Supplementary material

Equilibrium swelling of thermo-responsive copolymer microgels

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Governing equations

Inserting expressions (6), (7) and (11) into Eq. (5) for the specific Helmholtz free energy Ψ and using Eq. (12), we find that

$$\Psi = \mu^0 C + k_{\rm B}T_0 C\Bigl(\ln\frac{Cv}{1+Cv} + \frac{\chi}{1+Cv}\Bigr) + \sum_{m=1}^{2} W_m(I_{\rm e1}^{(m)}, I_{\rm e2}^{(m)}, I_{\rm e3}^{(m)}). \qquad \text{(S-1)}$$

Differentiation of Eq. (S-1) with respect to time implies that

$$\begin{aligned}\dot\Psi &= \Bigl[\mu^0 + k_{\rm B}T_0\Bigl(\ln\frac{Cv}{1+Cv} + \frac{1}{1+Cv} + \frac{\chi}{(1+Cv)^2}\Bigr)\Bigr]\dot C \\ &\quad + \sum_{m=1}^{2}\Bigl(\frac{\partial W_m}{\partial I_{\rm e1}^{(m)}}\dot I_{\rm e1}^{(m)} + \frac{\partial W_m}{\partial I_{\rm e2}^{(m)}}\dot I_{\rm e2}^{(m)} + \frac{\partial W_m}{\partial I_{\rm e3}^{(m)}}\dot I_{\rm e3}^{(m)}\Bigr), \qquad \text{(S-2)}\end{aligned}$$

the superscript dot stands for the derivative with respect to time t. In derivation of Eq. (S-2), χ is treated as a constant due to condition (13).

The derivatives of the principal invariants $I_{\rm e1}^{(m)}$, $I_{\rm e2}^{(m)}$, $I_{\rm e3}^{(m)}$ of the tensors $\mathbf{B}_{\rm e}^{(m)}$ $(m = 1, 2)$ read

$$\dot I_{\rm e1}^{(m)} = 2\mathbf{B}_{\rm e}^{(m)} : \mathbf{D}, \quad \dot I_{\rm e2}^{(m)} = 2\Bigl(I_{\rm e2}^{(m)}\mathbf{I} - I_{\rm e3}^{(m)}(\mathbf{B}_{\rm e}^{(m)})^{-1}\Bigr) : \mathbf{D}, \qquad \dot I_{\rm e3}^{(m)} = 2I_{\rm e3}^{(m)}\mathbf{I} : \mathbf{D}, \qquad \text{(S-3)}$$

where the colon denotes convolution, $\mathbf{L} = \dot{\mathbf{F}} \cdot \mathbf{F}^{-1}$ is the velocity gradient, and $\mathbf{D} = \frac{1}{2}(\mathbf{L} + \mathbf{L}^\top)$ is the rate-of-strain tensor. It follows from Eqs. (S-2) and (S-3) that

$$\dot\Psi = K\dot C + 2\mathbf{K} : \mathbf{D}, \qquad \text{(S-4)}$$

where

$$\begin{aligned} K &= \mu^0 + k_{\rm B}T_0\Bigl[\ln\frac{Cv}{1+Cv} + \frac{1}{1+Cv} + \frac{\chi}{(1+Cv)^2}\Bigr], \\ \mathbf{K} &= \sum_{m=1}^{2}\Bigl[\frac{\partial W_m}{\partial I_{\rm e1}^{(m)}}\mathbf{B}_{\rm e}^{(m)} - I_{\rm e3}^{(m)}\frac{\partial W_m}{\partial I_{\rm e2}^{(m)}}(\mathbf{B}_{\rm e}^{(m)})^{-1} + \Bigl(I_{\rm e2}^{(m)}\frac{\partial W_m}{\partial I_{\rm e2}} + I_{\rm e3}^{(m)}\frac{\partial W_m}{\partial I_{\rm e3}^{(m)}}\Bigr)\mathbf{I}\Bigr]. \qquad \text{(S-5)}\end{aligned}$$

To develop constitutive equations for a TR gel, we apply the free energy imbalance inequality

$$\dot\Psi - u_{\rm mec} - u_{\rm dif} \le 0, \qquad \text{(S-6)}$$

where $u_{\rm mec}$ and $u_{\rm dif}$ denote works (per unit volume in the initial state and unit time) produced by stresses and diffusion of solvent molecules.

