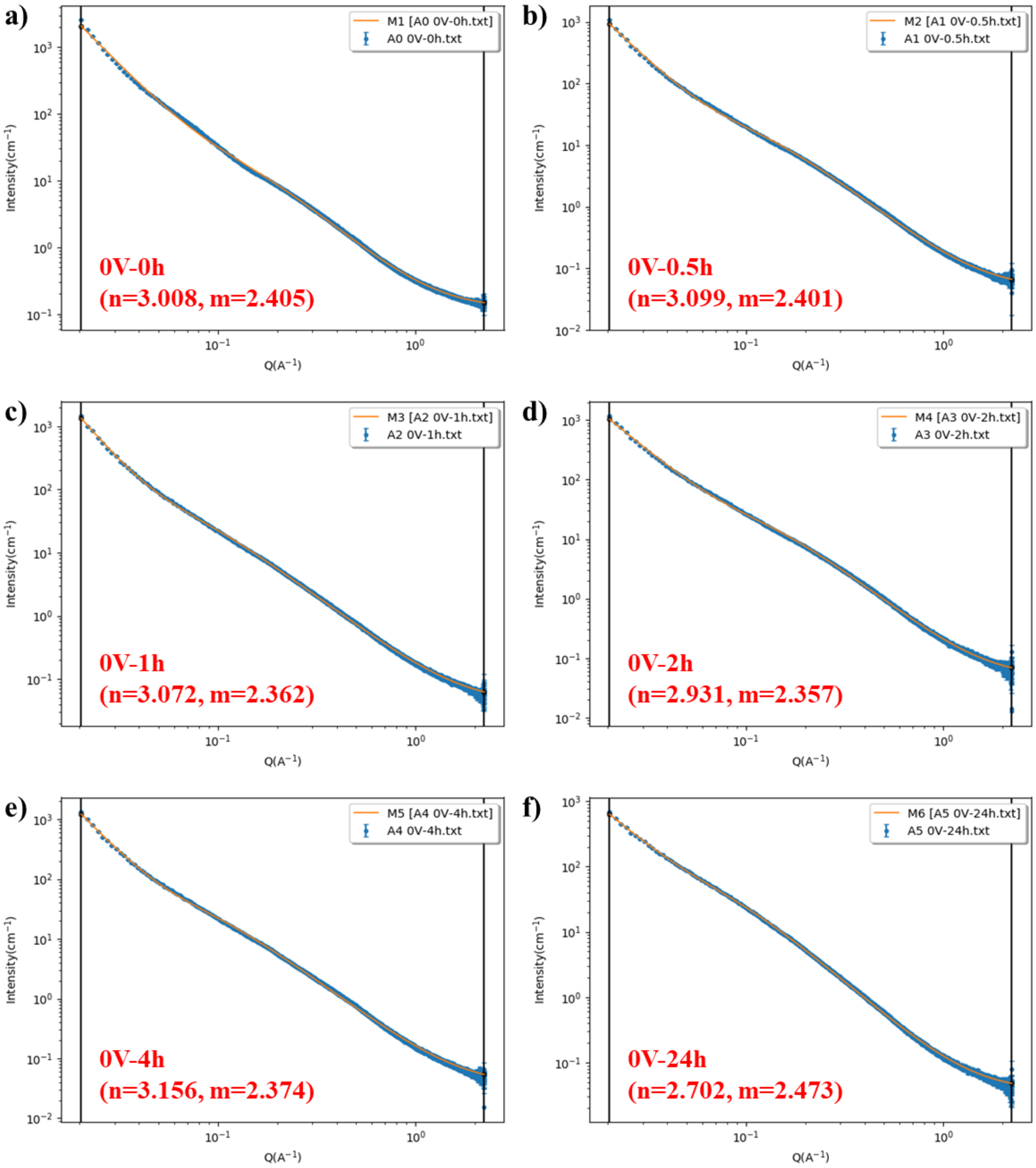

Figure S4. The SAXS data (blue scatter points) and fitted curves (orange lines) of the PVA-BA-QCSPA hydrogel at 0 V over time by the correlation length model (Eq. S2).

