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Mechanical response and equilibrium swelling of thermo-responsive copolymer hydrogels

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Abstract

Covalently cross-linked thermo-responsive (TR) gels form a special class of hydrogels that swell noticeably below their volume phase transition temperature T_c and shrink above T_c. As the critical temperature is weakly affected by the preparation conditions and molar fractions of monomers and cross-linkers in a pre-gel solution, a facile method to modulate T_c (which is required for biomedical applications of TR gels and their use as temperature-triggered actuators) is to incorporate relatively small amounts of neutral monomers whose hydrophilicity differs from that of the basic monomers. Although observations on copolymer gels confirm the effectiveness of this method, molar fractions of comonomers necessary for tuning of T_c remain unknown.

A model is developed for the mechanical response and equilibrium swelling of TR gels. Adjustable parameters in the governing relations are found by fitting equilibrium swelling diagrams on poly(*N*-isopropylacrylamide) homo- and copolymer gels. Good agreement is demonstrated between the experimental data and results of simulation. Based on the model, an analytical formula is derived that expresses the volume phase transition temperature in terms of the molar fraction of comonomers. Its ability to predict the critical temperature is confirmed by comparison with observations on several copolymer gels.

1. Introduction

Hydrogels are three-dimensional networks of polymer chains bridged by chemical and/or physical bonds. Due to the hydrophilic nature of segments of chains, they swell substantially being immersed into water, but preserve their structural integrity. Thermo-responsive (TR) gels form a special class of hydrogels whose equilibrium degree of swelling is strongly affected by temperature. At temperatures *T* below the volume phase transition temperature T_c, TR gels swell noticeably. When *T* exceeds the critical temperature, these gels shrink [1]. Equilibrium and transient swelling of TR

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gels has recently become a focus of attention due to a wide range of industrial and biomedical applications of these materials [2, 3, 4].

Poly(*N*-isopropylacrylamide) (PNIPA) is one of the most extensively studied TR gels that exhibits a sharp volume phase transition at temperatures in the vicinity of $T_c = 32$ to 34 °C accompanied by good mechanical properties below and above T_c and a fast response to changes in temperature [5]. Applications of TR hydrogels in the biomedical field [6], for DNA and proteins electrophoretic separation [7] and manufacture of temperature-triggered actuators [8] require modulation of the volume phase transition temperature T_c in a rather wide interval. Preparation of TR gels with tunable volume phase transition temperatures has been analyzed in a number of studies [9-13]. It is found that (i) T_c is practically unaffected by molar fractions of monomers and cross-linkers and preparation conditions (temperature at which cross-linking polymerization is performed and solvent for synthesis), (ii) it changes weakly with addition of polymer chains into a pre-gel solution to form semi-interpenetrating polymer networks, and (iii) T_c changes pronouncedly when TR monomers are mixed with relatively small amounts of monomers whose hydrophilicity differs from that of the basic monomers.

Although the qualitative trend in alternation of T_c is clear: the volume phase transition temperature decreases under insertion of hydrophobic monomers and increases when hydrophilic monomers are incorporated, no explicit relations have been proposed for the quantitative description of this phenomenon. The aim of this study is to develop a constitutive model able to predict changes in T_c with molar fraction of comonomers ψ in TR gels.

Experimental and theoretical studies on water uptake by TR gels have been initiated about 40 years ago [14, 15]. Changes in the equilibrium degree of swelling Q with temperature T are conventionally described within the Flory-Rehner theory, where the Flory-Huggins (FH) parameter χ is replaced with an ``effective" coefficient $\chi(T, \phi_n)$, where ϕ_n denotes volume fraction of polymer network. Evolution of the effective FH parameter with temperature is described by the equation

$$\chi = \chi_0(T) + \chi_1(T)\phi_n \tag{1}$$

where the coefficients χ_0 and χ_1 evolve linearly with T or T^{-1} [16, 17]. A constitutive framework for the analysis of solvent transport and the mechanical response of TR gels under three-dimensional deformations with finite strain grounded on Eq. (1) was developed in [18-22], see recent reviews [23, 24]. A phenomenological approach to the description of equilibrium swelling of TR gels based on the Landau theory of phase transition was proposed in [25, 26]. A model for equilibrium swelling of TR gels, where the Flory expression for the specific energy of interaction between monomers and solvent molecules was replaced with more sophisticated relations based on the double lattice concept, was developed in [27].

Although the models grounded on the Flory-Rehner concept reveal an acceptable agreement with observations in swelling tests (in particular, when higher order terms with respect to ϕ_n are introduced into Eq. (1) [28]), they were criticized for two reasons. First, the coefficients in Eq. (1) (these parameters are expressed in terms of the specific enthalpy and specific entropy of a polymer network) that ensure good fit of experimental data adopt unrealistic values [29, 30]. Secondly, this concept implies that the shear modulus G evolves with volume fraction of polymer network ϕ_n following the pattern

$$\frac{G(\phi_{n1})}{G(\phi_{n2})} = (\frac{\phi_{n2}}{\phi_{n1}})^{\frac{1}{3}} \qquad (2)$$

where ϕ_{n1} and ϕ_{n2} are volume fractions of polymer at temperatures T_1 and T_2. Although Eq. (2) predicts adequately mechanical properties of swollen elastomers [31], substantial (by an order of magnitude) deviations from this law were reported in tensile tests on PNIPA gels [32-35]. A pronounced increase in the elastic modulus of TR gels $T > T_c$ was recently observed by means of small-amplitude oscillatory shear tests in [36-40], see Fig. 1. For the purposes of this study (analysis of the volume phase transition temperature of copolymer gels), an important shortcoming of the models based on the Flory-Rehner theory is that they do not involve T_c explicitly, and, as a consequence, cannot predict how this quantity is affected by chemistry and molar fraction of comonomers.

To describe a strong decay in the equilibrium degree of swelling of a TR gel above T_c accompanied by a substantial growth of its shear modulus, we presume polymer chains in a network to be composited of hydrophilic and hydrophobic segments and adopt a concept of thermally-induced breakage of cages formed by water molecules around hydrophobic segments [41, 42], see also recent reviews [43, 44]. At temperatures below T_c , each hydrophobic segment is surrounded by a cage-like structure formed by water molecules bridged by hydrogen bonds [45]. When temperature grows, these clusters of water molecules are destabilized by thermal fluctuations. Their breakage induces agglomeration of hydrophobic segments and formation of aggregates from which water molecules are expelled. At temperatures above T_c , when cage-like structures are broken, a TR gel consists of a number of deswollen hydrophobic aggregates bridged by hydrophilic segments and separated by nano-channels in which water molecules are located [46].

The objective of this work is three-fold: (i) to derive a mean-field model for the elastic response and equilibrium swelling of TR gels that takes into account formation of physical bonds due to aggregation of hydrophobic segments above T_c, (ii) to determine adjustable parameters in the governing equations by fitting observations on several homo- and copolymer gels, and (iii) to derive a simple relation that expresses the volume phase transition temperature of copolymer gels T_c in terms of molar fraction of comonomers ψ.

The novelty of our study consists in treatment of the polymer network in a TR gel as a superposition of two networks: the first is formed under preparation when chains are chemically cross-linked, while the other is developed when temperature exceeds T_c and new physical bonds between chains arise due to aggregation of hydrophobic segments. These two networks have different reference (stress-free) states and different elastic moduli (the modulus of the network with covalent cross-links is temperature-independent, while that of the network with physical bonds increases with temperature).

Another approach to the analysis of swelling diagrams for stimuli-sensitive gels is grounded on ab initio calculations and Monte Carlo simulation of their deformation, see recent reviews [47, 48]. We do not apply these techniques as our purpose is to develop analytical expressions for the degree of swelling and volume phase transition temperature.