The specific mechanical work is determined by the conventional formula

$$u_{\rm mec} = J\mathbf{\Sigma} : \mathbf{D}, \tag{S-7}$$

where $J = \det \mathbf{F}$, and $\mathbf{\Sigma}$ is the Cauchy stress tensor.

The specific work produced by solvent transport is determined by

$$u_{\rm dif} = \mu\dot{C} + \bar{u}_{\rm dif} \tag{S-8}$$

with

$$\bar{u}_{\rm dif} \geq 0. \tag{S-9}$$

Eq. (S-6) is satisfied when the functions C and $\mathbf{F}$ are connected by the molecular incompressibility condition (1). To account for this connection, we differentiate Eq. (1) with respect to time and find that

$$\dot{C}v - J\mathbf{I} : \mathbf{D} = 0. \tag{S-10}$$

We now multiplying Eq. (S-10) by an arbitrary function Π (pressure treated as a Lagrange multiplier) and add the result to Eq. (S-6). Using Eqs. (S-4), (S-7) and (S-8), we arrive at the formula

$$(K + \Pi v - \mu)\dot{C} + [2\mathbf{K} - J(\mathbf{\Sigma} + \Pi\mathbf{I})] : \mathbf{D} - \bar{u}_{\rm dif} \leq 0. \tag{S-11}$$

Keeping in mind that C and $\mathbf{D}$ are arbitrary functions and using Eq. (S-9), we conclude that inequality (S-11) is fulfilled, provided that the chemical potential μ of water molecules reads

$$\mu = \mu^0 + k_{\rm B}T_0\bar{\mu}, \qquad \bar{\mu} = \ln\frac{Q}{1+Q} + \frac{1}{1+Q} + \frac{\chi}{(1+Q)^2} + \frac{\Pi v}{k_{\rm B}T_0}, \tag{S-12}$$

and the Cauchy stress tensor $\mathbf{\Sigma}$ is given by

$$\mathbf{\Sigma} = -\Pi\,\mathbf{I} + \frac{2}{1+Q}\sum_{m=1}^{2}\Big[\frac{\partial W_m}{\partial I_{\rm e1}^{(m)}}\mathbf{B}_{\rm e}^{(m)} - I_{\rm e3}^{(m)}\frac{\partial W_m}{\partial I_{\rm e2}^{(m)}}(\mathbf{B}_{\rm e}^{(m)})^{-1} + \Big(I_{\rm e2}^{(m)}\frac{\partial W_m}{\partial I_{\rm e2}} + I_{\rm e3}^{(m)}\frac{\partial W_m}{\partial I_{\rm e3}^{(m)}}\Big)\mathbf{I}\Big], \tag{S-13}$$

where degree of swelling Q is given by Eq. (15).

Eqs. (S-12) and (S-13) provide constitutive equations for the mechanical response of a TR gel. Adopting the neo-Hookean expressions (9) for the functions W_m, we present Eq. (S-13) in the form

$$\mathbf{\Sigma} = -\Pi\,\mathbf{I} + \frac{1}{1+Q}\Big[G_1(\mathbf{B}_{\rm e}^{(1)} - \mathbf{I}) + G_2(\mathbf{B}_{\rm e}^{(2)} - \mathbf{I})\Big]. \tag{S-14}$$

We consider unconstrained equilibrium swelling of a TR gel in a water bath with a fixed temperature T when pressure in the bath is disregarded,

$$\Pi^{\rm bath} = 0. \tag{S-15}$$

Under equilibrium, Q is independent of spatial coordinates (it depends on temperature T only), and the deformation gradient reads

$$\mathbf{F} = (1+Q)^{\frac{1}{3}}\mathbf{I}. \tag{S-16}$$

Combining Eqs. (S-14) and (S-16) and using Eqs. (3) and (4), we find that

$$\boldsymbol{\Sigma} = \Sigma\mathbf{I}, \qquad \Sigma = -\Pi + \frac{1}{1+Q}\Big\{G_1\Big[\Big(\frac{1+Q}{1+Q_0}\Big)^{\frac{2}{3}} - 1\Big] + G_2\Big[(1+Q)^{\frac{2}{3}} - 1\Big]\Big\}. \tag{S-17}$$

