Supporting Information for *Disentangling Polymer Network and Hydration Water Dynamics in pHEMA Physical and Chemical Hydrogels*

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1 Polymer network EISF fitting parameters

The elasitc incoherent structure factor related to the H-atoms of the polymer network, $EISF(Q)$, was analysed according to Eq. 14 and Eq. 15. Such equations represent the hypothesis that the observed quasi-elastic broadening reflects only the motion of the side-chain or to both the side-chain and the methyl group, respectively (see text in the paper and Figure 5). In Figure S1, we report the weights of the different parts of the polymer chain, as obtained from the fit parameters A and B of Eq. 14 and Eq.15, and the dimension of the region of space explored by the side-chain and the backbone, R_{SC} and R_B, respectively. All the parameters are obtained from the fits shown in Figure 5. The expected values on the basis of stoichiometric or geometric considerations (dashed lines) are also reported for comparison.

2 Jump-diffusion models

For the fit of the quasi-elastic broadening, we used the models developed by Chudley and Elliot (CEM) [S1], Singwi and Sjölander (SSM) [S2], and Hall and Ross (HRM) [S3]. Such models assume a diffusive motion *via* successive jumps. In between two jumps, the particle rests on a given site for a residence time τ.

In the CEM, the jump distance l_{CEM} is a constant and the corresponding half width at half maximum of the Lorentzian quasi-elastic component is given by

$$\frac{\Gamma}{2} = \frac{\hbar}{\tau}\left(1 - \frac{\sin(Ql_{\mathrm{CEM}})}{Ql_{\mathrm{CEM}}}\right), \tag{1}$$

In the SSM, the jump distance $\rho(r)$ is exponentially distributed,

$$\rho(r) = \frac{r}{r_0^2}\exp\left(-\frac{r}{r_0}\right), \tag{2}$$

and the broadening is given by

$$\frac{\Gamma}{2} = \frac{\hbar}{6\tau}\frac{Q^2 l_{\mathrm{SSM}}^2}{1+\frac{Q^2 l_{\mathrm{SSM}}^2}{6}}, \tag{3}$$

where l_{SSM}^2 is the mean square jump length, which is equal to $\int_0^\infty r^2\rho(r)dr = 6r_0^2$.

In the HRM, the jump distance is defined by a Gaussian distribution,

$$\rho(r) = \frac{2r^2}{r_0^3(2\pi)^{1/2}\exp\left(-\frac{r^2}{2r_0^2}\right)}, \tag{4}$$

and the broadening is given by

$$\frac{\Gamma}{2} = \frac{\hbar}{\tau}\left[1 - \exp\left(-\frac{Q^2 l_{\mathrm{HRM}}^2}{6}\right)\right]. \tag{5}$$

The mean square jump length for this model, l_{HRM}^2, is equal to $\int_0^\infty r^2\rho(r)dr = 3r_0^2$.

2.1 Jump-diffusion fit parameters

The residence times and jump lengths obtained by fitting the quasi-elastic broadening using the CEM, SSM and HRM are given in Tab. S1 and Tab. S2, respectively.

The residence times and the diffusion coefficients were fitted according to an Arrhenius law (see paper, Figure 10). Table S3 lists the derived activation energies and high temperature limits.

3 DSC thermograms

Figures S2 and S3 show the most representative DSC heating scans for the pHEMA chemical and physical hydrogels.