2. Model

A gel is modeled as a two-phase medium composed of solid (an equivalent polymer network) and fluid (water) constituents. The solid and fluid phases are treated as immiscible interpenetrating continua. The polymer network in a TR gel consists of two components. The first (covalent) network is formed under preparation when cross-linking polymerization of a pre-gel solution is conducted. The other (physical) network is formed at temperatures $T > T_c$ due to aggregation of hydrophobic segments of chains. Both networks are treated as permanent. Their deformations obey the affinity hypothesis and the molecular incompressibility condition.

The initial configuration of a gel coincides with that of an undeformed dry specimen at some temperature $T_0 < T_c$. Transformation of the initial configuration into the reference (stress-free) configuration of the first (covalently cross-linked) network is described by the deformation gradient $\boldsymbol{f}_1 = f_1^{\frac{1}{3}}\,\boldsymbol{I}$, where $\boldsymbol{I}$ is the unit tensor, $f_1 = 1 + Q_0$ is a coefficient of inflation under transition from the initial to the reference configuration, and Q_0 is the degree of swelling in the reference state. The reference state of the second network (with physical junctions) coincides with the initial state of the gel (all water molecules are expelled from hydrophobic clusters).

For definiteness, the neo-Hookean formulas are adopted for the strain energy densities of polymer networks with covalent and physical bonds

$$W_m = \frac{1}{2}\,G_m\left[\left(I_{e1}^{(m)} - 3\right) - \ln I_{3e}^{(m)}\right], \qquad (m = 1{,}2) \qquad (3)$$

where G_m stands for the shear modulus of the mth network, and $I_{e1}^{(m)}, I_{e2}^{(m)}, I_{e3}^{(m)}$ are the principal invariants of the Cauchy-Green tensors for elastic deformation. The physical meaning of these relations was discussed in [49], where Eq. (3) was derived within the concept of entropic elasticity. More sophisticated expressions for the functions W_m were developed and verified by comparison with observations in [50, 51].

The elastic modulus G_1 of the covalently cross-linked network is presumed to be independent of temperature. The elastic modulus G_2 of the network with physical junctions vanishes below T_c and grows with the difference $T - T_c$ above the volume phase transition temperature following the pattern

$$G_2(T) = 0, \qquad (T < T_c), \;\; G_2(T) = \bar{G}_2 \left[1 - \exp(-\beta\sqrt{T - T_c}\,)\right], \;\; (T \geq T_c) \qquad (4)$$

where $\bar{G}_2$ and β are adjustable parameters. Eq. (4) differs from the equation for evolution of elastic modulus with temperature proposed in [52]. The ability of Eq. (4) to described observations is verified in Fig. 1, where experimental data in shear oscillatory tests on PNIPA gels are approximated by this relation with the material constants listed in Tab. S1.

The specific Helmholtz free energy (per unit volume of a gel in its initial configuration) Ψ equals the sum of the energies of phases not interacting with each other and the energy of their interaction, $\Psi = \Psi_1 + \Psi_2 + \Psi_3$, where Ψ_1 is the specific energy of water molecules not interacting with the polymer network, Ψ_2 is the specific energy of the polymer network not interacting with water, and Ψ_3 is the specific energy of mixing of water molecules with segments of chains.

The specific energy of water reads $\Psi_1 = \mu^0 C$, where μ^0 denotes chemical potential of water molecules not interacting with the polymer network, and C stands for their concentration (number of molecules per unit volume in the initial state).

The specific energy of the polymer network (consisting of two parts with chemical and physical bonds) is given by $\Psi_2 = \sum_{m=1}^{2} W_m$, where the specific mechanical energy stored in chains of the mth network W_m is given by Eq. (3).

The specific energy of mixing of water molecules with segments of polymer chains is accepted in the Flory-Huggins form

$$\phi_n \Psi_3 = \frac{k_B T_0}{v} (\, \phi_w \ln \phi_w + \chi \phi_w \phi_n), \qquad (5)$$

where k_B is the Boltzmann constant, v is the characteristic volume of a water molecule, χ is the effective Flory-Huggins parameter, and ϕ_n, ϕ_w are volume fractions of polymer and water molecules

$$\phi_n = \frac{1}{1 + C\,v}, \qquad \phi_w = \frac{C\,v}{1 + C\,v}.$$

The coefficient ϕ_n is introduced in the left-hand side of Eq. (5) because the right-hand side of this equation equals the specific energy of mixing per unit volume in the actual configuration.

The following expression is accepted for the effective Flory-Huggins parameter

$$\chi = \chi_0 + \chi_1 T \quad (T < T_c)\,, \qquad \chi = \chi_{max} \quad (T \geq T_c)\,, \tag{6}$$

where T and T_c are measured in ˚C, and the material constants $\chi_0, \chi_1, \chi_{max}$ obey the condition

$$\chi_{max} = \chi_0 + \chi_1 T_c\,. \tag{7}$$

Eq. (7) means that breakage of cages formed by water molecules around hydrophobic segments under heating of a gel induces an increase in χ below T_c. When T exceeds the volume phase transition temperature T_c, further increase in χ is prohibited by formation of aggregates of hydrophobic segments from which water molecules are expelled.

Under unconstrained equilibrium swelling of a TR gel, its degree of swelling $Q = C\,v$ at an arbitrary temperature T obeys the nonlinear equation

$$\ln\frac{Q}{1+Q} + \frac{1}{1+Q} + \frac{\chi}{(1+Q)^2} + \frac{g_1}{1+Q}\left[\left(\frac{1+Q}{1+Q_0}\right)^{\frac{2}{3}} - 1\right]$$

$$+\frac{g_2}{1+Q}\left[(1+Q)^{\frac{2}{3}} - 1\right] = 0 \tag{8}$$

where

$$g_m = \frac{G_m\,v}{k_B T_0} \qquad (m = 1,2)$$

are dimensionless elastic moduli. A detailed derivation of Eq. (8) is given in Supplementary Material.

Eq. (8) together with Eq. (6) for the effective Flory-Huggins parameter χ and Eq. (4) for the elastic modulus g_2 provide the governing equations for the equilibrium degree of swelling Q. These relations involve seven adjustable parameters: (i) coefficients χ_0 and χ_1 describe how hydrophilicity of chains is affected by temperature below the critical temperature T_c, (ii) parameter χ_{max} characterizes their hydrophilicity above the volume phase transition temperature, (iii) g_1 and Q_0 stand for the dimensionless shear modulus of the covalently cross-linked network and its degree of swelling in the reference state, and (iv) coefficients $\bar{g}_2$ and β describe an increase in the dimensionless shear modulus of the network with physical bonds above T_c. The volume phase transition temperature T_c is calculated from Eq. (7).

3. Comparison with experimental data

To examine the ability of the model (4), (6) and (8) to describe experimental swelling diagrams, we focus on observations on poly(*N*-isopropylacrylamide) homopolymer and copolymer gels as these materials are widely used in biomedical applications [2].

In the conventional treatment of observations in swelling tests, the effective Flory-Huggins parameter χ is thought of as an adjustable function of two variables T and ϕ_n. Unlike this approach, we consider χ as a material function of temperature T only. The dependence $\chi(T)$ is found by fitting the equilibrium swelling diagram on a special gel prepared by γ-irradiation of an aqueous solution of PNIPA chains (this treatment excludes the effects of chemistry and concentration of cross-linker on the hydrophilicity of polymer chains). Afterwards, the ``universal" coefficients χ_0 and χ_1 in Eq. (6) are fixed and used without changes for other hydrogels under investigation. This allows elastic moduli of the polymer networks with covalent and physical bonds to be determined with high accuracy.

For each set of observations, adjustable parameters are found by the nonlinear regression method to minimize the expression $\sum(Q_{exp} - Q_{sim})^2$, where summation is performed over all temperatures T under consideration, Q_{exp} stands for the degree of swelling measured in a test, and Q_{sim} is determined by Eq. (8), which is solved by means of the Newton-Raphson algorithm.

3.1 The Flory-Huggins parameter

We begin with matching experimental data on PNIPA gel prepared by irradiation cross-linking of an aqueous solution of PNIPA chains with the irradiation dose $\Gamma = 20$ kGy [53]. Observations in equilibrium water uptake tests are depicted in Fig. 2, where Q is plotted versus temperature T.