It follows from the equilibrium conditions and Eq. (S-15) that

$$\Sigma = 0.$$

Insertion of Eq. (S-17) into this equality implies that

$$\Pi = \frac{1}{1+Q}\Big\{G_1\Big[\Big(\frac{1+Q}{1+Q_0}\Big)^{\frac{2}{3}} - 1\Big] + G_2\Big[(1+Q)^{\frac{2}{3}} - 1\Big]\Big\}. \tag{S-18}$$

The chemical potential of water molecules in a gel is determined by Eq. (S-12). Its chemical potential in the bath is given by the same equality where the terms describing interactions between water molecules and segments of chains are disregarded,

$$\mu^{\rm bath} = \mu^0. \tag{S-19}$$

Substituting expressions (S-12) and (S-19) into the equilibrium condition

$$\mu = \mu^{\rm bath}, \tag{S-20}$$

and using Eq. (S-18), we arrive at the nonlinear equation for the equilibrium degree of swelling,

$$\ln\frac{Q}{1+Q} + \frac{1}{1+Q} + \frac{\chi}{(1+Q)^2} + \frac{g_1}{1+Q}\Big[\Big(\frac{1+Q}{1+Q_0}\Big)^{\frac{2}{3}} - 1\Big] + \frac{g_2}{1+Q}\Big[(1+Q)^{\frac{2}{3}} - 1\Big] = 0, \tag{S-21}$$

where dimensionless elastic moduli g_m are given by Eq. (17).

Tables

Table S-1: Material parameters for copolymer gels

Comonomer	Q_0	g_1	$\chi_{\max}$	$\tilde{\chi}_{\mathrm{co}}$	$\bar{g}_2$	β	Fig.
tBA	1.0	0.01	0.64	4.17	4.0	0.04	1A
NtBAm	0.1	0.009–0.017	0.58	4.06	4.0	0.08	2A
HEMA	2.7–9.5	0.12	0.58	1.56	0.3	0.09	3A
HEMA	0.5–1.2	0.04	0.54	1.56	0.5	0.10	S-3A
TREGMA	12.0–17.3	0.10	0.63	−1.11	3.5	0.10	4A
DMAAm	3.5–4.0	0.06	0.58	−1.81	0.8	0.09	5A
DMAAm	1.7–3.1	0.03	0.50	−1.81	3.2	0.10	6A
AAm	7.0–10.1	0.03	0.51	−4.12	2.8	0.09	7A

Table S-2: The FH parameter for comonomers $\tilde{\chi}_{\mathrm{co}}$ versus their Hildebrand solubility δ_{H}.

Comonomer	$\tilde{\chi}_{\mathrm{co}}$	δ_{H} $(\mathrm{MPa})^{\frac{1}{2}}$
tBA	4.17	16.74
NtBAm	4.06	20.43
HEMA	1.56	23.81
TREGMA	−1.11	21.73
DMAAm	−1.81	24.26
AAm	−4.12	25.71