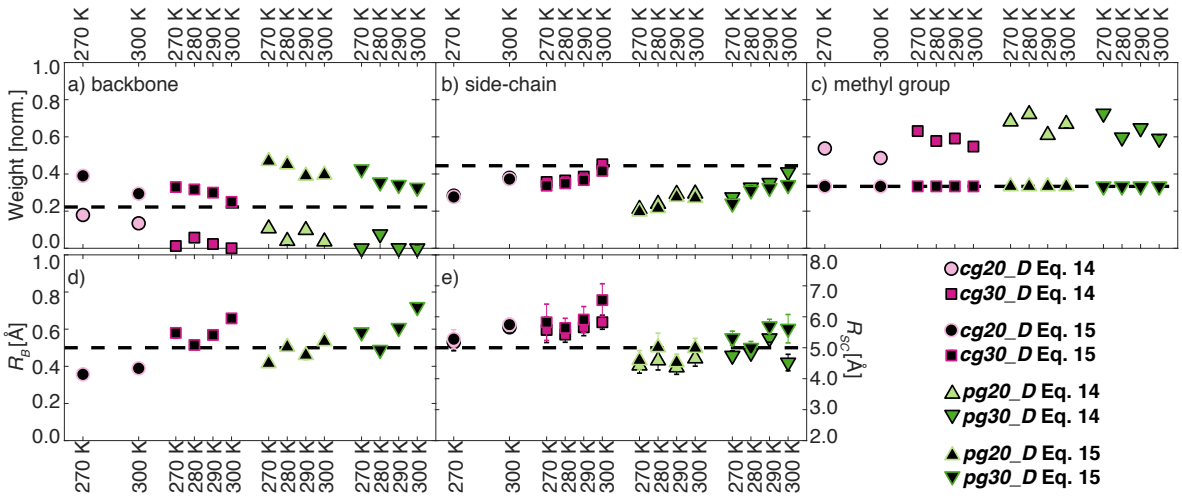

Fig. S1 Weights of the different parts of the polymer chain: a) backbone, b) side-chain, and c) methyl group. In d) and e), there are shown the regions of space explored by the backbone and the side-chain, respectively. All the parameters are obtained from the fits shown in Figure 5 in the paper and Eq. 14 and 15. Dashed lines represent the expected values on the basis of stoichiometric or geometric considerations. When not visible, error bars are within the symbols.

	CEM				SSM				HRM			
	270K	280K	290K	300K	270K	280K	290K	300K	270K	280K	290K	300K
cg20_w	-	-	-	0.09(3)	-	-	-	0.03(1)	-	-	-	0.06(2)
cg30_w	0.061(3)	0.051(3)	0.047(3)	0.041(2)	0.037(3)	0.030(2)	0.028(2)	0.024(2)	0.049(3)	0.040(3)	0.037(2)	0.032(2)
pg20_w	0.099(3)	0.081(2)	0.072(2)	0.063(1)	0.062(3)	0.055(2)	0.050(3)	0.045(3)	0.079(3)	0.067(1)	0.060(2)	0.053(2)
pg30_w	0.065(3)	0.056(2)	0.050(2)	0.045(2)	0.036(3)	0.033(1)	0.030(2)	0.028(2)	0.049(3)	0.044(1)	0.039(1)	0.036(1)

Tab. S1 Residence times τ (in ns) obtained by fitting $\frac{\Gamma}{2}$ according to Eq. (1), (3), and (5).

	l_{CEM}				l_{SSM}				l_{HRM}			
	270K	280K	290K	300K	270K	280K	290K	300K	270K	280K	290K	300K
cg20_w	-	-	-	2.4(4)	-	-	-	1.5(4)	-	-	-	1.9(4)
cg30_w	3.9(2)	3.9(2)	3.9(2)	4.1(2)	3.5(3)	3.4(2)	3.5(2)	3.6(2)	3.7(2)	3.6(2)	3.7(2)	3.8(2)
pg20_w	3.7(1)	4.0(1)	4.1(1)	4.25(9)	3.6(2)	4.1(2)	4.5(5)	4.7(6)	3.6(1)	4.0(1)	4.2(2)	4.3(3)
pg30_w	3.6(1)	3.9(1)	4.1(1)	4.3(1)	2.9(2)	3.3(1)	3.6(2)	3.9(3)	3.2(1)	3.6(1)	3.8(1)	4.1(1)

Tab. S2 Jump lengths (in Å) obtained by fitting $\frac{\Gamma}{2}$ according to Eq. (1), (3), and (5).