The swelling diagram in Fig. 2 is matched by means of a two-step procedure. At the first step, we approximate observations below T_c (where $g_2 = 0$), set $Q_0 = 12.81$ (which means that the reference state coincides with the as-prepared state [32]), determine χ from Eq. (8), and fit the experimental dependence $\chi(T)$ by means of Eq. (6), where χ_0 and χ_1 are calculated by the least-squares technique. The dimensionless elastic modulus g_1 is found from the condition of the best-fit of the experimental function $\chi(T)$ by linear Eq. (6). At the other step, the experimental data above T_c are matched with the help of two parameters, β and $\bar{g}_2$ with $\bar{g}_2 = \bar{G}_2\, v/(k_B T_0)$.

Fig. 2A demonstrates good agreement between the observations in equilibrium swelling tests and results of numerical simulation with the material constants collected in Tab. S2. Fig. 2B shows that the growth of χ with temperature below T_c is described adequately by Eq. (6).

3.2 Copolymer gels

We approximate four sets of experimental data on PNIPA copolymer gels prepared with incorporation of hydrophobic and hydrophilic monomers.

We begin with the analysis of swelling diagrams on a homopolymer PNIPA gel and copolymer gels synthesized with addition of 4 mol.% of hydrophobic butyl methacrylate (BMA) and hydrophilic acrylamide (AAm) monomers [54]. The gels were prepared by cross-linking polymerization (18 h at 80 ˚C) of solutions of monomers in 1,4-dioxane (molar fraction $m_{mon} = 0.884$ M) by using ethylene glycol dimethacrylate (EGDMA, molar fraction $m_{cr} = 8.8$ mM) as a cross-linker.

First, we fit observations on homopolymer PNIPA gel (Fig. 3A) by using the coefficients χ_0 and χ_1 reported in Tab. S2, and find g_1 and Q_0 from the best-fit condition for the dependence $\chi(T)$ below T_c . The coefficient χ_{max} is determined from measurements of T_c , and the parameters β and $\bar{g}_2$ are found by matching the experimental swelling diagram above T_c .

We proceed with fitting experimental data on PNIPA-BMA (Fig. 3B) and PNIPA-AAm (Fig. 3C) copolymer gels. As molar fractions of hydrophobic and hydrophilic comonomers are low, we disregard their influence on the degree of swelling in the reference state Q_0 and the elastic modulus of the covalently cross-linked network g_1. For each set of observations, we calculate χ_0 and χ_1 by matching the dependence $\chi(T)$ below T_c (using Q_0 and g_1 determined in fitting observations on the homopolymer gel), find χ_{max} from measurement of T_c , and determine β and $\bar{g}_2$ by matching the equilibrium swelling curve above T_c . The best-fit material constants are listed in Tab. S3.

We now approximate observations on double-network semi-interpenetrating PNIPA gels prepared in aqueous solutions of poly(*N*-vinylpyrrolidone) (PVP, molecular weight $M_w = 1.3 \cdot 10^6$ g/mol) with various mass fractions of PVP chains ψ ranging from 0 to 3 wt.%. The hydrogels were prepared by cross-linking polymerization (24 h at 4 ˚C) of NIPA monomers (molar fraction $m_{mon} = 0.885$ M) by using *N*,*N*′-methylenebisacrylamide (BIS, $m_{cr} = 35.4$ mM) as a cross-linker [55]. Equilibrium swelling diagrams on gels with the lowest ($\psi = 0$) and highest ($\psi = 3$ wt.%) mass fractions of PVP chains are depicted in Figs. 4A and 4B together with results of numerical simulation, and those on gels with intermediate ψ values ($\psi = 1$ and 2 wt.%) are presented in Figs. S1A and S1B.

Material parameters are determined by means of the same procedure that is used to fit observations in Fig. 3. We begin with the swelling diagram on homopolymer PNIPA gel, find g_1 and Q_0 by matching observations below T_c with the ``universal" coefficients χ_0 and χ_1, determine χ_{max}

from measurements of T_c , and calculate β and $\bar{g}_2$ by fitting data above T_c. Afterwards, experimental data on the double-network hydrogels with various ψ are approximated by using the same algorithm with the fixed values of g_1 and Q_0. Each set of observations is matched separately.

The coefficients g_1, Q_0, χ_{max} and β are found to be independent of ψ. Their values are listed in Tab. S4. The remaining parameters, χ_0, χ_1 and $\bar{g}_2$, are affected by mass fraction ψ of PVP chains in pre-gel solutions. Evolution of these quantities with ψ is illustrated in Fig. S1C, where the data are approximated by the relations

$$\chi_0 = \chi_0^0 - \psi\, \chi_0^1 , \quad \chi_1 = \chi_1^0 + \psi \chi_1^1 , \quad \log \bar{g}_2 = \log \bar{g}_2^0 - \psi \log \bar{g}_2^1 \qquad (9)$$

with the coefficients calculated by the least-squares technique.

We proceed with fitting experimental data on PNIPA-*N,N'*-dimethyl aminoethyl methacrylate (DMAEMA) copolymer gels with mass fractions of DMAEMA monomers (with respect to NIPA) $\psi = 0$, 0.1 and 0.2. The hydrogels were synthesized by free-radical cross-linking polymerization (at 80 ˚C) of solutions of monomers in 1,4-dioxane (molar fraction of NIPA monomers $m_{mon} = 2.68$ M) by using BIS as a cross-linker (molar fraction $m_{cr} = 53.6$ mM) [56]. The experimental swelling diagrams on gels with the lowest ($\psi = 0$) and highest ($\psi = 0.2$) mass fractions of comonomers are depicted in Figs. 5A and 5B, and that on the gel with $\psi = 0.1$ is presented in Fig. S2A. Each curve is matched separately by means of the same procedure that is used to fit experimental data in Figs. 3 and 4.

The best-fit coefficients g_1, Q_0, χ_{max} and β are independent of ψ. Their values are listed in Tab. S5. The effect of ψ on parameters χ_0 , χ_1 and $\bar{g}_2$ is illustrated in Fig. S2B, where the data are approximated by Eq. (9).

Finally, we match experimental data on PNIPA-acrylamide (AAm) graft copolymer gels with various mass fractions of AAm monomers (with respect to NIPA) $\psi = 0$, 0.2, 0.35 and 0.5. The gels were prepared by cross-linking polymerization (4 h at 4 ˚C) of aqueous solutions of NIPA (molar fraction $m_{mon} = 0.74$ M) and AAm monomers by using BIS (molar fraction $m_{cr} = 54$ mM) as a cross-linker [57]. Experimental data in equilibrium swelling tests on gels with the lowest ($\psi = 0$) and highest ($\psi = 0.5$) mass fractions of AAm monomers are presented in Figs. 6A and 6B. The other two sets of observations on gels with $\psi = 0.2$ and 0.35 are reported in Figs. S3A and S3B. Each swelling diagram is fitted separately with the help of the same algorithm that is used to approximate observations in Figs. 3 to 5.

The best-fit material constants g_1, Q_0, χ_{max} and β are collected in Tab. S6. Evolution of parameters χ_0 , χ_1 and $\bar{g}_2$ with mass fraction of comonomers ψ is demonstrated in Fig. S3C, where the data are approximated by Eq. (9).

The following conclusions are drawn from Figs. 3 to 6:

(I) Incorporation of hydrophobic monomers induces a reduction in the volume phase transition temperature of copolymer gels, whereas addition of hydrophilic monomers into a pre-gel solution causes an increase in T_c.

(II) The shift of the critical temperature is explained by changes in hydrophilicity of polymer chains described by evolution of the coefficients χ_0 and χ_1 with molar fraction of comonomers ψ.

(III) When hydrophilic comonomers are added into a pre-gel solution, the coefficient χ_0 decreases strongly with ψ, while the coefficient χ_1 increases weakly. According to the thermodynamic theory of mixtures [17], these changes reflect the growth of the entropic and enthalpic components of the energy of interactions between water molecules and segments of chains.