Figures

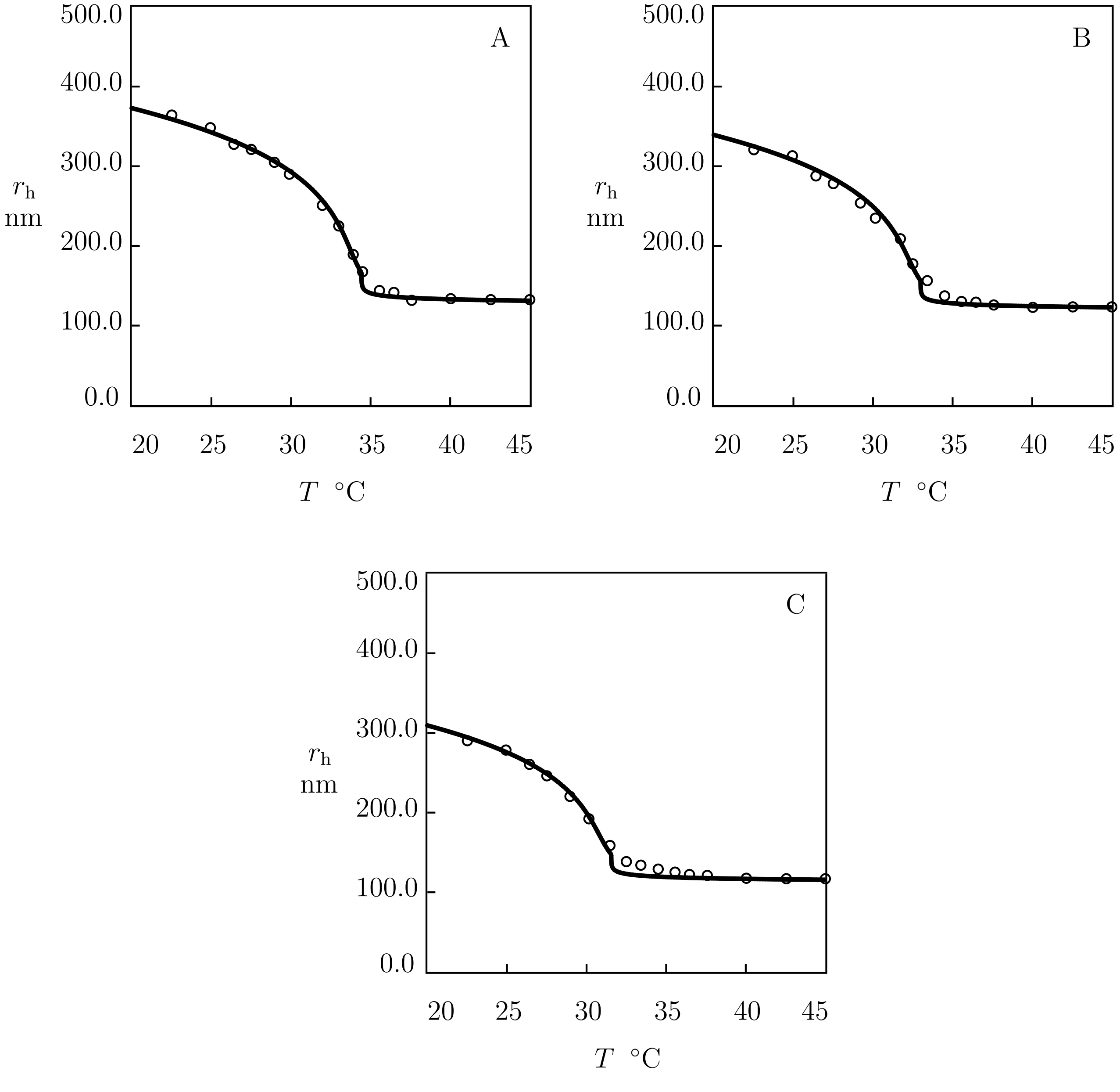

Figure S-1: Hydrodynamic radius r_h of microgel particles versus temperature T. Circles: experimental data [53] on P(NIPAm-tBA) microgels with molar fractions of comonomers $c_{co} = 0.11$ (A), $c_{co} = 0.16$ (B), and $c_{co} = 0.21$ (C). Solid lines: results of simulation.