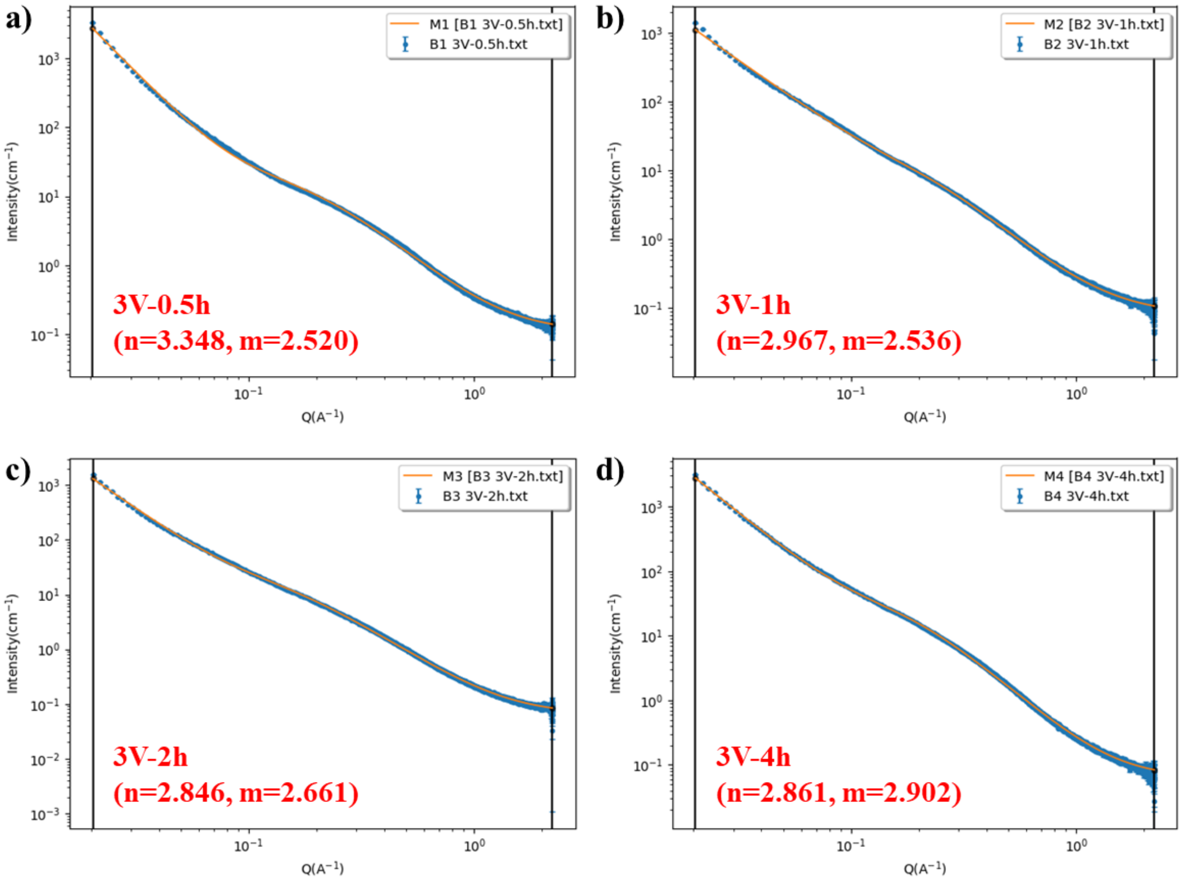

Figure S5. The SAXS data (blue scatter points) and fitted curves (orange lines) of the PVA-BA-QCSPA hydrogel at 3 V over time by the correlation length model (Eq. S2).

