ADVANCED MATERIALS

Supporting Information

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Unusual Temperature Dependence of Water Sorption in Semicrystalline Hydrogels

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This Supporting Information includes

1. **Detailed Thermodynamic Analysis**
2. **Tables S1 to 3**
3. **Figures S1 to 15**

1. Detailed Thermodynamic Analysis.

We formulated a thermodynamic theory to analyze and predict the vapor uptake in the hydrogel at different temperatures and different RHs. As the water vapor molecules in the air are adsorbed and condensed on the solid surface of the dry polymers, the liquid water molecules on the surface start to mix with the dry polymers and further induce the volumetric expansion of the polymer network. The interaction between water molecules and polymers depends on the polymer structures. For example, polymers in the crystalline state are not permeable to water molecules, but amorphous polymers can be subject to water diffusion, dissolution, and deformation. Therefore, our model considers the effects of water vapor adsorption, polymer-water mixing, polymer network deformation, and polymer melting. The equilibrium water uptake is set by these effects. At equilibrium, the chemical potentials of water molecules in the hydrogel $\mu_{1,\text{hydrogel}}$ and in the gas phase $\mu_{1,\text{gas}}$ are equal, that is,

$$\mu_{1,\text{gas}}(p,T) = \mu_{1,\text{hydrogel}}(p,T) \quad \text{[S1]}$$

where p is the current vapor pressure and T is the current temperature.

Chemical potentials of the water. The chemical potential of water molecules in the gas phase $\mu_{1,\text{gas}}(p,T)$ can be calculated by

$$\mu_{1,\text{gas}}(p,T) = \mu_1^0(p_0,T_0) + c_p(T-T_0) - c_pT\ln\left(\frac{T}{T_0}\right) + RT\ln\left(\frac{p}{p_0}\right) \quad \text{[S2]}$$

where p_0 is the reference pressure (generally the standard pressure of 1 atm), T_0 is the reference temperature (373 K), $\mu_1^0(p_0,T_0)$ is the chemical potential of pure water species at the reference state, which is assumed to zero, and c_p is the specific heat capacity of water. The saturated vapor pressure of water is 1 atm at T_0, and the enthalpy of vaporization ΔH_{vap} is 40.7 kJ mol^{-1}. We are able to obtain the saturated vapor pressure at the current temperature according to the Clausius-Clapeyron equation[1],

$$\ln\left(\frac{p_{\text{sat}}(T)}{p_0}\right) = -\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right) \quad \text{[S3]}$$

The RH is defined as the ratio of the current vapor pressure and the saturated vapor pressure at the current temperature, that is,

$$\text{RH} = \frac{p}{p_{\text{sat}}(T)} \quad \text{[S4]}$$

By inserting Eqs. S3 and S4 into Eq. S2, the chemical potential of water molecules in the gas phase can be expressed as

$$\mu_{1,\text{gas}}(p,T) = c_p(T-T_0) - c_pT\ln\left(\frac{T}{T_0}\right) - \Delta H_{\text{vap}}\left(1-\frac{T}{T_0}\right) + RT\ln(\text{RH}) \quad \text{[S5]}$$

Compared to the last two terms, the sum of the first two terms is one order of magnitude smaller for the temperature range $T \in$ [273 K, 373 K]. Therefore, we can simplify Eq. S5 to be

$$\mu_{1,\text{gas}}(p,T) = -\Delta H_{\text{vap}}\left(1-\frac{T}{T_0}\right) + RT\ln(\text{RH}) \quad \text{[S6]}$$

To introduce water molecules in the gas phase into the hydrogel, the chemical potential of water molecules in the hydrogel $\mu_{1,\text{hydrogel}}$ is equal to the partial molar Gibbs free energy by its definition

$$\mu_{1,\text{hydrogel}}(p,T) = \left(\frac{\partial G_{\text{hydrogel}}}{\partial n_1}\right)_{p,T} \quad \text{[S7]}$$

where n_1 is the number of moles of water. To calculate the chemical potential of water molecules in the hydrogel, the Gibbs free energy G_{hydrogel} after water vapor uptake should be understood. The vapor uptake in the hydrogel involves multiple processes such as vapor adsorption, polymer-water mixing, polymer network deformation, and polymer melting. The Gibbs free energy for 1 mol of the dry hydrogel can be written as

$$G_{\mathrm{hydrogel}} = G^0_{\mathrm{hydrogel}} + \Delta G_{\mathrm{ads}} + \Delta G_{\mathrm{mix}} + \Delta G_{\mathrm{def}} + \Delta G_{\mathrm{melt}} \quad [S8]$$

where G^0_{hydrogel} is the Gibbs free energy at the reference state, ΔG_{ads} is the Gibbs free energy change for adsorbing n_1 mol of water vapor on the surface of 1 mol of the dry hydrogel, ΔG_{mix} is the Gibbs free energy change for mixing n_1 mol of liquid water with 1 mol of the dry hydrogel, ΔG_{def} is the Gibbs free energy change for deforming the polymer chains in 1 mol of the dry hydrogel due to water uptake, and ΔG_{melt} is the Gibbs free energy change for melting the crystalline polymer in 1 mol of the dry hydrogel. The partial molar Gibbs free energy of water in the hydrogel at the reference state, $\left(\frac{\partial G^0_{\mathrm{hydrogel}}}{\partial n_1}\right)$, is equal to $\mu_1^0(p_0, T_0)$, which is assumed to be zero. Combing Eqs. S7 and S8, we can reach

$$\mu_{1,\mathrm{hydrogel}}(p,T) = \left(\frac{\partial \Delta G_{\mathrm{ads}}}{\partial n_1}\right)_{p,T} + \left(\frac{\partial \Delta G_{\mathrm{mix}}}{\partial n_1}\right)_{p,T} + \left(\frac{\partial \Delta G_{\mathrm{def}}}{\partial n_1}\right)_{p,T} + \left(\frac{\partial \Delta G_{\mathrm{melt}}}{\partial n_1}\right)_{p,T} \quad [S9]$$

In the equilibrium state of water uptake, the hydrogel contains n_1 mol of water and 1 mol of polymer effective strands (including n_2 mol of amorphous polymers and n_3 mol of crystalline polymers, $n_2 + n_3 = 1$). When we adopt the lattice model for each component [2], ϕ_1, ϕ_2, and ϕ_3 are the volume fractions of each component, and $\phi_1 + \phi_2 + \phi_3 = 1$. We choose the lattice site to have the volume of one water molecule and each polymer occupies N_e lattice sites, and N_e is the degree of polymerization in each polymer effective strand. Accordingly, the volume fractions are defined as

$$\begin{cases} \phi_1 = \dfrac{n_1}{n_1 + N_{\mathrm{e}}} \\ \phi_2 = \dfrac{n_2 N_{\mathrm{e}}}{n_1 + N_{\mathrm{e}}} \\ \phi_3 = \dfrac{n_3 N_{\mathrm{e}}}{n_1 + N_{\mathrm{e}}} \end{cases} \quad [S10]$$

The water uptake can be expressed as

$$w = \frac{\phi_1}{1 - \phi_1} \quad [S11]$$

Vapor adsorption. For adsorbing n_1 mol of water vapor on the surface of 1 mol of the dry hydrogel, the Gibbs free energy change is

$$\Delta G_{\mathrm{ads}} = (\Delta H_{\mathrm{ads}} - T\Delta S_{\mathrm{ads}})n_1 \quad [S12]$$

where ΔH_{ads} is the molar enthalpy of water adsorption on the hydrogel surface, ΔS_{ads} is the molar entropy of water adsorption on the hydrogel surface. At the normal boiling point of water (T_0 = 373 K), the vapor condensation and evaporation are at equilibrium, that is,

$$\Delta G_{\mathrm{liq}}\big|_{T_0} = (\Delta H_{\mathrm{liq}} - T_0 \Delta S_{\mathrm{liq}})n_1 = 0 \quad [S13]$$

where ΔH_{liq} is the molar enthalpy of water condensation (i.e., $\Delta H_{\mathrm{liq}} = -\Delta H_{\mathrm{vap}}$), ΔS_{liq} is the molar entropy of water condensation. We assume that the entropy change per mole of water is the same for condensation and adsorption, and obtain

$$\Delta S_{\mathrm{ads}} = \Delta S_{\mathrm{liq}} = \Delta H_{\mathrm{liq}}/T_0 \quad [S14]$$