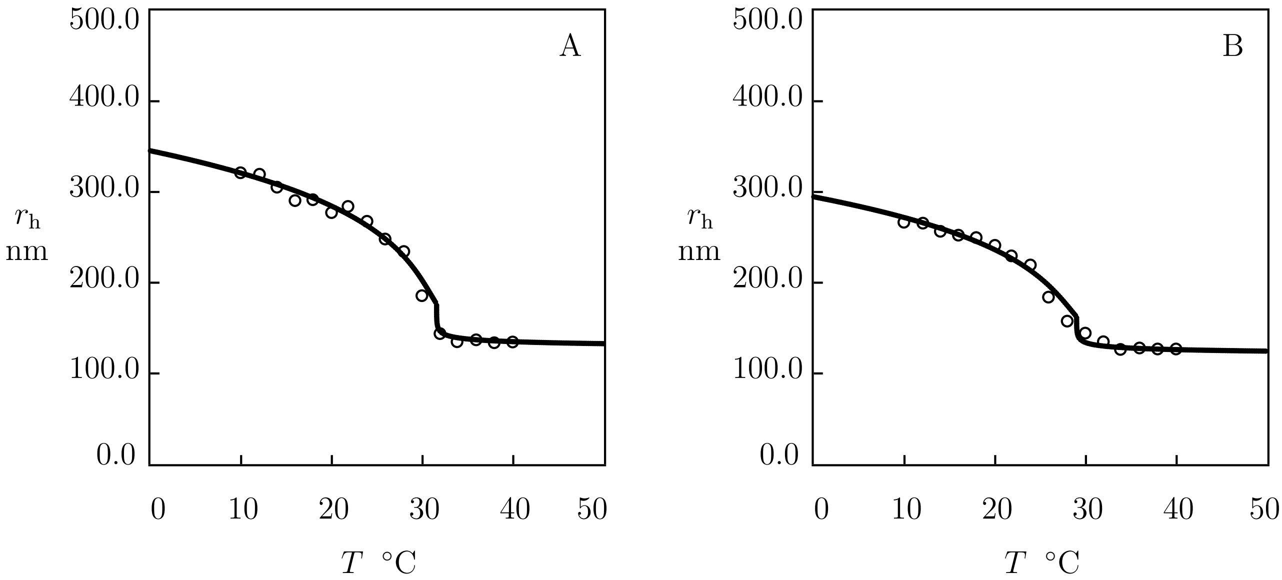

Figure S-2: Hydrodynamic radius r_2 of microgel particles versus temperature T. Symbols: experimental data [55] on P(NIPAm-NtBAm) microgels with molar fractions of comonomers $c_{co} = 0.05$ (A) and $c_{co} = 0.10$ (B). Solid lines: results of simulation.