(IV) Evolution of parameters χ_0 and χ_1 with ψ is accompanied by a reduction in the shear modulus $\bar{g}_2$ of the polymer network with physical bonds. This decrease may be explained by a decay (caused by the presence of hydrophilic segments) in the number of hydrophobic aggregates served as physical junctions between chains above the volume phase transition temperature.

3.3 Homopolymer gels

Figs. 3 to 6 show that inclusion of hydrophilic and hydrophobic monomers under polymerization affects strongly equilibrium swelling diagrams of PNIPA gels (below and above T_c) and leads to noticeable shifts of the volume phase transition temperature. Our aim now is to demonstrate that modification of the preparation conditions for homopolymer gels induces substantial changes in their equilibrium degree of swelling, but does not affect the critical temperature T_c. For this purpose, two sets of experimental data are analyzed.

First, observations in equilibrium swelling tests are fitted on PNIPA gels prepared in aqueous solutions of sucrose with various concentrations ψ ranging from 0 to 1.5 M. The hydrogels were synthesized by free radical cross-linking polymerization (24 h at 20 ˚C) of NIPA monomers (molar fraction $m_{mon} = 0.59$ M) in aqueous solutions of sucrose by using BIS (molar fraction $m_{cr} = 21.6$ mM) as a cross-linker [58]. Experimental swelling diagrams together with results of simulation are reported in Fig. 7.

Each set of data in Fig. 7 is matched separately by means of the following algorithm. Keeping in mind that polymer chains contain only NIPA monomers and molar fraction of cross-linker is low, we adopt the ``universal" values of χ_0 and χ_1 found by fitting data in Fig. 2. Coefficients g_1 and Q_0 are calculated by matching experimental data below the volume phase transition temperature, T_c is measured in the swelling test, and parameters $\bar{g}_2$ and β are determined by approximation of observations above T_c.

Material parameters $\chi_0, \chi_1, \chi_{max}$ and β are independent of molar fraction of sucrose in aqueous solutions ψ. Their best-fit values are listed in Tab. S7. The effect of ψ on parameters $g_1, \bar{g}_2$ and Q_0 is illustrated in Fig. S4. The data are approximated by the phenomenological equations

$$\log g_1 = \log g_1^0 + \psi \log g_1^1, \qquad \log \bar{g}_2 = \log \bar{g}_2^0 - \psi \log \bar{g}_2^1,$$
$$Q_0^{-1} = q^0 - \psi\, q^1, \tag{10}$$

where the coefficients are determined by the least-squares method.

We proceed with the analysis of equilibrium swelling diagrams on nanocomposite PNIPA cryogels with various mass fractions ψ of colloidal silica particles (Ludox AS-40, average diameter 20 nm) with ψ ranging from 0 to 0.35. The gels were prepared by cross-linking polymerization (24 h at 15 ˚C at the first stage and -18 ˚C at the other stage) of NIPA monomers (molar fraction $m_{mon} = 0.97$ M) in aqueous dispersions of SiO_2 nanoparticles by using BIS (molar fraction $m_{cr} = 15$ mM) as a cross-linker [59].

Observations in equilibrium swelling tests on the nanocomposite gels are reported in Fig. 8 together with results of simulation. Each swelling curve is matched separately by applying the same approach that is used to approximate experimental data in Fig. 7. The best-fit values of material parameters $\chi_0, \chi_1, \chi_{max}$ and β are listed in Tab. S8. The effect of mass fraction ψ on silica nanoparticles on $g_1, \bar{g}_2$ and Q_0 is illustrated in Fig. S5, where the data are approximated by Eq. (10).

The following conclusions are drawn from Figs. 7 and 8:

(i) Synthesis of PNIPA gels in aqueous solutions of sucrose and dispersions of colloidal particles does not induce changes in the volume phase transition temperature T_c, but affects strongly their mechanical properties, and, as a consequence, degree of swelling.

(ii) Addition of sucrose to a pre-gel solution results in a pronounced reduction of the shear modulus g_1 of the covalently cross-linked network, whereas insertion of nanoparticles induces a strong increase in g_1. The decay in g_1 with ψ in sucrose solutions can be explained by collapse of PNIPA chains at high concentrations of sucrose [58] that leads to a decrease in the number of cross-links formed under preparation. The growth of g_1 with ψ in silica dispersions reflects stiffening of nanocomposite hydrogels due to the presence of filler.

(III) Dissolution of sucrose as well as dispersion of silica nanoparticles in a pre-gel solution induce a substantial decrease in the elastic modulus $\bar{g}_2$ of the polymer network developed above the critical temperature T_c . This conclusion is explained by the growth of porosity of gels [58, 59] treated as an increase in the characteristic distance between segments of neighboring chains. The latter results in a reduction in concentration of aggregates formed by hydrophobic segments above the volume phase transition temperature, which, in turn, is proportional to $\bar{g}_2$.

(IV) The growth of ψ causes an increase in the degree of swelling Q_0 in the reference (stress-free) state of the gels. This growth is strong for gels prepared in aqueous solutions of sucrose (due to the collapse of polymer chains) and becomes negligible for nanocomposite gels.

3.4 Discussion

Figs. 2 to 8 demonstrate good agreement between experimental data on homo- and copolymer hydrogels and results of numerical simulation. This confirms the ability of the model to describe observations in equilibrium swelling tests on thermo-responsive gels.

Unlike the conventional models that require very high values of the Flory-Huggins parameter χ to ensure good quality of fitting, the coefficient χ_{max} adopts reasonable values in the interval between 0.46 and 0.62 for all hydrogels under consideration, see Tabs. S2 to S8.

Figs. S2B, S3C, S4 and S5 show that adjustable parameters found by fitting experimental data change consistently with concentrations of comonomers and mass fractions of additives in pre-gel solutions. Their evolution with ψ is described adequately by phenomenological Eqs. (9) and (10). However, some scatter of the experimental data should be mentioned that may be ascribed to inaccuracies of measurements.

To assess how these inaccuracies affect the quality of prediction by the model, we calculate the volume phase transition of copolymer gels T_c as a function of concentration of hydrophilic monomers ψ. It follows from Eqs. (7) and (9) that

$$T_c = \frac{\chi_{max} - \chi_0^0 + \psi\chi_0^1}{\chi_1^0 + \psi\chi_1^1} \quad . \tag{11}$$

We calculate T_c for PNIPA-PVP, PNIPA-DMAEMA and PNIPA-AAm copolymer gels by means of Eq. (11) (the coefficients in the right-hand side are taken from Figs. S1C, S2B and S3C) and plot the results together with experimental data in Figs. 4C, 5C and 6C, respectively. These figures show the ability of the model not only to describe experimental data in equilibrium swelling tests, but also to predict the effect of comonomers on the volume phase transition temperature.

4 Conclusions

A model is developed for the mechanical response and equilibrium swelling of thermo-responsive gels. Unlike conventional approaches grounded on the Flory-Rehner concept, our model accounts for a pronounced increase in the elastic modulus above the volume phase transition temperature observed in monotonic tensile tests and shear oscillatory tests. Its material parameters adopt physically reasonable values (in particular, the Flory-Huggins parameter χ does not exceed 0.62 for all hydrogels under investigation).

Polymer chains in a thermo-response gel are presumed to involve hydrophilic and hydrophobic segments. Below the volume phase transition temperature T_c, each hydrophobic segment is surrounded by a cage-like structure formed by water molecules bridged by hydrogen bonds. With an increase in temperature, thermal fluctuations induce breakage of these structures accompanied by aggregation of hydrophobic segments and formation of clusters from which water molecules are expelled. Above T_c, when most cage-like structures are broken, a gel consists of a number of deswollen hydrophobic aggregates bridged by hydrophilic segments and separated by nano-channels in which water molecules are located. With reference to this scenario, constitutive equations for an arbitrary three-dimensional deformation of a thermo-responsive hydrogel are derived by means of the free energy imbalance inequality.