According to the multilayer adsorption in the Brunauer–Emmett–Teller (BET) theory [3], the enthalpy change per mole of water for condensation and adsorption is different in particular at the first layer, that is,

$$\Delta H_{\mathrm{ads}} = \Delta H_{\mathrm{liq}} - RT\ln c \quad [S15]$$

where c is the BET constant. Combining the expressions for ΔS_{ads} and ΔH_{ads}, we arrive at the final result:

$$\Delta G_{\mathrm{ads}} = \left[\Delta H_{\mathrm{liq}}\left(1 - \frac{T}{T_0}\right) - RT\ln c\right] n_1 \quad [S16]$$

Since $\Delta \bar{H}_{\mathrm{liq}} = -\Delta \bar{H}_{\mathrm{vap}}$, the partial molar Gibbs free energy change due to vapor sorption is

$$\left(\frac{\partial \Delta G_{\mathrm{ads}}}{\partial n_1}\right)_{p,T} = -\Delta H_{\mathrm{vap}}\left(1 - \frac{T}{T_0}\right) - RT\ln c \quad [S17]$$

where the BET constant $c = \exp\left(\frac{\Delta H_{\mathrm{liq}} - \Delta H_{\mathrm{ads}}}{RT}\right)$.

Polymer-water mixing. For dissolving n_1 mol of liquid water by 1 mol of the dry hydrogel, the Gibbs free energy change is

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \quad [S18]$$

where ΔH_{mix} is the enthalpy change due to polymer-water mixing, ΔS_{mix} is the entropy change due to polymer-water mixing. Because crystalline polymers are not involved in polymer dissolution, we can write down the Gibbs free energy change due to mixing between amorphous polymers and water, based on the Flory-Huggins theory [4, 5]

$$\Delta G_{\mathrm{mix}} = RT(n_1 \ln \phi_1{}' + n_2 \ln \phi_2{}' + n_1 \phi_2{}' \chi) \quad [S19]$$

where χ is the interaction parameter between amorphous polymers and water, $\phi_1{}'$ is the volume fraction of water after mixing, and $\phi_2{}'$ is the volume fraction of amorphous polymers after mixing (crystalline polymers excluded, $\phi_1' + \phi_2{}' = 1$), that is,

$$\begin{cases} \phi_1' = \dfrac{n_1}{n_1 + n_2 N_{\mathrm{e}}} = \dfrac{\phi_1}{\phi_1 + \phi_2} = \dfrac{1}{1 + (1 - n_3)/w} \\ \phi_2' = \dfrac{n_2 N_{\mathrm{e}}}{n_1 + n_2 N_{\mathrm{e}}} = \dfrac{\phi_2}{\phi_1 + \phi_2} = \dfrac{(1 - n_3)/w}{1 + (1 - n_3)/w} \end{cases} \quad [S20]$$

Taking the derivative with respect to ΔG_{mix}, we can obtain the partial molar Gibbs free energy change due to polymer mixing,

$$\left(\frac{\partial \Delta G_{\mathrm{mix}}}{\partial n_1}\right)_{p,T} = RT[ln\phi_1{}' + (1 - \phi_1{}')\left(1 - \frac{1}{N_{\mathrm{e}}}\right) + \chi(1 - \phi_1{}')^2] \quad [S21]$$

Since $\frac{1}{N_e} \ll 1$, we can simplify it to be

$$\left(\frac{\partial \Delta G_{\mathrm{mix}}}{\partial n_1}\right)_{p,T} = RT[ln\phi_1{}' + (1 - \phi_1{}') + \chi(1 - \phi_1{}')^2] \quad [S22]$$

We further substitute $\phi_1{}'$ with water uptake w and crystallinity n_3 and obtain

$$\left(\frac{\partial \Delta G_{\mathrm{mix}}}{\partial n_1}\right)_{p,T} = RT[ln\frac{1}{1 + (1 - n_3)/w} + \left(1 - \frac{1}{1 + (1 - n_3)/w}\right) + \chi\left(1 - \frac{1}{1 + (1 - n_3)/w}\right)^2] \quad [S23]$$

Polymer network deformation. For deforming the polymer network per mol of the dry hydrogel, the Gibbs free energy change is

$$\Delta G_{\mathrm{def}} = \Delta H_{\mathrm{def}} - T\Delta S_{\mathrm{def}} \quad [S24]$$

Since the deformation is assumed to be purely entropic, we can obtain

$$\Delta G_{\mathrm{def}} = -T\Delta S_{\mathrm{def}} \quad [S25]$$

The deformation-induced entropy change follows the rubber elasticity [6], that is,

$$\Delta S_{\mathrm{def}} = -\frac{k v_{\mathrm{e}}}{2}\left[{\lambda_x}^2 + {\lambda_y}^2 + {\lambda_z}^2 - 3 - \ln\left(\lambda_x \lambda_y \lambda_z\right)\right] \quad [S26]$$

where v_{e} is the number of effective strands, and λ_x, λ_y, λ_z are the extension ratios in different directions. When the deformation is not constrained, it shows isotropic expansion (i.e., $\lambda_x = \lambda_y = \lambda_z = \lambda$). The volumetric expansion can be given by

$$\lambda^3 = \frac{1}{\phi_2 + \phi_3} \quad [S27]$$

The one-dimensional extension ratio is

$$\lambda = (1 + w)^{\frac{1}{3}} \quad [S28]$$

The Gibbs free energy due to polymer network deformation can be written as

$$\Delta G_{\mathrm{def}} = \frac{kTv_{\mathrm{e}}}{2}[3\lambda^2 - 3 - 3\ln\lambda] \quad [S29]$$

Taking the derivative with respect to ΔG_{def}, we can obtain the partial molar Gibbs free energy change is

$$\left(\frac{\partial \Delta G_{\mathrm{def}}}{\partial n_1}\right)_{p,T} = kTv_{\mathrm{e}}\left(3\lambda - \frac{3}{2\lambda}\right)\frac{\partial \lambda}{\partial n_1} \quad [S30]$$

Due to the volume conservation, we obtain

$$\lambda^3 = \frac{n_1 V_1 + V_0}{V_0} \quad [S31]$$

where V_1 is the molar volume of water and V_0 is the molar volume of the dry hydrogel. If we differentiate this expression with respect to n_1, we obtain

$$\left(\frac{\partial \lambda}{\partial n_1}\right) = \frac{1}{3\lambda^2}\frac{V_1}{V_0} \quad [S32]$$

By incorporating the above expressions for λ (Eq. S28) and its partial derivative (Eq. S32) into the partial molar Gibbs free energy change (Eq. S30), we arrive at the result of

$$\left(\frac{\partial \Delta G_{\mathrm{def}}}{\partial n_1}\right)_{p,T} = kTv_{\mathrm{e}}\frac{V_1}{V_0}\left((1 + w)^{-\frac{1}{3}} - \frac{(1 + w)^{-1}}{2}\right) \quad [S33]$$