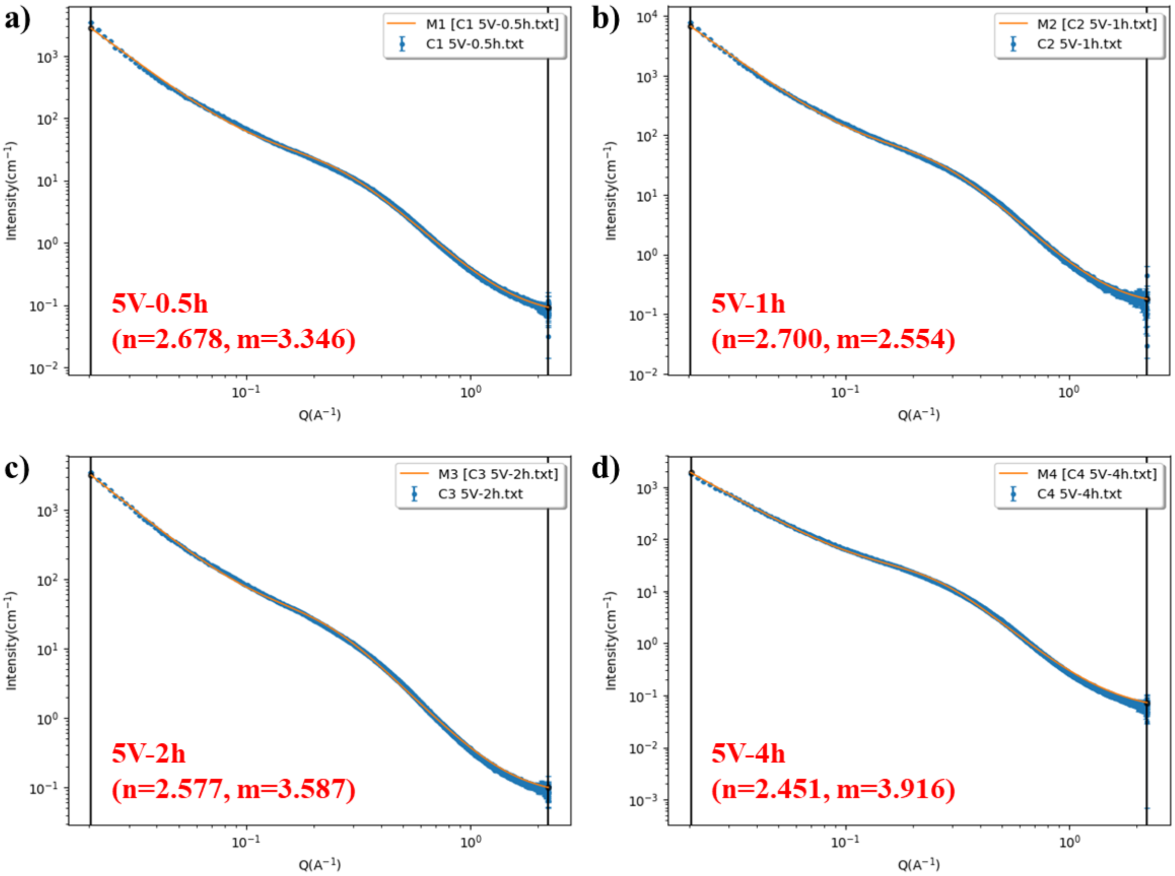

Figure S6. The SAXS data (blue scatter points) and fitted curves (orange lines) of the PVA-BA-QCSPA hydrogel at 5 V over time by the correlation length model (Eq. S2).

Model of Gaussian spherical domains

An alternative approach to the correlation length model was to analyze in particular the single broad peak seen in the Kratky plots by globular domains within the hydrogel. As such domains are not expected to have sharp boundaries they were assumed to be described as spherical structures with a diffuse scattering length density (SLD) profile. For this we choose a spherically symmetric Gaussian profile [3, 4] which is given by the following equation:

$$SLD(r) = \rho_0 \cdot e^{\left(-\frac{r^2}{2R^2}\right)} \#(S4)$$

where ρ_0 represents the SLD value at the center of the sphere, r is the radial distance from the domain center, and R denotes the characteristic radius of the spherical domain, where the SLD has fallen to a value of 60.6% of that of the center. The scattering amplitude is obtained by the radial Fourier transform:

$$F(q) = 4\pi \int_0^{\infty} SLD(r) \cdot \frac{\sin(qr)}{qr} \cdot r^2 dr \#(S5)$$

After integration:

$$F(q) = (2\pi)^{3/2} \rho_0 \cdot R^3 \cdot e^{\left(-\frac{q^2 R^2}{2}\right)} \#(S6)$$

The total scattering intensity is obtained from the ensemble average of the squared amplitude:

$$I(q) = N|F(q)|^2 S(q) \#(S7)$$

where N is the number density of domains. For non-interacting domains, structure factor $S(q)$ = 1. The scattering intensity as a function of the sphere radius is therefore obtained as:

$$I(q) = I_2 \cdot \left(R^3 \cdot e^{\left(-\frac{q^2 R^2}{2}\right)}\right)^2 \#(S8)$$

where $I_2 = N(2\pi)^3 \rho_0^2$ absorbs pre-factors and constants.