The governing equations for equilibrium swelling of a hydrogel involve seven material parameters with transparent physical meaning: (i) coefficients χ_0 and χ_1 describe how hydrophilicity of chains is affected by temperature below T_c, (ii) parameter χ_{max} characterizes their hydrophilicity at and above T_c, (iii) g_1 and Q_0 stand for the shear modulus of the covalently cross-linked network and its degree of swelling in the reference state, and (iv) coefficients $\bar{g}_2$ and β characterize an increase in the shear modulus of polymer chains bridged by deswollen hydrophobic aggregates above T_c. These quantities are found by matching experimental swelling diagrams on homopolymer PNIPA gels cross-linked by γ-radiation, covalently cross-linked in water, 1,4-dioxane, aqueous sucrose solution and dispersion of silica colloidal particles, as well as on copolymer PNIPA-BMA, PNIPA-PVP, PNIPA-DMAEMA and PNIPA-AAm gels. Figs. 2 to 8 demonstrate good agreement between the experimental data and results of numerical simulation.

An analytical formula, Eq. (11), is derived for the volume phase transition temperature of copolymer gels. Figs. 4C, 5C and 6C confirms the ability of the model to predict the effect of concentration of comonomers on T_c.

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Figure 1: The ratio of storage moduli $R = G'(T)/G'(T_0)$ with $T_0 = 22$ ˚C versus temperature T. Circles: experimental data on PNIPA gels in shear oscillatory tests. Solid lines: results of simulation. A – [36], B –[40].

Figure 2: A - Degree of swelling Q versus temperature T. Circles: experimental data [53] on PNIPA gel prepared by irradiation of polymer solution. Solid line: results of simulation. B - Parameter χ versus temperature T. Circles: treatment of observations. Solid line: approximation of the data by Eq. (6).

Figure 3: Degree of swelling Q versus temperature T. Circles: experimental data [54]. Solid lines: results of simulation. A - PNIPA gel, B - PNIPA-BMA gel, C - PNIPA-AAm gel.

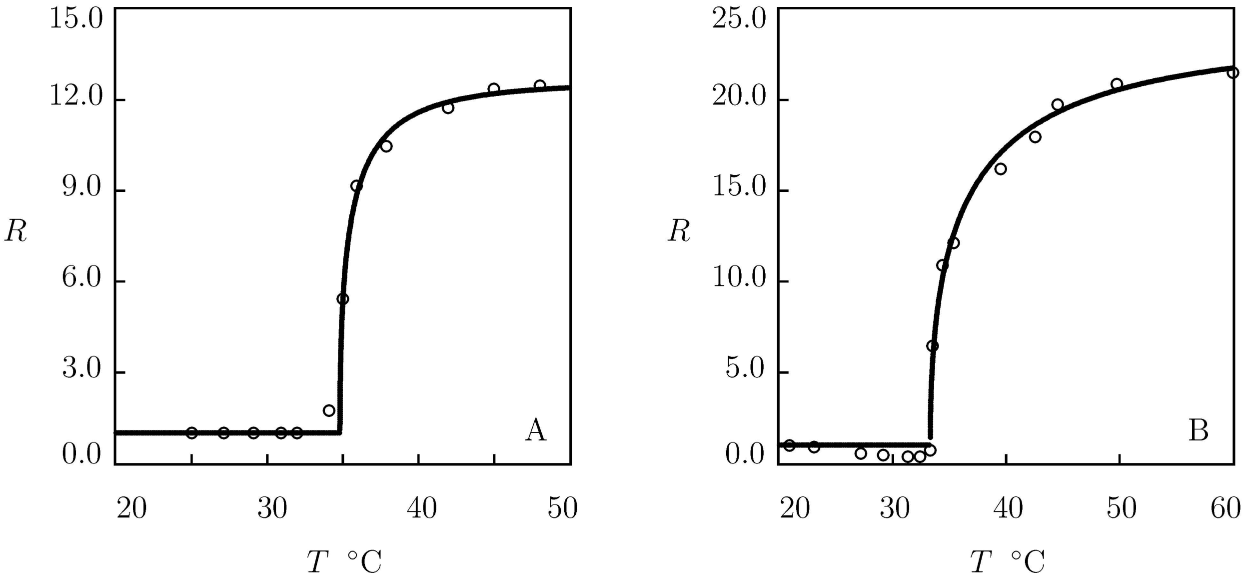
Figure 4: A, B - Degree of swelling Q versus temperature T. Circles: experimental data [55] on interpenetrating PNIPA-PVP gels with various mass fractions ψ of PVP (A - $\psi = 0$, B - $\psi = 3$ wt.%). Solid lines: results of simulation. C - Volume phase transition temperature T_c versus mass fraction ψ of PVP. Circles: treatment of observations. Solid line: prediction of the model.

Figure 5: A, B - Degree of swelling Q versus temperature T. Circles: experimental data [56] on PNIPA-DMAEMA gels with various mass fractions ψ of DMAEMA monomers (A - $\psi = 0$, B - $\psi = 0.2$). Solid lines: results of simulation. C - Volume phase transition temperature T_c versus mass fractions ψ of DMAEMA monomers. Circles: treatment of observations. Solid line: prediction of the model.

Figure 6: A, B - Degree of swelling Q versus temperature T. Circles: experimental data [57] on PNIPA-AAm gels with various molar fractions ψ of AAm monomers. (A -$\psi = 0$, B - $\psi = 0.5$). Solid lines: results of simulation. C - Volume phase transition temperature T_c versus molar fraction ψ of AAm monomers. Circles: treatment of observations. Solid line: prediction of the model.

Figure 7: Degree of swelling Q versus temperature T. Circles: experimental data [58] on PNIPA gels prepared in aqueous solutions of sucrose with various concentrations ψ (A - $\psi = 0$, B - $\psi = 0.5$, C - $\psi = 1.0$, D - $\psi = 1.5$ M). Solid lines: results of simulation.