In hydrogels, both chemical and physical crosslinkers contribute to the final hydrogel elasticity. In semi-crystalline hydrogels, the number of polymer effective strands is higher than purely chemically crosslinked polymers due to the presence of crystalline lamellae. We use a measurable parameter, Young's modulus, to represent the number of effective strands. The expression for Young's modulus is [7]

$$E = \frac{3kT}{\lambda}\frac{v_{\mathrm{e}}}{V_0} \quad [S34]$$

By substituting v_{e} with Young's modulus, we can obtain

$$\left(\frac{\partial \Delta G_{\mathrm{def}}}{\partial n_1}\right)_{p,T} = \frac{EV_1}{3}\left(1 - \frac{1}{2(1 + w)^{2/3}}\right) \quad [S35]$$

Polymer melting. For melting the crystalline polymer in 1 mol of the dry hydrogel, the Gibbs free energy change is

$$\Delta G_{\mathrm{melt}} = (\Delta H_{\mathrm{melt}} - T\Delta S_{\mathrm{melt}})n_3 \quad [S36]$$

At the melting point T_m of polymer, the polymer melting and crystallization are at equilibrium, that is,

$$\Delta G_{\mathrm{melt}}|_{T_{\mathrm{m}}} = (\Delta H_{\mathrm{melt}} - T_{\mathrm{m}}\Delta S_{\mathrm{melt}})n_3 = 0 \quad [S37]$$

We obtain the entropy change due to melting as

$$\Delta S_{\mathrm{melt}} = \Delta H_{\mathrm{melt}}/T_{\mathrm{m}} \quad [S38]$$

Then we can get the simplified Gibbs free energy change due to melting

$$\Delta G_{\mathrm{melt}} = \Delta H_{\mathrm{melt}}(1 - \frac{T}{T_{\mathrm{m}}})n_3 \quad [S39]$$

We assume the quantities of crystalline polymers and water are independent, that is, $\frac{\partial n_3}{\partial n_1} = 0$. Therefore, melting of the crystalline polymers in 1 mol of the dry hydrogel is independent of the water content, the partial molar Gibbs free energy change due to polymer melting is 0, so that,

$$\left(\frac{\partial \Delta G_{\mathrm{melt}}}{\partial n_1}\right)_{p,T} = 0 \quad [S40]$$

Final equation. By substituting Eqs. S6, S9, S17, S23, S35, S40 into Eq. S1, we arrive at the final equation

$$\begin{aligned}\ln(\mathrm{RH}) = &-\left(\frac{\Delta H_{\mathrm{liq}} - \Delta H_{\mathrm{ads}}}{RT}\right) + ln\left(\frac{1}{1+(1-n_3)/w}\right) \\ &+ \left(1 - \frac{1}{1+(1-n_3)/w}\right) + \chi\left(1 - \frac{1}{1+(1-n_3)/w}\right)^2 \\ &+ \frac{EV_1}{3RT}\left(1 - \frac{1}{2(1+w)^{2/3}}\right)\end{aligned} \quad [S41]$$

To obtain the water uptake as a function of environmental variables $w(\mathrm{RH}, T)$, we need the numerical quantities of ΔH_{ads}, χ, n_3, and E for specific materials.

Material parameters. ΔH_{ads} is the molar enthalpy of water adsorption on the hydrogel surface. Using the PEG hydrogel as an example, we first measure the water uptake isotherms at four different temperatures (5, 25, 50, and 75 °C) (Fig. S10A). The isotherms are converted to isosteres, that is, plots of $\ln(p)$ vs $1/T$ (Fig. S10B). We calculate the values of ΔH_{ads} through the Clausius-Clapeyron equation

$$\ln(p) = -\frac{\Delta H_{\mathrm{ads}}}{RT} + C \quad [S42]$$

where *p* is water vapor feed pressure, *T* is sorption temperature, *R* is the ideal gas constant, and *C* is an integration constant. From the Clausius-Clapeyron equation, we can obtain the values of ΔH_{ads} to be -41.95 kJ/mol, which is slightly lower than the condensation enthalpy of water ΔH_{liq}, which is -40.65 kJ/mol. The difference between adsorption and condensation enthalpy ($\Delta H_{\mathrm{ads}} - \Delta H_{\mathrm{liq}}$) is -1.3 kJ/mol. χ is the interaction parameter between amorphous polymers and water. According to the data in the literature[8], we can see χ for the PEG-water system is almost independent of temperature and significantly affected by the volume fraction of the polymer. In our work, we assume that χ = 2.1 for PEG-water mixing[8]. n_3 is the crystallinity of the hydrogel. Based on the TGA/DSC measurement, we obtain the numbers of n_3 at varied RHs and temperatures, and use linear dependence and Fermi-Dirac distribution to approximate the function of $n_3(\mathrm{RH})$ and $n_3(T)$, respectively (Fig. S9B,C). Therefore, the crystallinity can be estimated by

$$n_3(\mathrm{RH}, T) = \frac{n_{3,\max}}{2} * \left[1 - \mathrm{erf}\left(\frac{T - T_m}{\mu}\right)\right] \quad [S43]$$

where $n_{3,\max}$ is the maximum crystallinity, T_m is the melting temperature, and μ is a fitting parameter.

Furthermore, E, Young's modulus of the hydrogel, follows the similar temperature and humidity dependence as crystallinity, because of the crystalline lamellae as a major crosslinker in the semi-crystalline hydrogels. Therefore, we can write down the fitting function for Young's modulus as

$$E(\mathrm{RH},T) = \frac{E_{\max} n_{3,\max}}{2} * \left[1 - \mathrm{erf}\left(\frac{T - T_m}{\mu}\right)\right] + E_{\min} \qquad [S44]$$

2. Supplementary Tables

Table S1. Material parameters for PEG and PAAm hydrogels in the thermodynamic analysis.

Parameters	PEG	PAAm
$\Delta \boldsymbol{H}_{\mathbf{ads}}$ (kJ/mol)	-41.95	-43.65
$\Delta \boldsymbol{H}_{\mathbf{liq}}$ (kJ/mol)	-40.65	-40.65
$\boldsymbol{\chi}$	2.1	2.1
$\boldsymbol{V}_{\mathbf{1}}$ (m^3/mol)	1.8×10^{-5}	1.8×10^{-5}
$\boldsymbol{n}_{\mathbf{3,max}}$	0.66	0
$\boldsymbol{T}_{\mathbf{m}}$ (°C)	46.5	/
$\boldsymbol{\mu}$	2.0	/
$\boldsymbol{E}_{\mathbf{max}}$ (kPa)	77000	77000
$\boldsymbol{E}_{\mathbf{min}}$ (kPa)	46	77000

Table S2. Maximum polymer crystallinity and melting temperature of PEG hydrogels with different molecular weights of polymer chains.

Molecular weight of polymer chains	**Max polymer crystallinity, $n_{3,max}$**	**Melting temperature, T_m (°C)**
5kDa	0.44	25.6
10kDa	0.58	38.0
20kDa	0.66	46.5
40kDa	0.78	53.6

Table S3. Maximum polymer crystallinity and melting temperature of PEG hydrogels with different PEG mass ratios during sample preparation.