For fitting, the remaining gel network behavior was described by the power-law function (I_1/q^n), expressed as:

$$I(q) = \frac{I_1}{q^n} + I_2 \cdot \left(R^3 \cdot e^{\left(-\frac{q^2 R^2}{2}\right)}\right)^2 \#(S9)$$

where I_1 *and* I_2 represent the amplitudes associated with the residual network contribution and the Gaussian domain contribution, respectively. The fits in the Kratky peak region, where the scattering is dominated by the local density correlations of the polymer network, yielded as most interesting parameter the effective radius R.

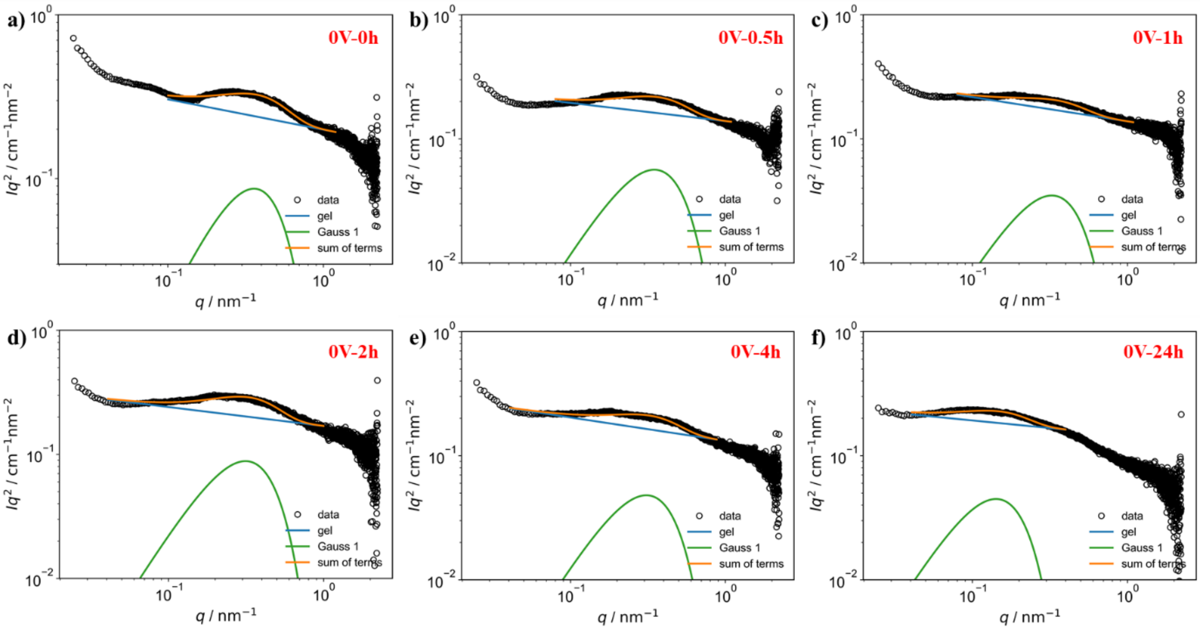

Figure S7. Kratky plots and fitting curves (orange curves) with gaussian spherical domain model by Eq. S9 for PVA-BA-QCSPA hydrogels swollen in 0.01 M PBS at 0 V for a) 0 h, b) 0.5 h, c) 1 h, d) 2 h, e) 4 h, and f) 24 h.

Table S1. Fitted results from the spherical domain function Eq. S9 for PVA-BA-QCSPA hydrogel with different time at 0 V.