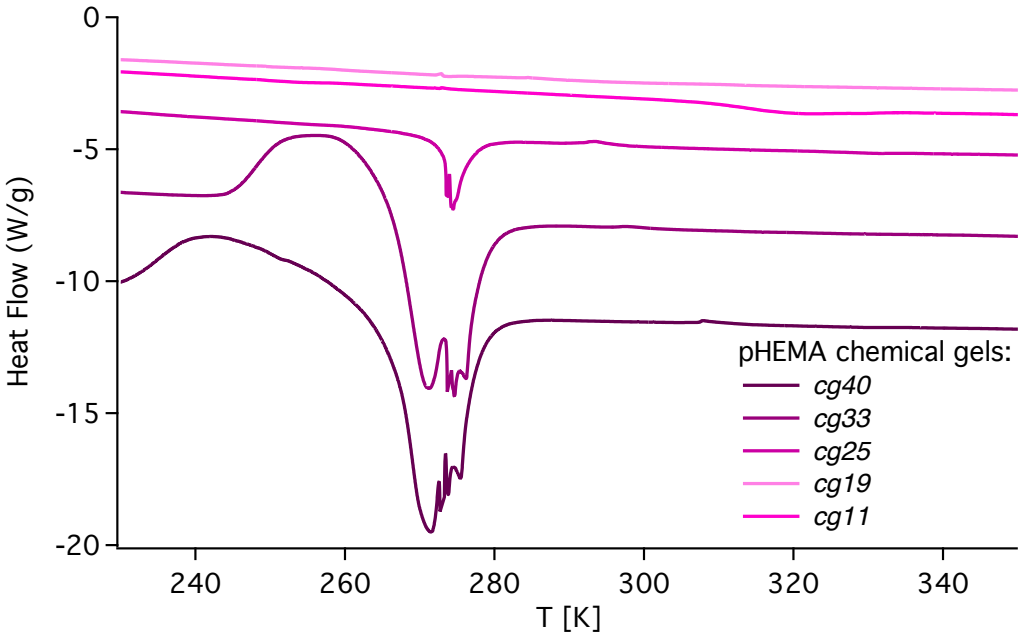

Fig. S2 DSC heating scans representative of water melting in chemical hydrogels with 10 to 40 % water content. Curves are offset along the y-axis for the sake of clarity.

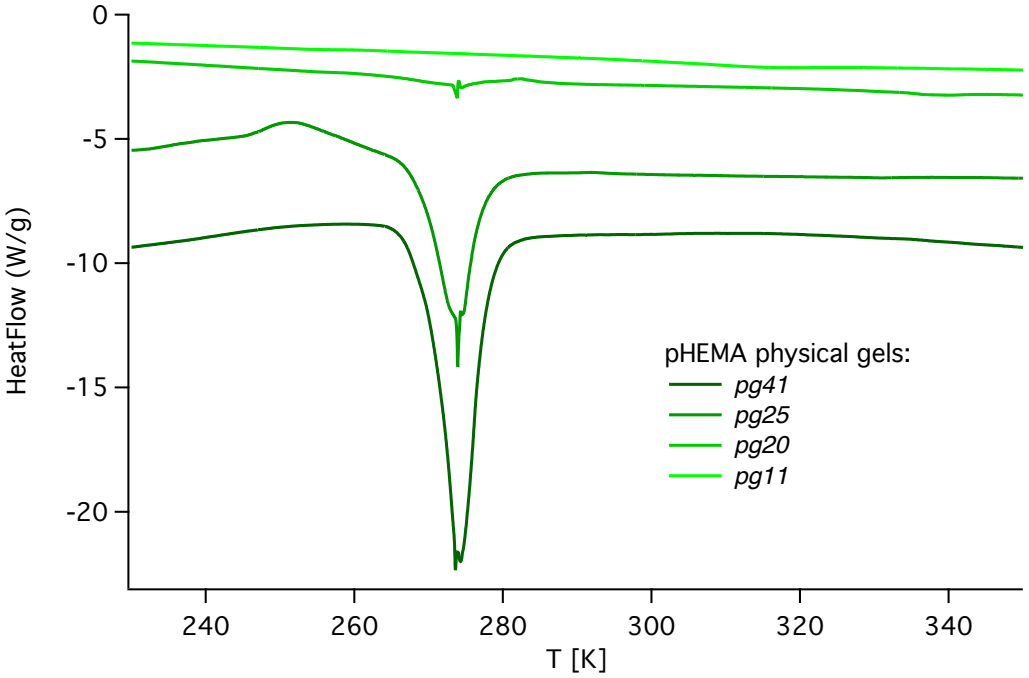

Fig. S3 DSC heating scans representative of water melting in physical hydrogels with 10 to 40 % water content. Curves are offset along the y-axis for the sake of clarity.

	τ_0 [ps]	E_τ [eV]	D_0 [10^{-3} cm^2 s^{-1}]	E_D [eV]
pg20_w (CEM)	1.5(5)	-0.097(8)	2(1)	0.15(2)
pg30_w (SSM)	2.5(4)	-0.062(4)	12(6)	0.18(1)
pg30_w(HRM)	2.0(2)	-0.075(3)	6(2)	0.17(1)
cg30_w (SSM)	0.6(2)	-0.09(1)	0.5(2)	0.11(1)
cg30_w (HRM)	0.9(3)	-0.092(7)	0.5(2)	0.11(1)

Tab. S3 Activation energies and high temperature limits for residence times and diffusion coefficients derived by Arrhenius law fits.

Note

Uncertainties and error bars represent one standard deviation.

References

S1 Chudley, C. T.; Elliott, R. J. Neutron Scattering from a Liquid on a Jump Diffusion Model. *Proc. Phys. Soc.* **1961**, *77*, 353–361.

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S3 Hall, P. L.; Ross, D. K. Incoherent Neutron Scattering Functions for Random Jump Diffusion in Bounded and Infinite Media. *Mol. Phys.* **1981**, *42*, 673–682.