PEG mass ratios during sample preparation	**Max polymer crystallinity, $n_{3,max}$**	**Melting point, T_m (°C)**
5 wt%	0.61	45.8
10 wt%	0.66	46.5
15 wt%	0.67	49.6

3. Supplementary Figures

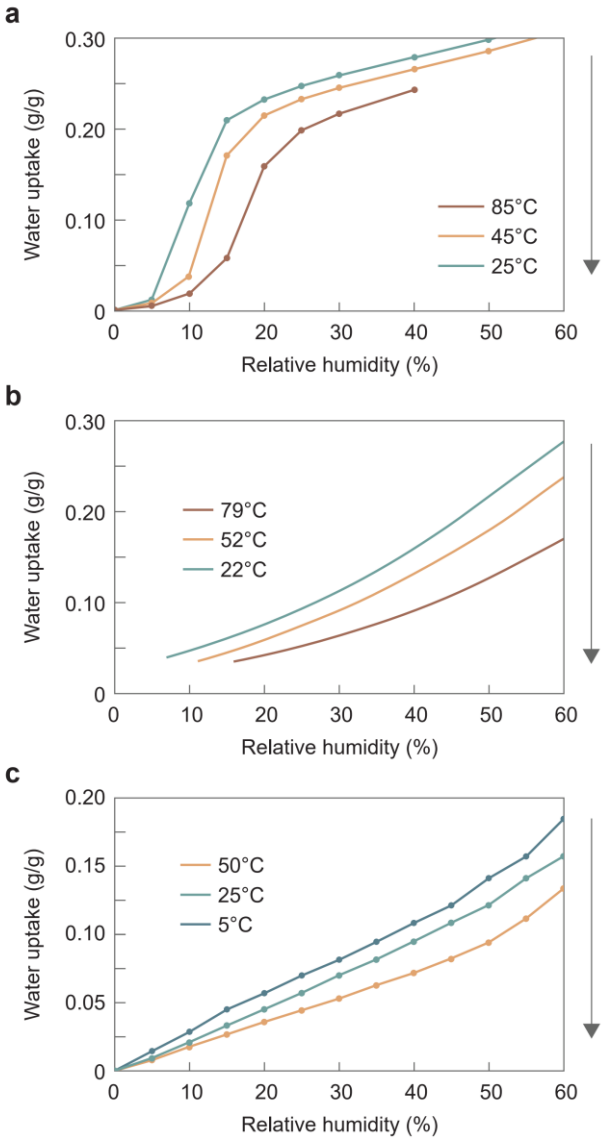


Figure S1. Water vapor uptake isotherms of the MOF-801 [9, 10] (a), silica gel [11] (b), and PAAm hydrogel (c) in g/g as a function of RH at different temperatures.

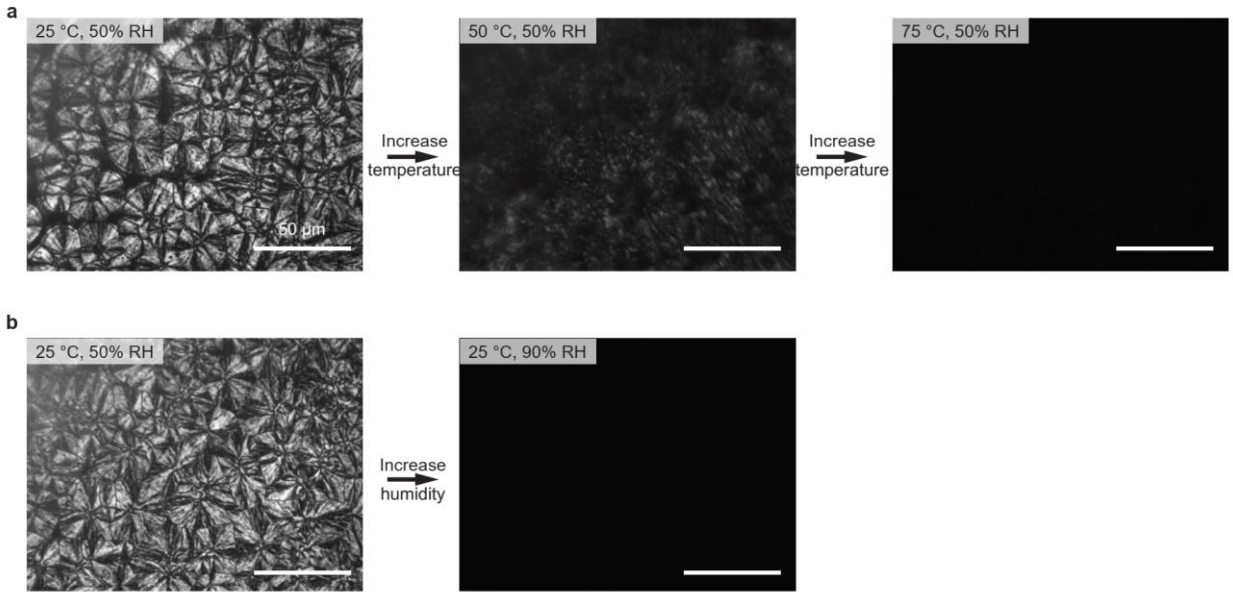


Figure S2. Polarized optical microscopic images showing the crystallization morphology of the PEG hydrogels at different temperatures (a) and RHs (b). There are highly ordered spherulites at 25 °C and 50% RH, while increasing temperature or RH will lead to the disappearance of the spherulites (all black images at 75 °C and 50%, as well as 25 °C and 90%).

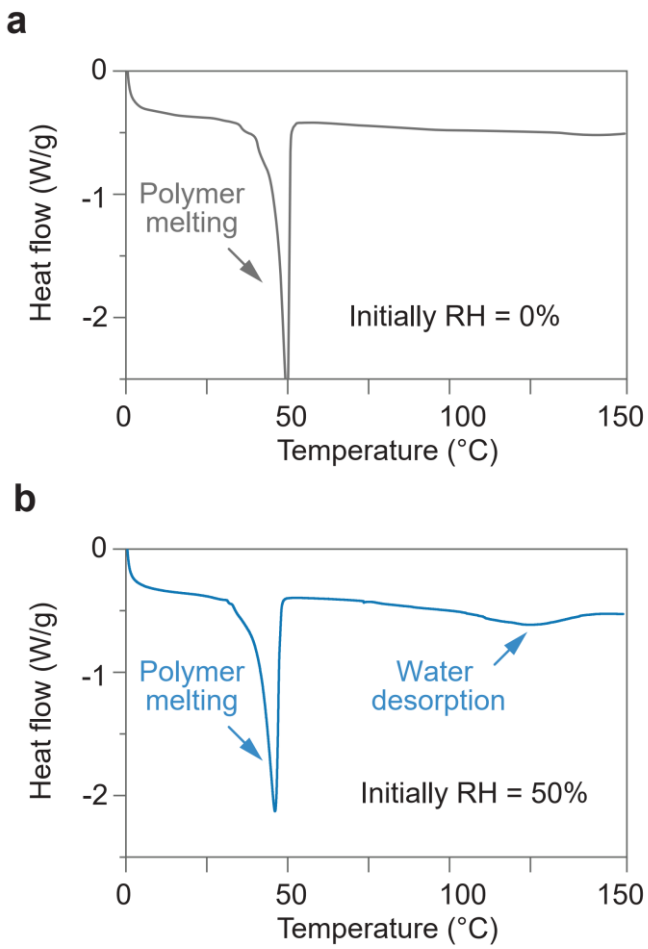


Figure S3. DSC thermographs of the PEG hydrogels when they are pre-incubated at the RH of 0% (a) and 50% (b) for 12 h.

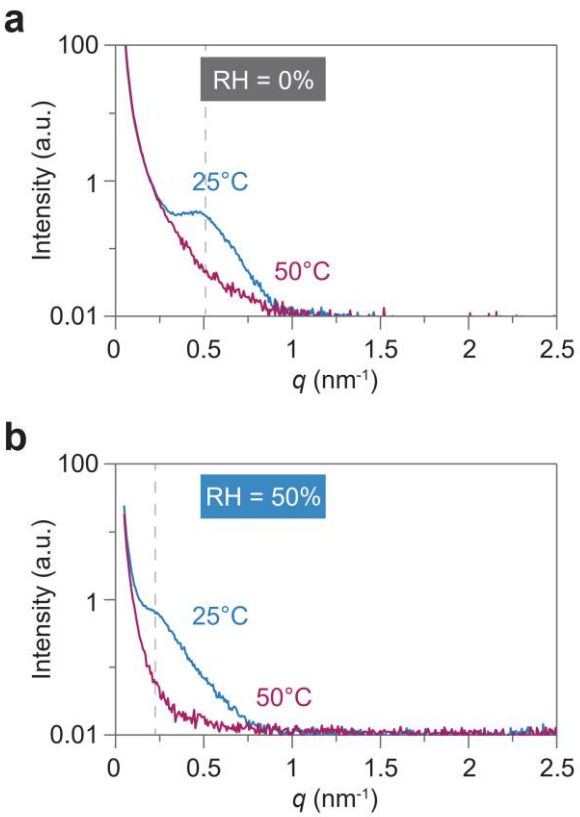


Figure S4. SAXS profiles of the PEG hydrogel at different temperatures when the RH is kept at 0% (a) and 50% (b).