Figure 8: Degree of swelling Q versus temperature T. Circles: experimental data [59] on PNIPA gels reinforced with various mass fractions ψ of silica nanoparticles (A - $\psi = 0$, B - $\psi = 5$, C - $\psi = 21$, D - $\psi = 35$ wt.%). Solid lines: results of simulation.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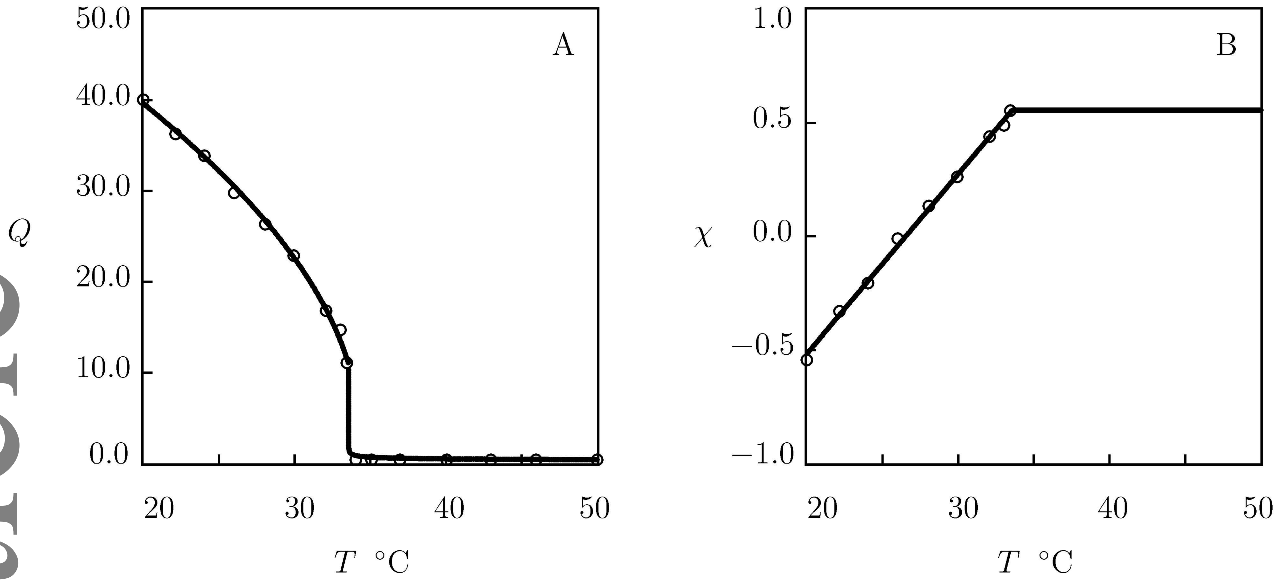