Gel code	Fitted q range / nm^{-1}	n	I_1 / cm^{-1}	I_2 / cm^{-1}	R / nm
0V-0h	0.1 - 1.2	2.19 ± 2e-03	0.20 ± 4e-04	3.9e-03 ± 7e-05	2.79 ± 0.01
0V-0.5h	0.08 - 1.1	2.15 ± 3e-03	0.14 ± 4e-04	2.3e-03 ± 5e-05	2.87 ± 0.02
0V-1h	0.08 - 1.1	2.20 ± 2e-03	0.14 ± 3e-04	1.1e-03 ± 3e-05	3.07 ± 0.02
0V-2h	0.04 - 1.0	2.15 ± 2e-03	0.17 ± 6e-04	2.3e-03 ± 5e-05	3.19 ± 0.02
0V-4h	0.04 - 1.0	2.18 ± 3e-03	0.14 ± 6e-04	1.0e-03 ± 4e-05	3.25 ± 0.03
0V-24h	0.04 - 0.4	2.12 ± 3e-03	0.15 ± 9e-04	5.0e-05 ± 2e-06	7.03 ± 0.06

(The reported errors are merely statistical errors, corresponding to the standard deviation from the covariance matrix of the least-squares fit. They reflect the internal fitting accuracy of the model and do not include systematic errors.)

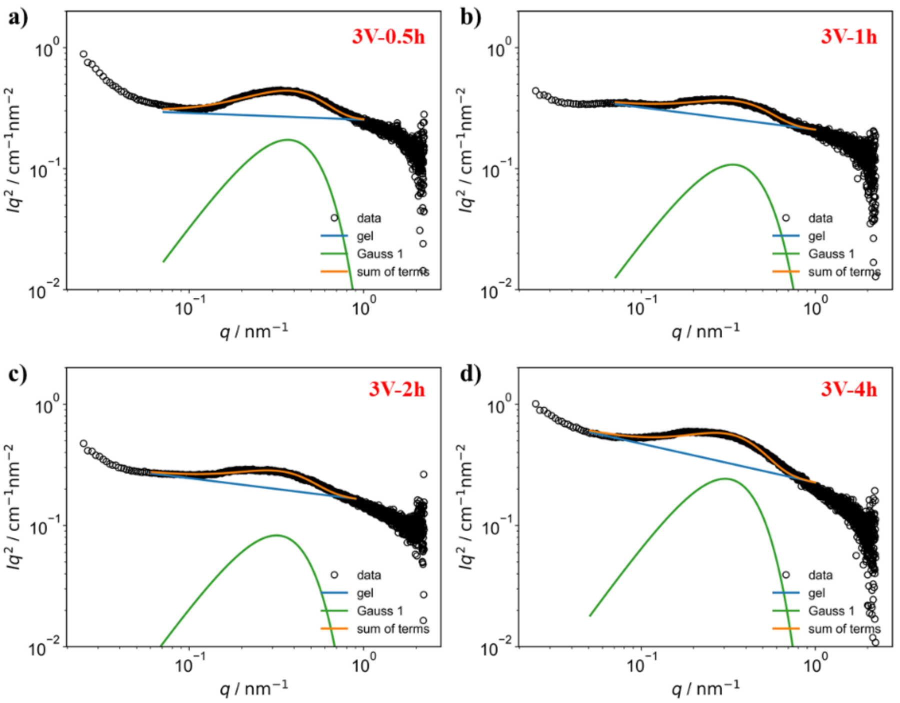

Figure S8. Kratky plots and fitting curves (orange curves) with gaussian spherical domain model by Eq. S9 for PVA-BA-QCSPA hydrogels swollen in 0.01 M PBS at 3 V for a) 0.5 h, b) 1 h, c) 2 h, and d) 4 h.

Table S2. Fitted results from the spherical domain function Eq. S9 for PVA-BA-QCSPA hydrogel with different time at 3 V.

Gel code	Fitted q range / nm^{-1}	n	I_1 / cm^{-1}	I_2 / cm^{-1}	R / nm
3V-0.5h	0.07 - 1.0	2.06 ± 2e-03	0.25 ± 9e-04	8.56e-03 ± 11e-05	2.72 ± 0.01
3V-1h	0.07 - 1.0	2.18 ± 2e-03	0.21 ± 6e-04	3.76e-03 ± 6e-05	2.97 ± 0.01
3V-2h	0.06 - 1.0	2.18 ± 2e-03	0.16 ± 5e-04	2.26e-03 ± 4e-05	3.16 ± 0.01
3V-4h	0.05 - 1.0	2.32 ± 3e-03	0.23 ± 1e-03	5.62e-03 ± 10e-05	3.29 ± 0.01

(The reported errors are merely statistical errors, corresponding to the standard deviation from the covariance matrix of the least-squares fit. They reflect the internal fitting accuracy of the model and do not include systematic errors.)