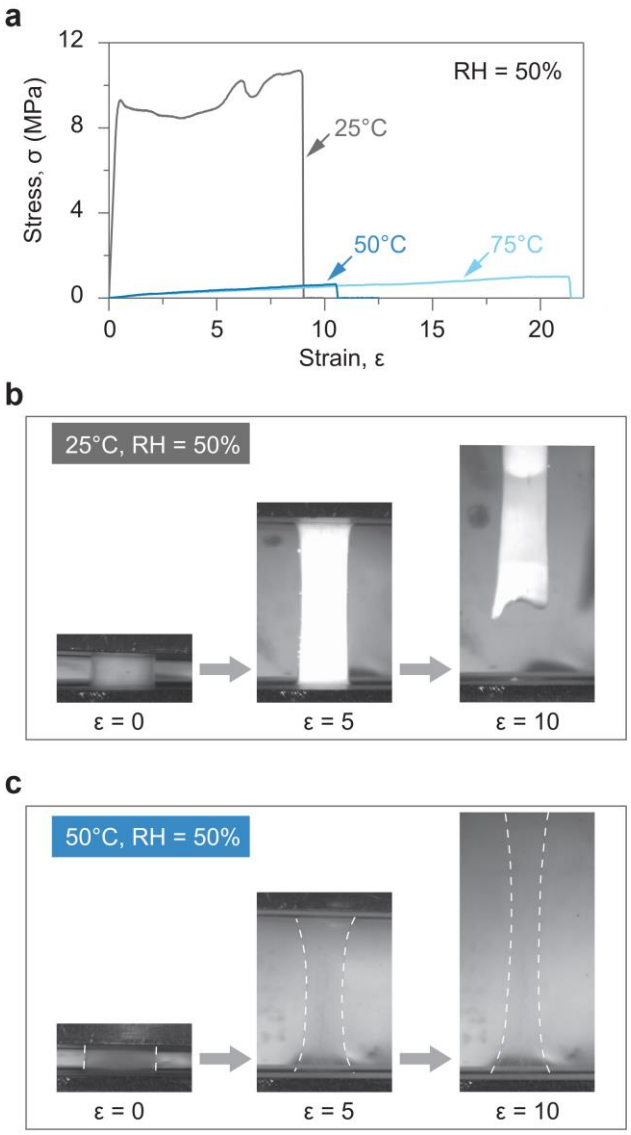


Figure S5. (a) Stress-strain curves of the PEG hydrogel when they are pre-incubated at the RH of 50% for 12 h, and tested at different temperatures of 25, 50, and 75°C. (b) Images of the PEG hydrogel at 25°C under uniaxial tension with the strains of 0, 5, and 10. (c) Images of the PEG hydrogel at 50°C under uniaxial tension with the strains of 0, 5, and 10.

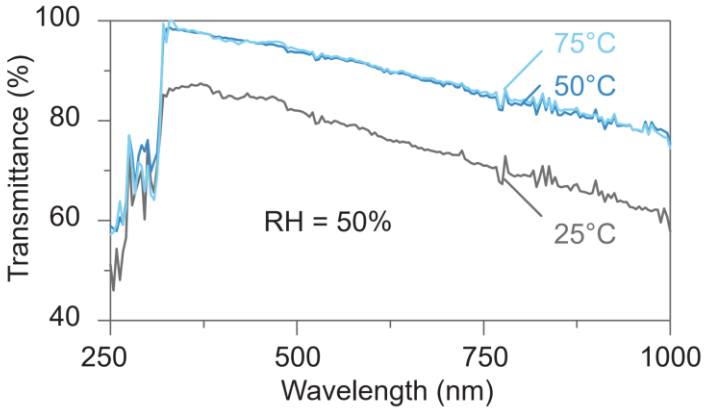


Figure S6. UV-visible transmittance spectra of the PEG hydrogels when they are pre-incubated at the RH of 50% and different temperatures of 25, 50, and 75°C for 12 h.

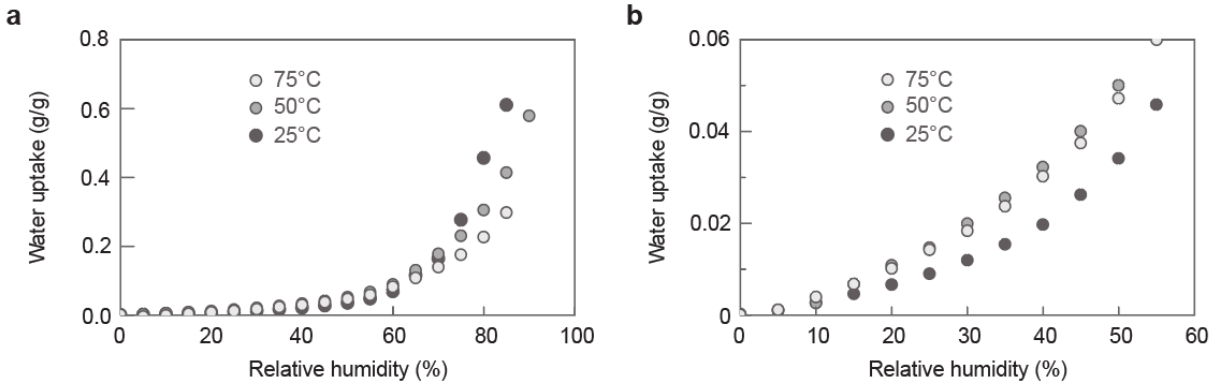


Figure S7. (a) Water uptake of the PEG hydrogel as a function of RH (RH range: 0-100%) at different temperatures. (b) Water uptake of the PEG hydrogel as a function of RH (RH range: 0-60%) at different temperatures. The water uptake shows the unusual temperature dependence within the RH range of 0-60%, but the normal negative dependence on temperature within the RH range of 60-100%.

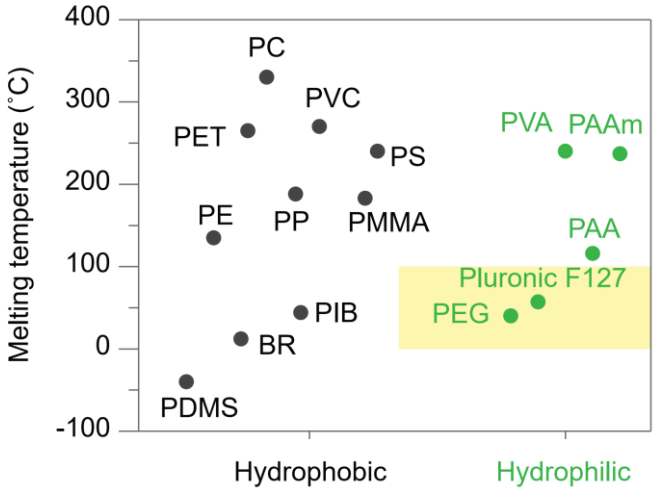


Figure S8. Melting temperatures and wettability information of common polymers. The yellow region highlights the polymers that are expected to exhibit the unusual temperature dependence of water sorption. The melting temperature and wettability data were obtained from Ref. [12]. PC, polycarbonates; PVC, *polyvinyl chloride; PET, polyethylene terephthalate; PS,* polystyrene; PE, polyethylene; PP, *polypropylene; PMMA, poly(methyl methacrylate); PIB, polyisobutylene; BR, polybutadiene; PDMS, polydimethylsiloxane; PVA, polyvinyl alcohol; PAAm, polyacrylamide; PAA, polyacrylic acid.*