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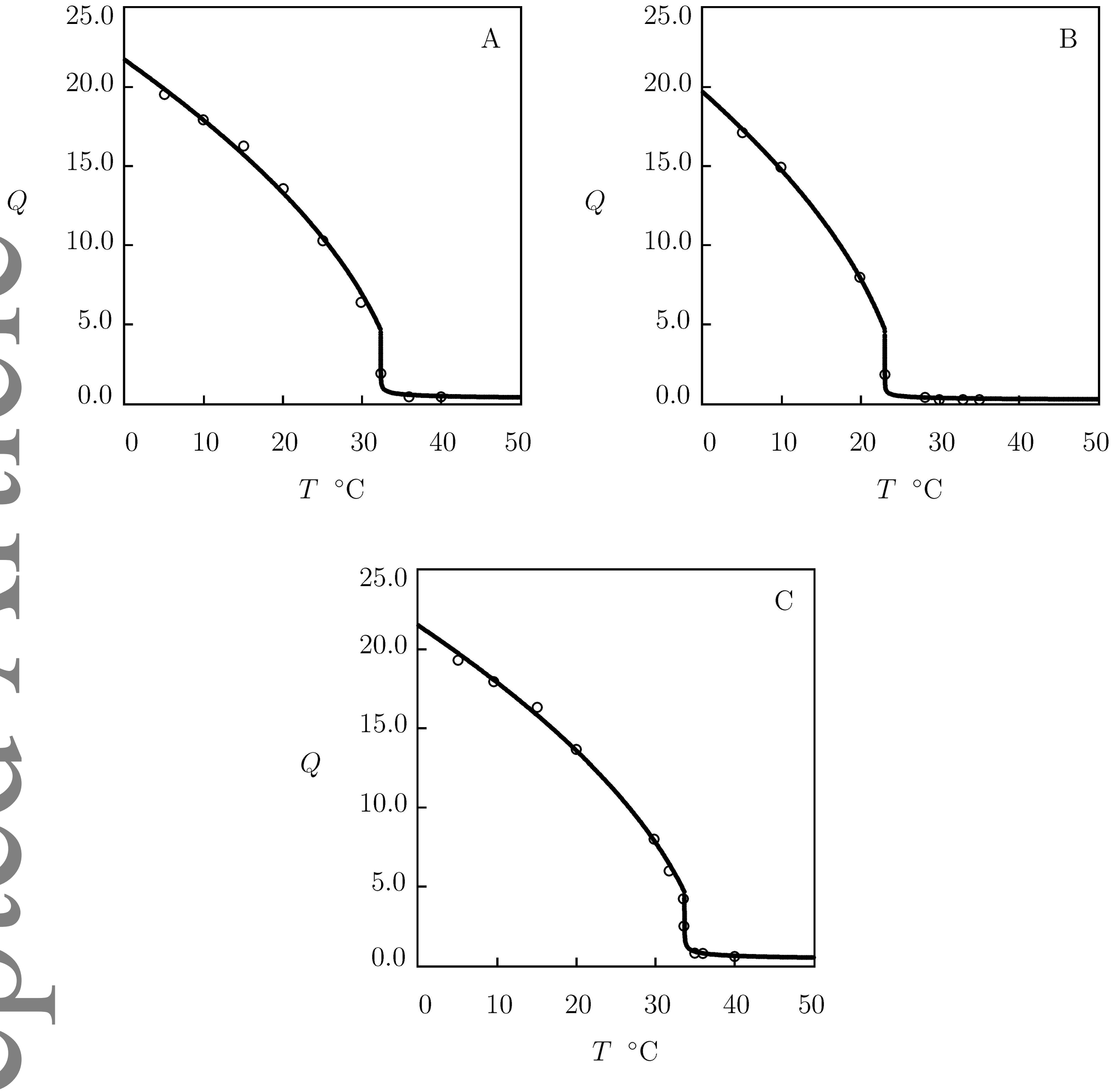
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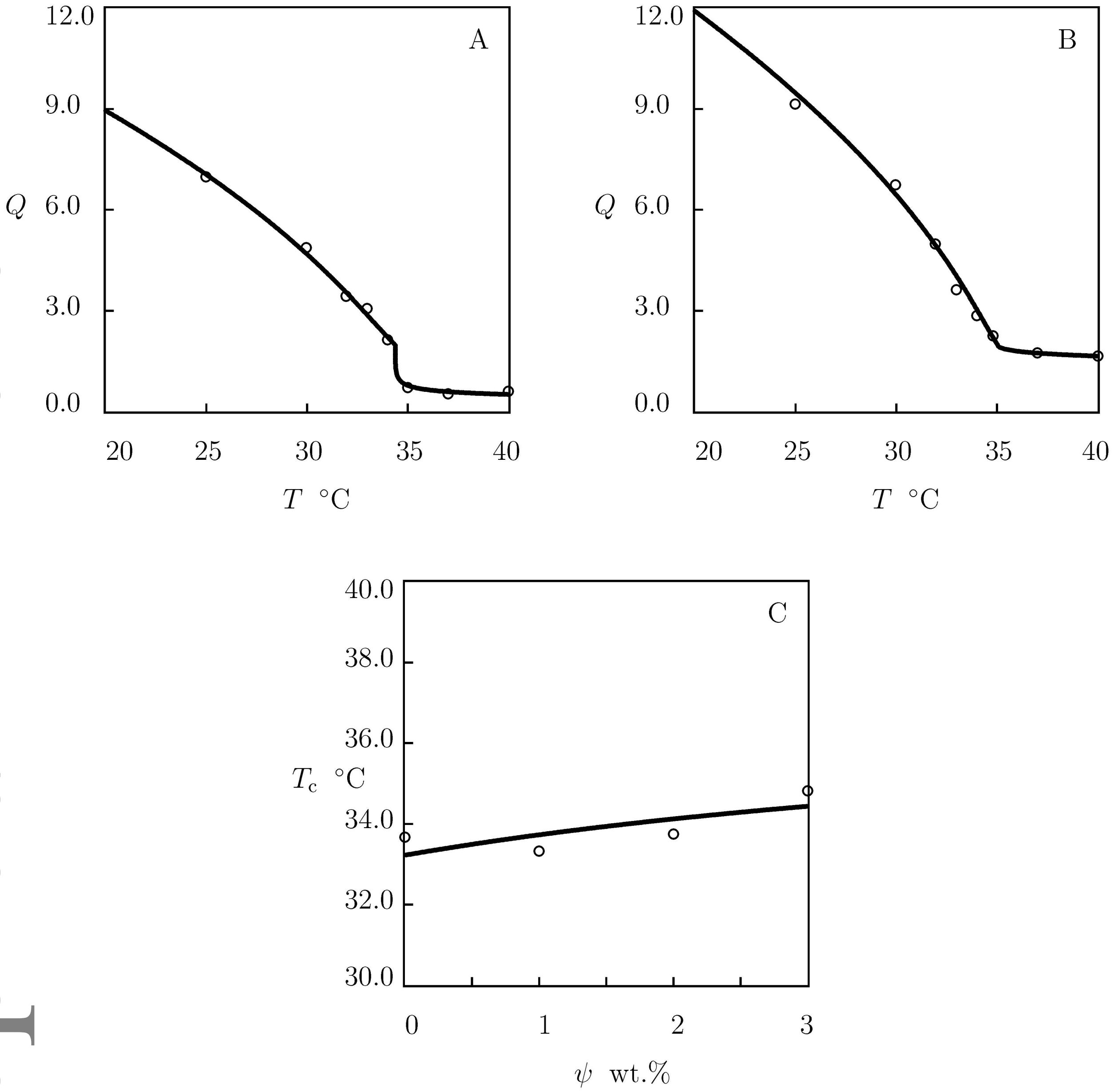
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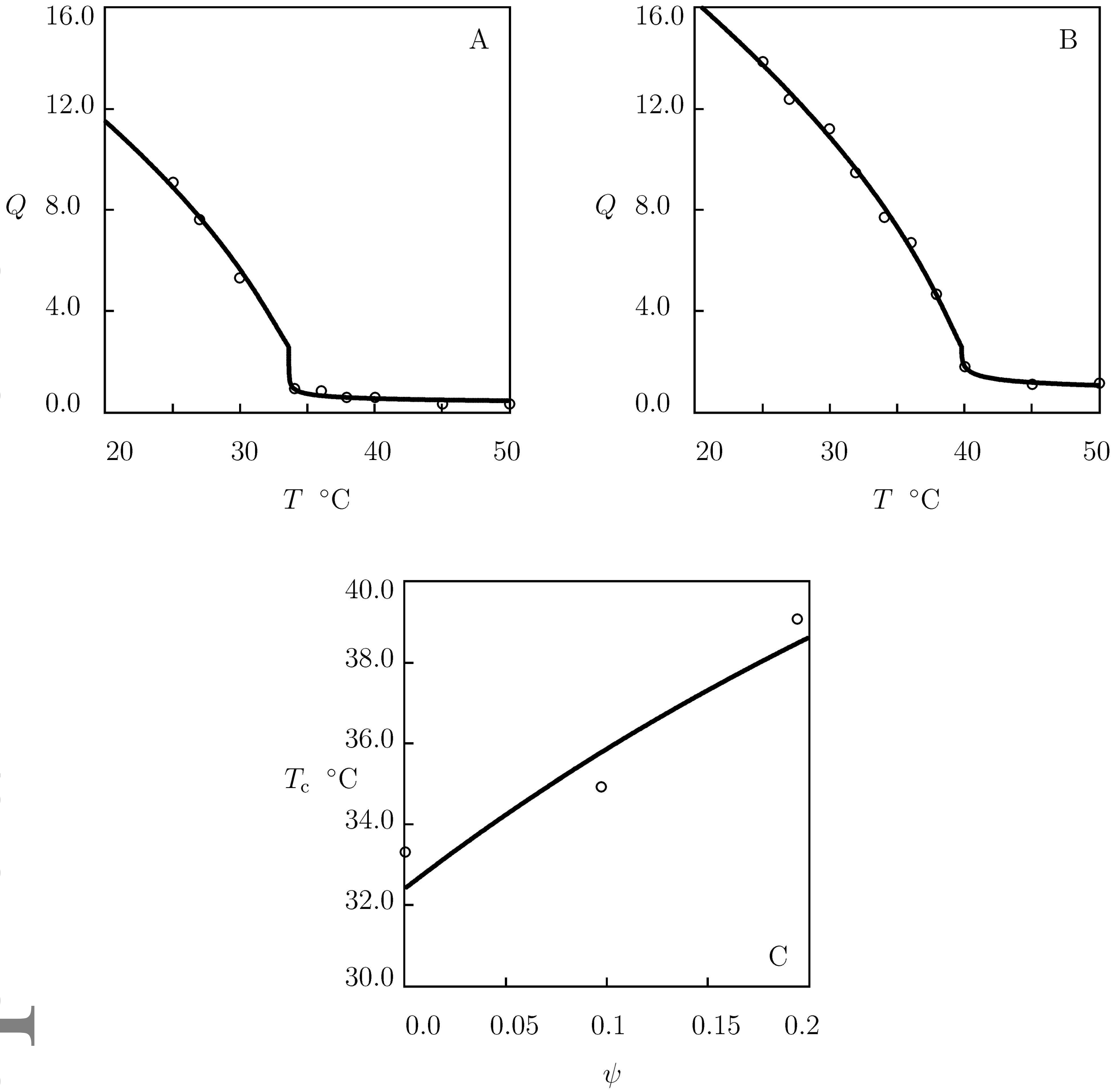