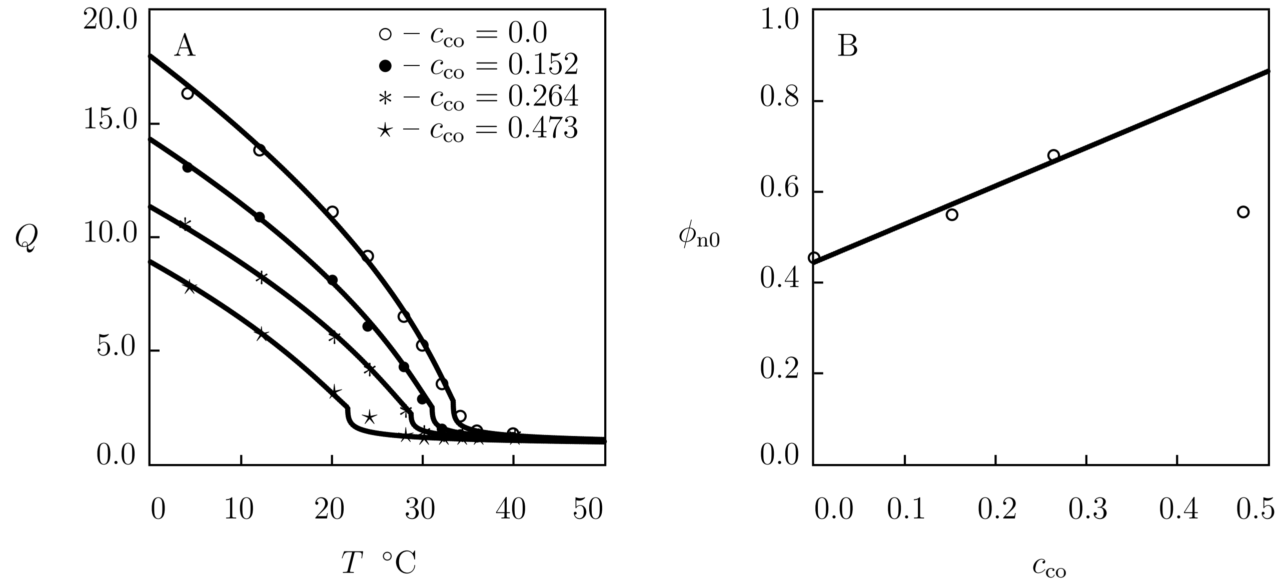

Figure S-3: A – Degree of swelling Q versus temperature T. Symbols: experimental data [59] on P(NIPAm-HEMA) gels with various molar fractions of comonomers c_{co}. Solid lines: results of simulation. B – Parameter ϕ_{n0} versus molar fraction of comonomers c_{co}. Circles: treatment of observations. Solid line: results of simulation.

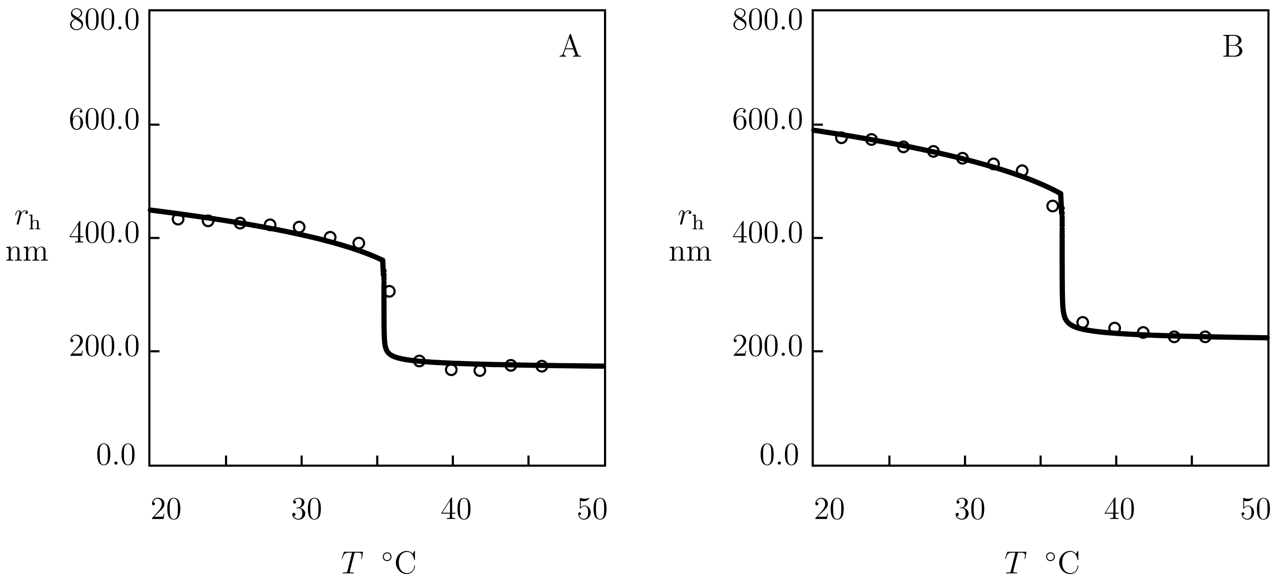

Figure S-4: Hydrodynamic radius r_h of microgel particles versus temperature T. Circles: experimental data [60] on P(NIPAm-TREGMA) microgels with molar fractions of comonomers $c_{co} = 0.04$ (A) and $c_{co} = 0.08$ (B). Solid lines: results of simulation.