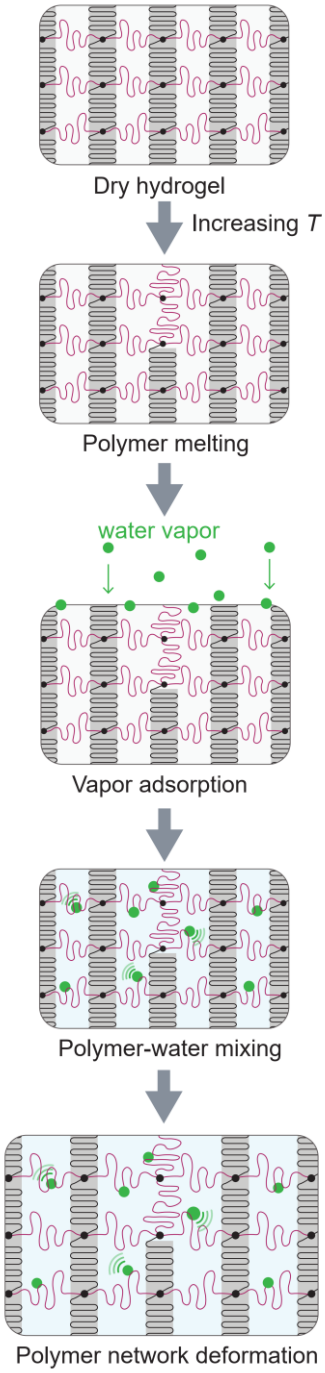


Figure S9. The model of water sorption by dry hydrogels accounts for the effects of vapor adsorption, polymer-water mixing, polymer network deformation, and polymer melting. The vapor adsorption process describes how the water vapor molecules interact with the polymer surface. The polymer-water mixing process describes that the adsorbed water molecules diffuse inside the polymer network, which is equivalent to the absorption process.

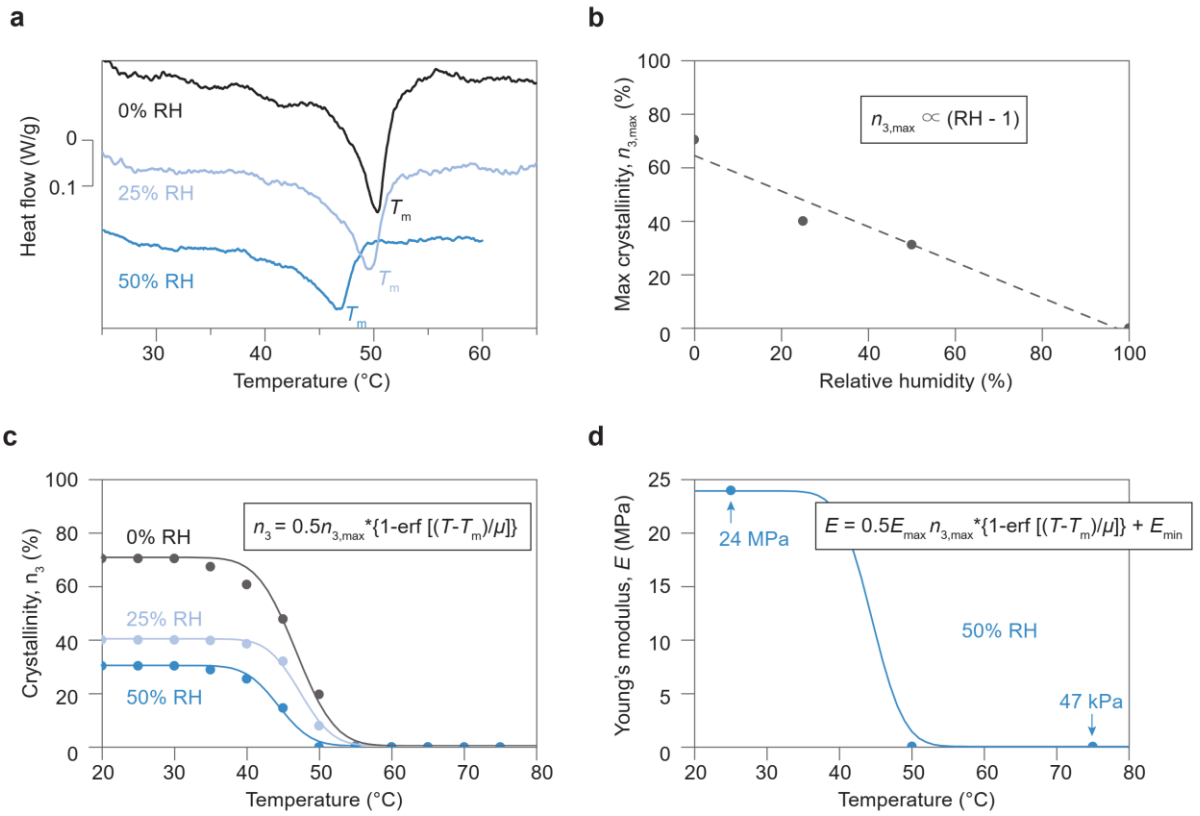


Figure S10. (a) DSC thermographs of the PEG hydrogel when the RH is kept at 0%, 25%, and 50%. (b) Maximum crystallinity as a function of RH. (c) Crystallinity as a function of temperature. (d) Young's modulus as a function of temperature. Solid dots: experimental data, dash line: fitting curves.

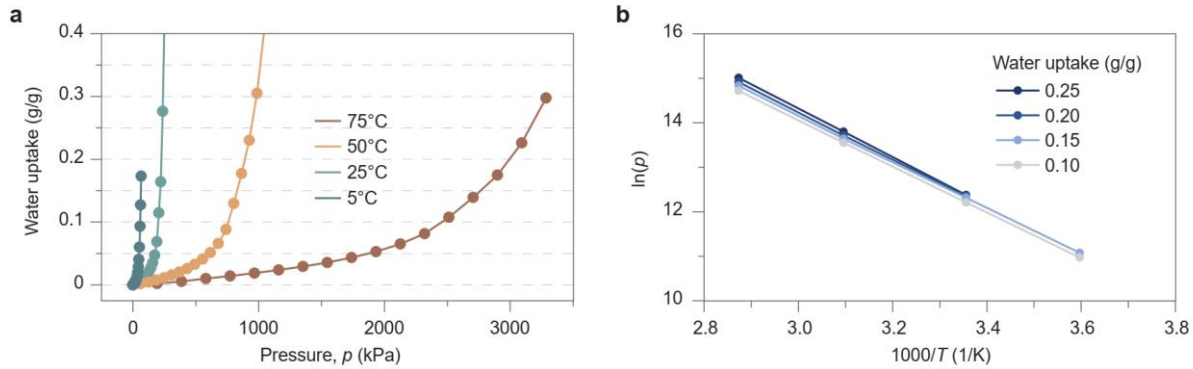


Figure S11. (a) Water vapor uptake isotherms of the PEG hydrogel as a function of vapor pressure at temperatures of 5, 25, 50, and 75°C. (b) $\ln(p)$ as a function of $1000/T$ at different level of water uptake.