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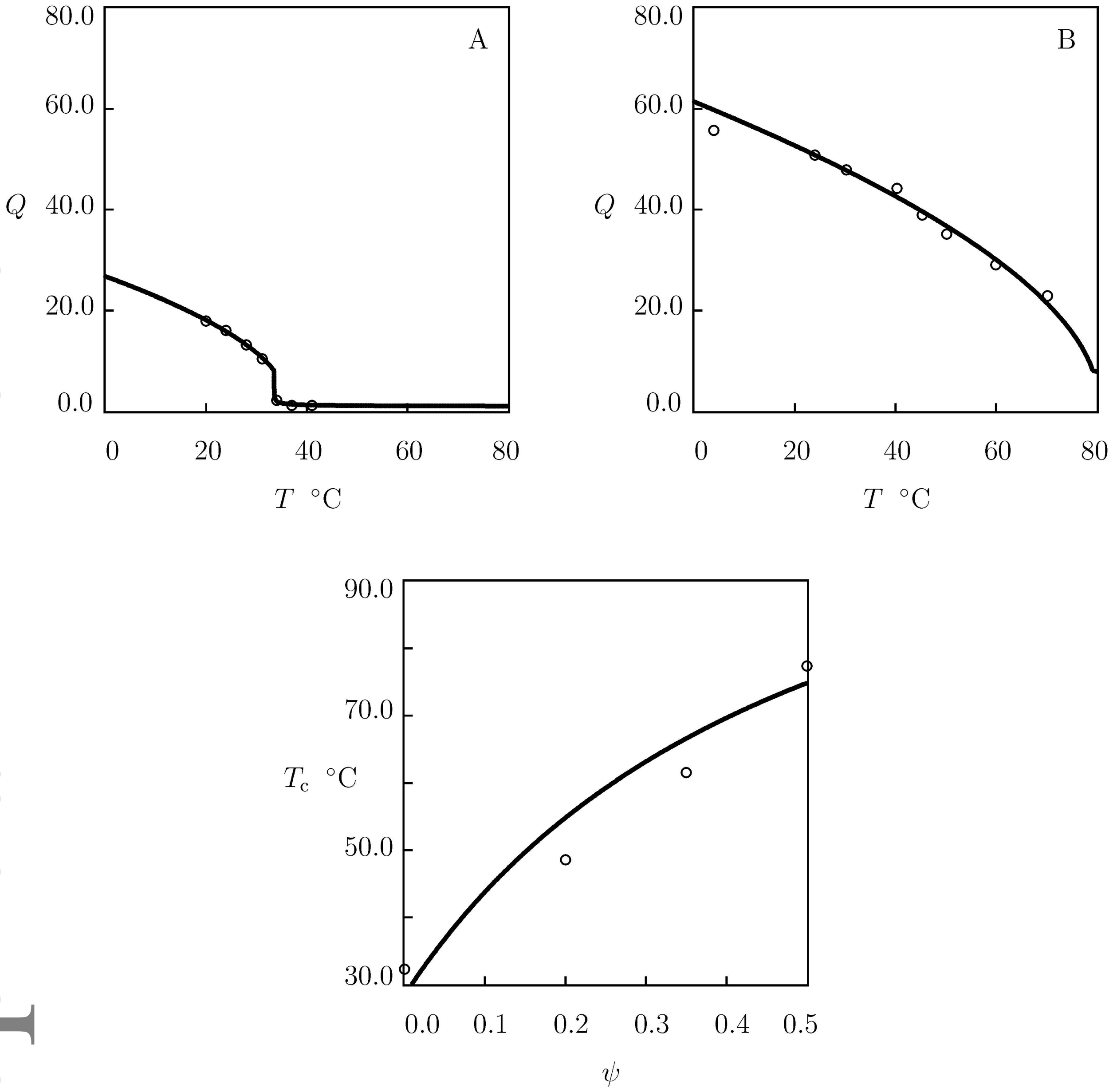
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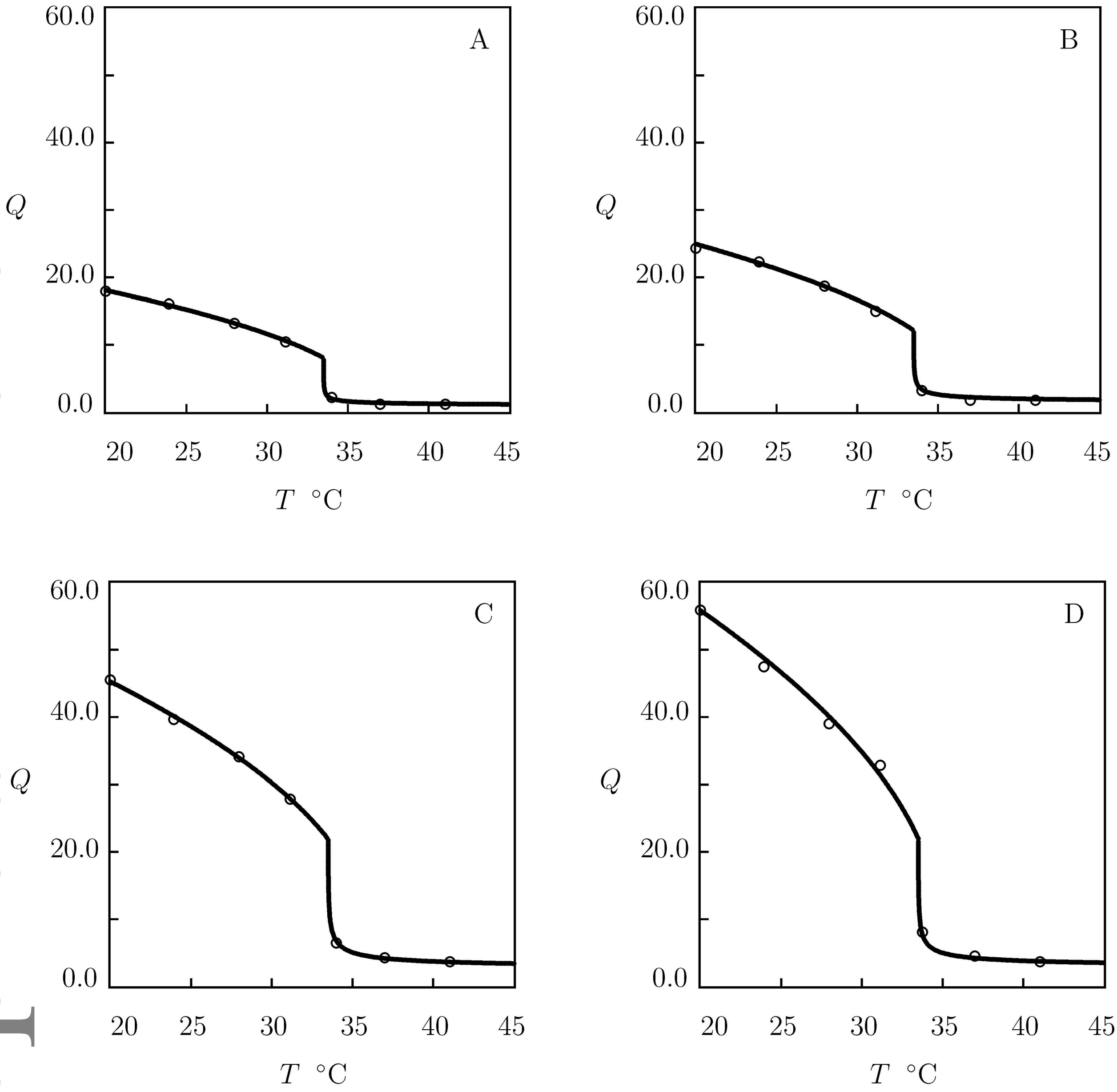
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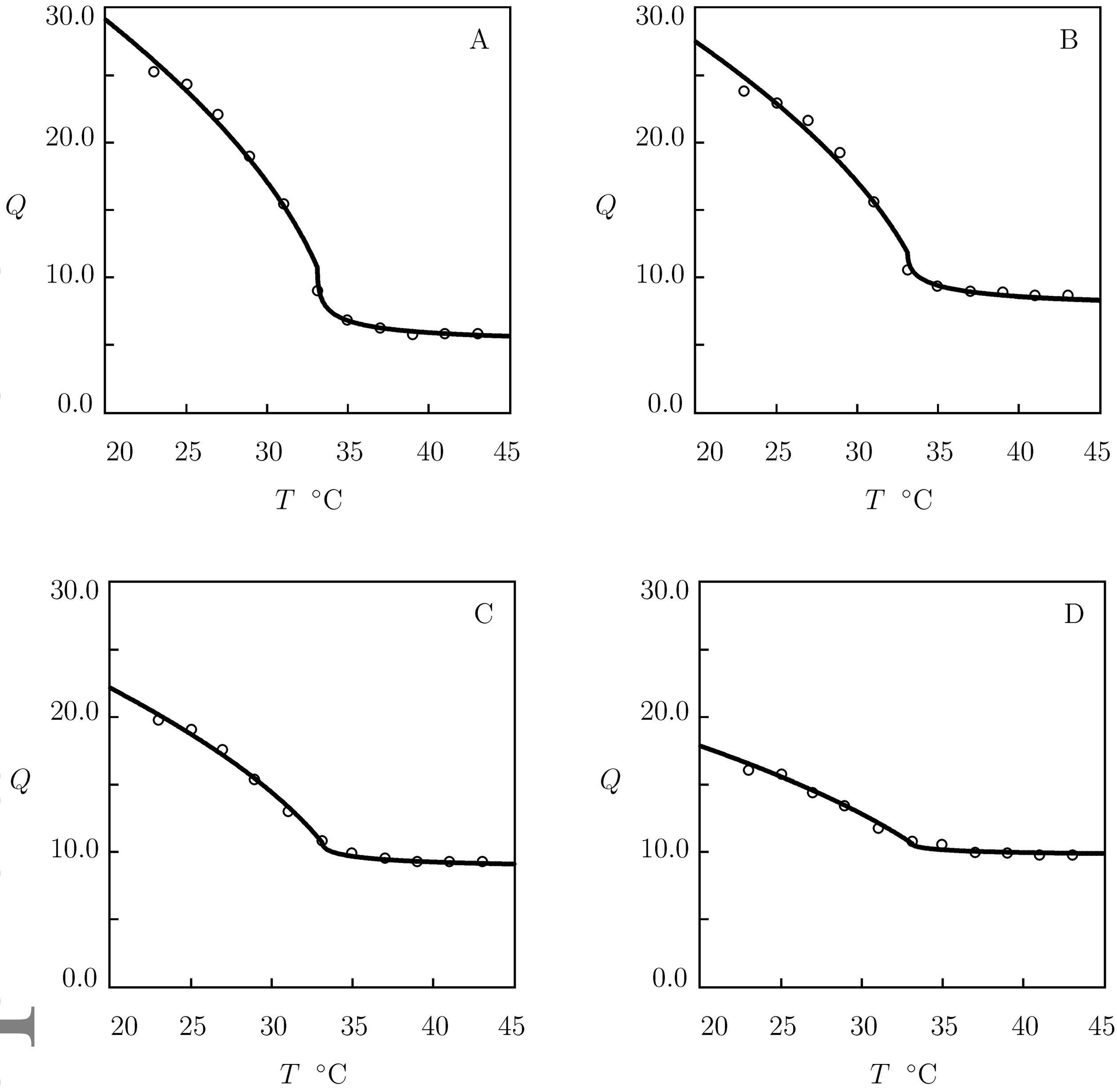
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