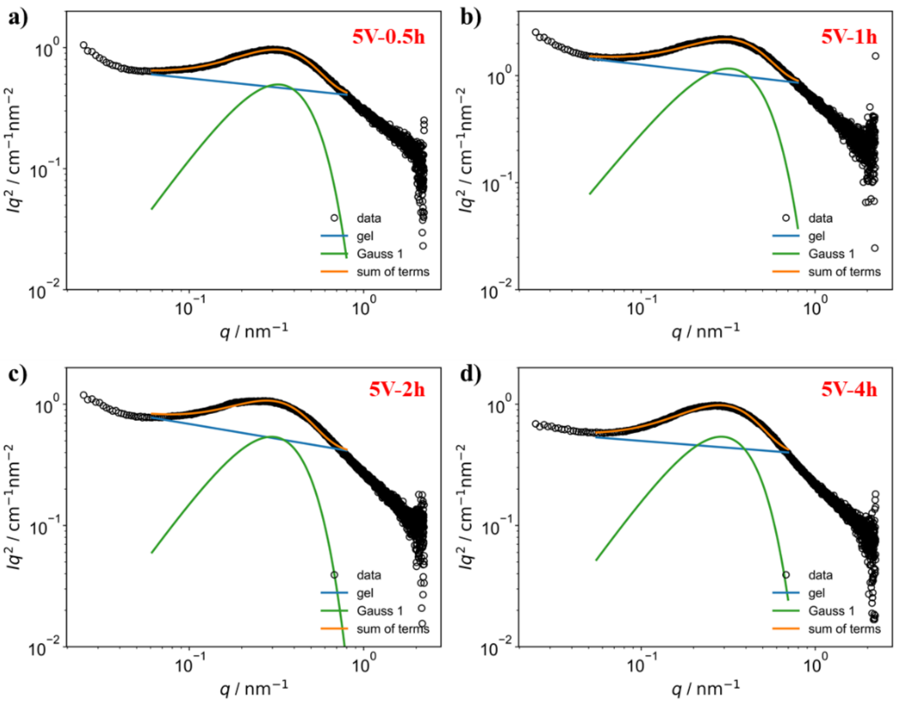

Figure S9. Kratky plots and fitting curves (orange curves) with gaussian spherical domain model by Eq. S9 for PVA-BA-QCSPA hydrogels swollen in 0.01 M PBS at 5 V for a) 0.5 h, b) 1 h, c) 2 h, and d) 4 h.

Table S3. Fitted results from the spherical domain function Eq. S9 for PVA-BA-QCSPA hydrogel with different time at 5 V.

Gel code	Fitted q range / nm^{-1}	n	I_1 / cm^{-1}	I_2 / cm^{-1}	R / nm
5V-0.5h	0.06 - 0.8	2.15 ± 2e-03	0.39 ± 2e-03	1.47e-02 ± 1e-04	3.10 ± 0.01
5V-1h	0.06 - 0.8	2.19 ± 3e-03	0.82 ± 5e-03	3.26e-02 ± 4e-04	3.14 ± 0.01
5V-2h	0.06 - 0.8	2.24 ± 4e-03	0.39 ± 3e-03	1.13e-02 ± 2e-04	3.38 ± 0.01
5V-4h	0.07 - 0.7	2.09 ± 4e-03	0.40 ± 3e-03	9.60e-03 ± 1e-04	3.50 ± 0.01

(The reported errors are merely statistical errors, corresponding to the standard deviation from the covariance matrix of the least-squares fit. They reflect the internal fitting accuracy of the model and do not include systematic errors.)

References

1. B. R. Pauw, J. S. Pedersen, S. Tardif, M. Takata and B. B. Iversen, *J Appl Crystallogr*, 2013, **46**, 365-371.
2. I. Bressler, B. R. Pauw and A. F. Thunemann, *J Appl Crystallogr*, 2015, **48**, 962-969.
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