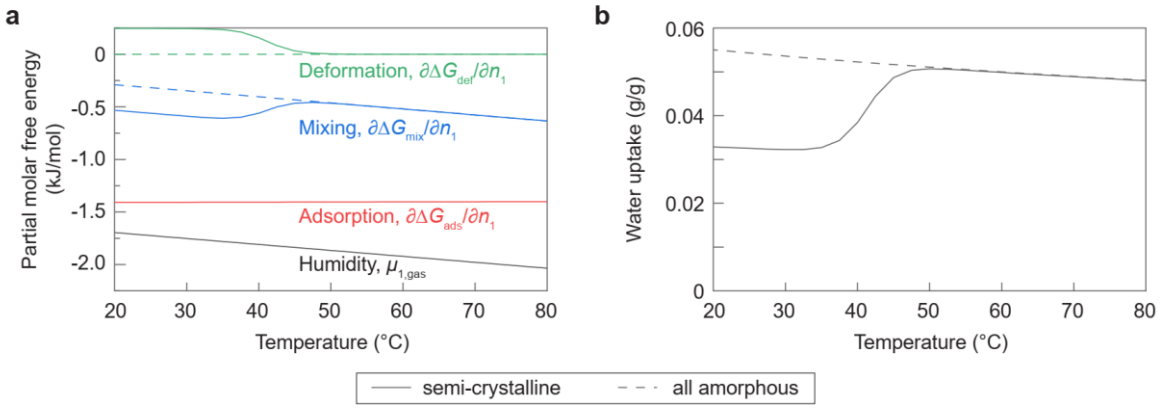


Figure S12. (a) Different terms of partial molar Gibbs free energy as a function of temperature, including $\left(\frac{\partial \Delta G_{\mathrm{def}}}{\partial n_1}\right)_{p,T}$ for polymer network deformation, $\left(\frac{\partial \Delta G_{\mathrm{mix}}}{\partial n_1}\right)_{p,T}$ for polymer-water mixing, $\left(\frac{\partial \Delta G_{\mathrm{ads}}}{\partial n_1}\right)_{p,T}$ for vapor adsorption, and chemical potential of water molecules in the gas phase $\mu_{1,\mathrm{gas}}$. (b) Water uptake of hydrogels as a function of temperature. Solid lines: semi-crystalline hydrogel. Dash lines: all amorphous hydrogel.

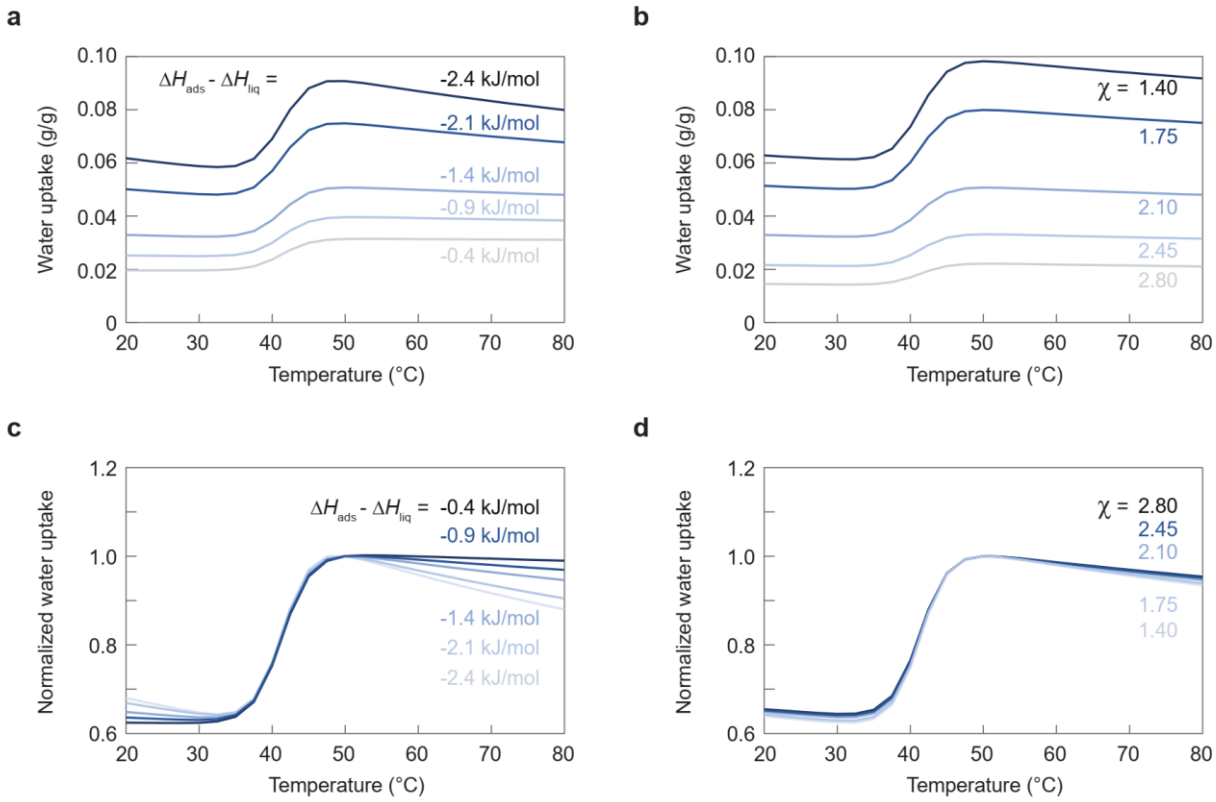


Figure S13. (a-b) Theoretical water uptake of the semi-crystalline hydrogel as a function of temperature in response to the changing enthalpy difference in adsorption and condensation ($\Delta H_{\mathrm{ads}} - \Delta H_{\mathrm{liq}}$, a) and interaction parameter between PEG and water (χ, b). (c-d) Theoretical normalized water uptake of the semi-crystalline hydrogel as a function of temperature in response to the changing enthalpy difference in adsorption and condensation ($\Delta H_{\mathrm{ads}} - \Delta H_{\mathrm{liq}}$, c) and interaction parameter between PEG and water (χ, d). The water uptake is normalized by the maximum water uptake.

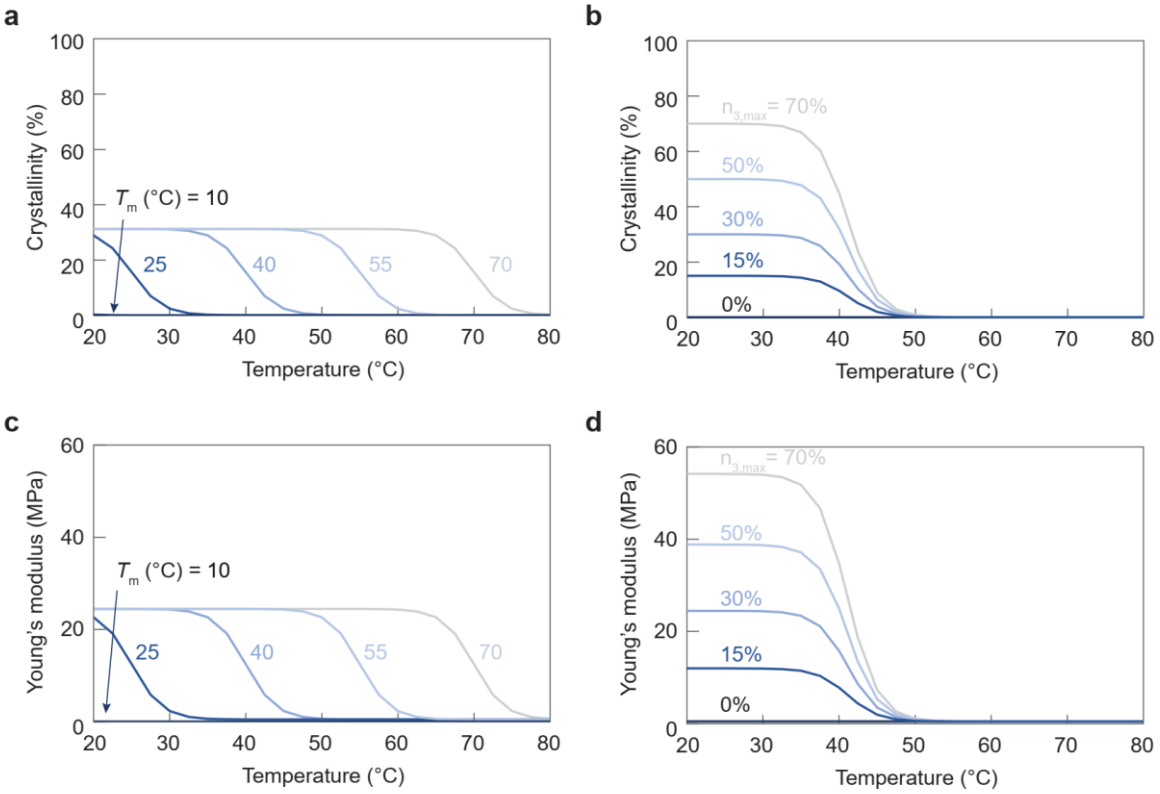


Figure S14. (a-b) Crystallinity as a function of temperature in response to the changing melting point (T_m, a) and maximum crystallinity ($n_{3,max}$, b). (c-d) Young's modulus as a function of temperature in response to the changing melting point (T_m, c) and maximum crystallinity ($n_{3,max}$, d).