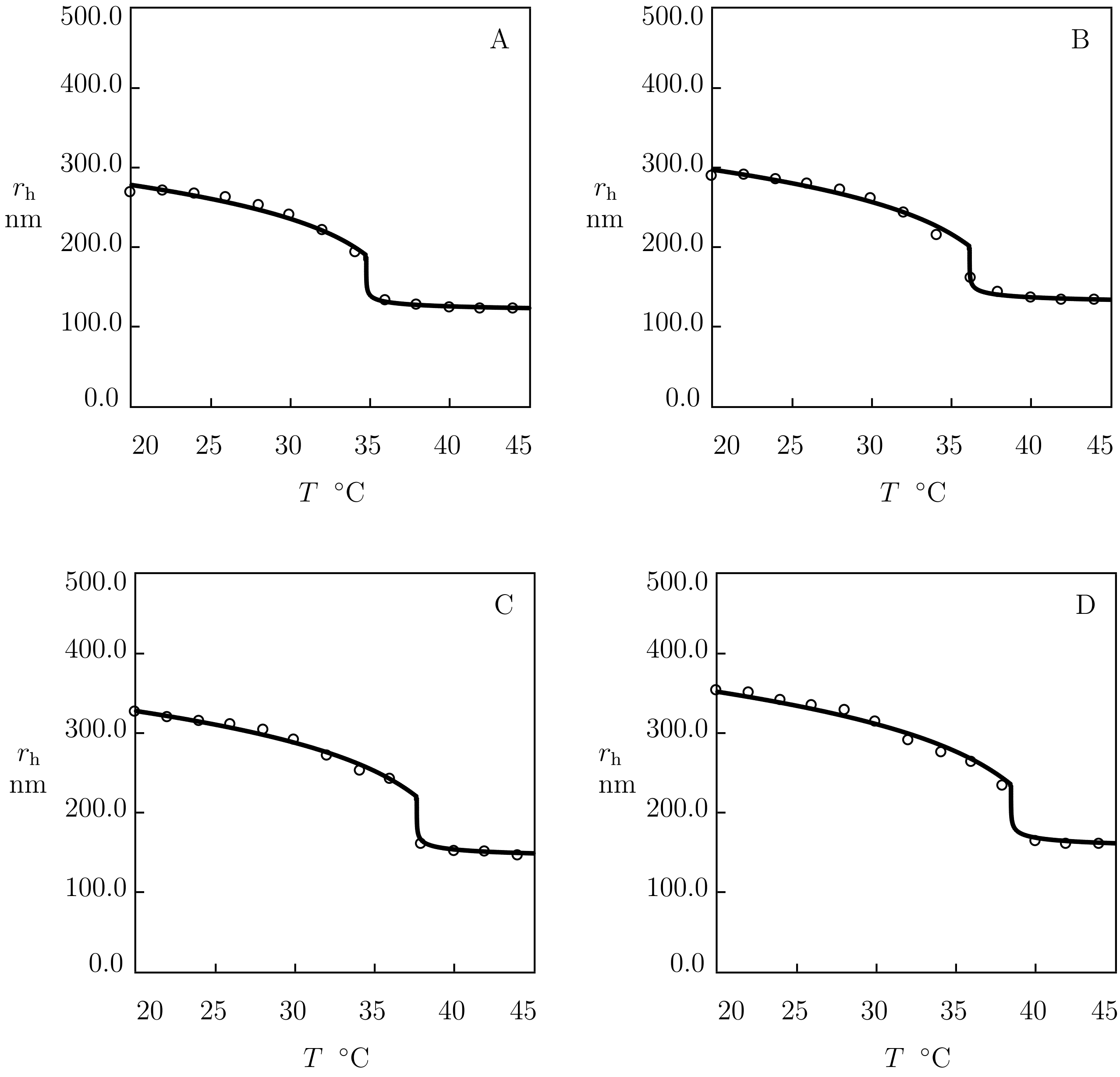

Figure S-5: Hydrodynamic radius r_{h} of microgel particles versus temperature T. Circles: experimental data [63] on P(NIPAm-DMAAm) microgels with molar fractions of comonomers $c_{\mathrm{co}} = 0.06$ (A), $c_{\mathrm{co}} = 0.10$ (B), $c_{\mathrm{co}} = 0.14$ (C) and $c_{\mathrm{co}} = 0.16$ (D). Solid lines: results of simulation.