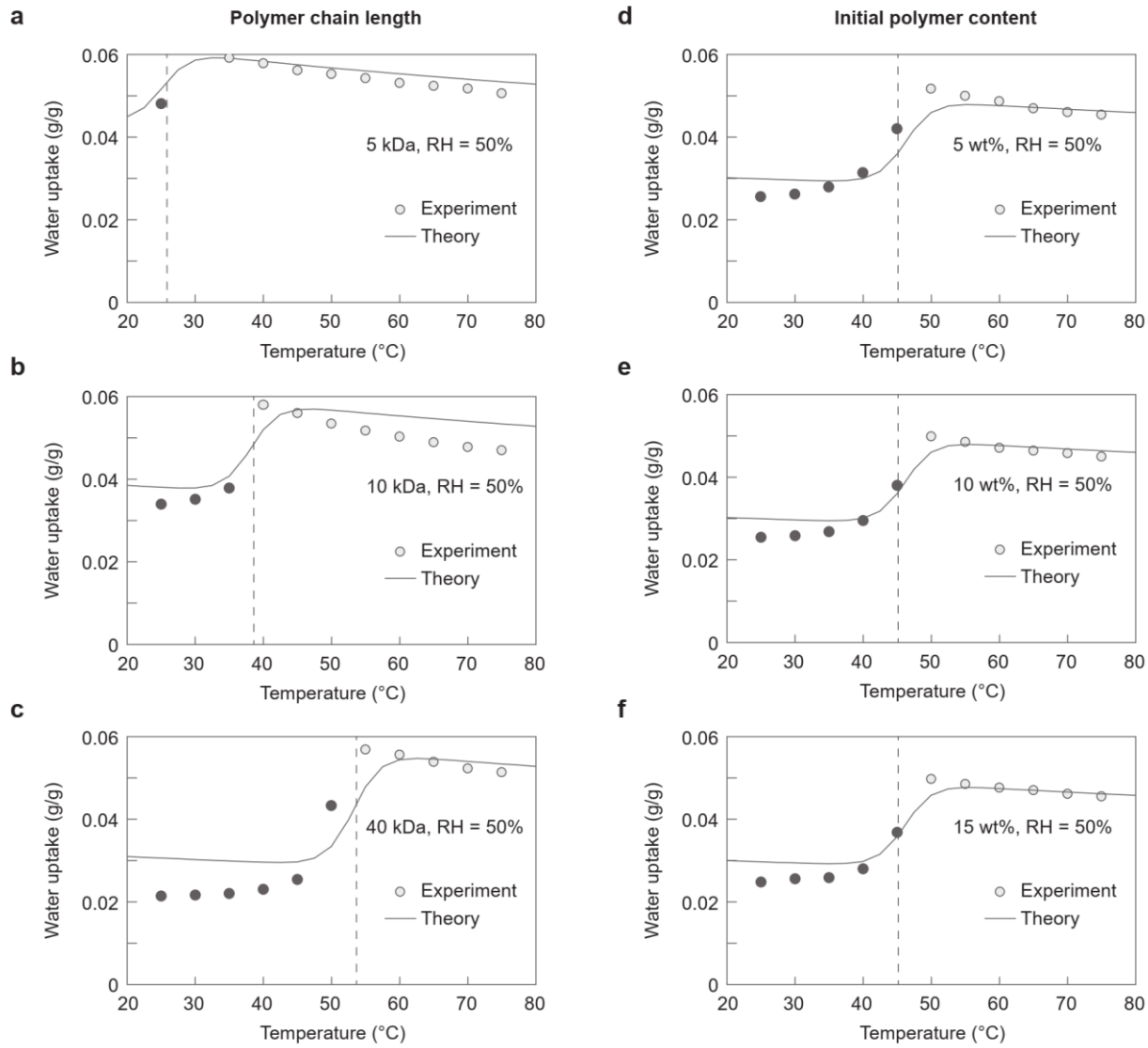


Figure S15. Water uptake of the PEG hydrogel samples as a function of temperature at RH = 50%. The PEG hydrogel samples have different molecular weights of polymer chains ranging from 5 kDa (a), 10 kDa (b), and 40 kDa (c) and the same PEG mass ratios during sample preparation (10 wt%, a-c). Other PEG hydrogel samples also have the same molecular weights of polymer chains (20 kDa, d-f) and different PEG mass ratios during sample preparation ranging from 5 wt% (d), 10 wt% (e), and 15 wt% (f). Vertical dash lines represent the melting temperatures (T_m), solid dots represent the water uptake below T_m, and hallow dots represent the water uptake above T_m.

References

1. Mittal H, Al Alili A, Alhassan SM. Adsorption isotherm and kinetics of water vapors on novel superporous hydrogel composites. *Microporous Mesoporous Materials* 2020, **299:** 110106.
2. Sariban A, Binder K. Critical properties of the Flory–Huggins lattice model of polymer mixtures. *The Journal of Chemical Physics* 1987, **86**(10)**:** 5859-5873.
3. Brunauer S, Emmett PH, Teller E. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society* 1938, **60**(2)**:** 309-319.
4. Flory PJ. Thermodynamics of high polymer solutions. *The Journal of Chemical Physics* 1942, **10**(1)**:** 51-61.
5. Huggins ML. Solutions of long chain compounds. *The Journal of Chemical Physics* 1941, **9**(5)**:** 440-440.
6. Flory PJ, Rehner Jr J. Statistical mechanics of cross-linked polymer networks I. Rubberlike elasticity. *The Journal of Chemical Physics* 1943, **11**(11)**:** 512-520.
7. Zhao X, Chen X, Yuk H, Lin S, Liu X, Parada G. Soft materials by design: unconventional polymer networks give extreme properties. *Chemical Reviews* 2021, **121**(8)**:** 4309-4372.
8. Bae Y, Shim J, Soane D, Prausnitz J. Representation of vapor–liquid and liquid–liquid equilibria for binary systems containing polymers: applicability of an extended Flory–Huggins equation. *Journal of Applied Polymer Science* 1993, **47**(7)**:** 1193-1206.
9. Kim H, Rao SR, Kapustin EA, Zhao L, Yang S, Yaghi OM, *et al.* Adsorption-based atmospheric water harvesting device for arid climates. *Nature Communications* 2018, **9**(1)**:** 1191.
10. Kim H, Yang S, Rao SR, Narayanan S, Kapustin EA, Furukawa H, *et al.* Water harvesting from air with metal-organic frameworks powered by natural sunlight. *Science* 2017, **356**(6336)**:** 430-434.
11. Dini S. Analysis of Cross-Cooled Desiccant Cooling Systems. Ph.D. thesis, Illinois Institute of Technology, 1982.
12. Hiemenz PC, Lodge TP. *Polymer Chemistry*. CRC press, 2007.