Structure-property relations for equilibrium swelling of cationic gels

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ABSTRACT

Governing equations are developed for equilibrium swelling of a cationic polyelectrolyte gel in aqueous solutions with various pH and molar fractions of a monovalent salt. Material constants are determined by fitting observations on several homo- and copolymer gels in two types of tests: when swelling is conducted in water baths with varied pH and a fixed molar fraction of salt, and when experiments are performed in water baths with a fixed pH and varied concentration of salt. Phenomenological relations are suggested for the effect of total volume fraction of monomers in a pre-gel solution, molar fraction of ionic monomers, and molar fraction of cross-linker on adjustable parameters in the model.

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1. Introduction

Hydrogels are three-dimensional networks of polymer chains connected by covalent bonds, physical cross-links and hydrogen bonds. When a dry gel is immersed into a water bath, it swells retaining structural integrity and ability to withstand large deformations. Stimuli-responsive gels form an important class of hydrogels whose equilibrium degree of swelling and kinetics of water uptake are strongly affected by temperature, pH, ionic strength, electric field, and light [1,2]. These materials have recently became a focus of attention as they demonstrate potential for a wide range of "smart" applications including biomedical devices, drug delivery carriers, scaffolds for tissue engineering, filters and membranes for selective diffusion, sensors for on-line process monitoring and soft actuators [3–8].

In polyelectrolyte gels, functional groups (attached to main or side chains of the polymer network) are ionized when pH of water is altered. Depending on the charge of bound groups, anionic, cationic, and ampholyte gels are distinguished. This study deals with water uptake by cationic gels whose functional groups are ionized due to proton exchange reaction with mobile hydronium ions.

We focus on the analysis of equilibrium swelling of cationic gels prepared by cross-linking polymerization of monomers in an aqueous solution. Composition of an homopolymer gel is characterized by two parameters: (i) volume fraction of monomers ϕ_{m} in a pre-gel solution and (ii) molar fraction of cross-linker ρ_{c} (the ratio of molar mass of a cross-linker to the molar mass of monomers). Composition of a copolymer gel is described by three parameters: (i) volume fraction of monomers ϕ_{m} in a pre-gel solution, (ii) molar fraction of ionic monomers ρ_{i} (the ratio of molar mass of ionic monomers to the total molar mass of monomers), and (iii) molar fraction of a cross-linker ρ_{c}. The effect of these quantities on degree of swelling of cationic gels under unconstrained swelling was analyzed experimentally in [9–20], to mention a few. To examine how degree of swelling is affected by parameters ϕ_{m}, ρ_{i}, and ρ_{c}, two types of water uptake tests are conventionally

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List of symbols

a_m, b_m, g_m	coefficients in Eqs. (7)–(9)
C	number of water molecules per unit volume in the initial state
C_b	number of functional groups per unit volume in the initial state
f	coefficient of volume expansion of the polymer network
G	elastic modulus
g	dimensionless elastic modulus
J_{em}	the principal invariants of the Cauchy–Green measure for elastic deformation
k_B	Boltzmann's constant
n_+	fraction of positive mobile ions
n_+^{bath}	fraction of positive ions in the bath
pK_b	base dissociation constant
pK_w	water ionization constant
q_0	degree of swelling in the as-prepared state
q_1, q	parameters characterizing expansion of the network driven by electrostatic repulsion of bound charges
Q	degree of swelling
R_b	volume fraction of functional groups in the initial state
R_b^0	volume fraction of functional groups in a pure cationic gel
S	parameter characterizing formation of ion pairs
T	absolute temperature
v	volume of a water molecule
W	strain energy density
$\mathbf{B}_e$	the Cauchy–Green measure of elastic deformation
$\mathbf{F}$	the deformation gradient for macro-deformation
$\mathbf{F}_e$	the deformation gradient for elastic deformation
α	degree of ionization of chains
α_{max}	maximum degree of ionization of chains
α_0	parameter characterizing hydrophobic interactions between segments of chains
θ	molar fraction of salt in an aqueous solution
κ	molarity of water
ρ_c	molar fraction of a cross-linker
ρ_i	molar fraction of ionic monomers
ρ_m	molar fraction of monomers in a pre-gel solution
ϕ_m	volume fraction of monomers in a pre-gel solution
χ	the Flory–Huggins parameter

employed. In the first type of experiments, degree of swelling Q is measured as a function of pH of water, whereas in the other type of tests, this quantity is determined as a function of molar fraction θ of a monovalent salt in an aqueous solution with a fixed pH. In this study, a constitutive model is reported that allows observations in one type of experiments to be predicted by using experimental data in the other type of tests, and its adjustable parameters are determined by fitting experimental swelling diagrams.

Modeling and simulation of the mechanical response of pH-sensitive gels under three-dimensional deformations with finite strains accompanied by swelling has attracted substantial attention in the past decade when it has been recognized that their equilibrium water uptake is strongly affected by geometrical constraints [21,22]. Coupled equations for the elastic behavior of polyelectrolyte gels and transport of solvent and solutes were recently developed in [23–33].

In our previous study [33], a model has been derived for anionic gels that allows an equilibrium swelling diagram in water uptake tests with varying pH to be re-calculated into that in experiments with varying θ and vice versa. The aim of this work is (i) to report an analog of this model for cationic gels, (ii) to validate the governing equations by comparison of results of simulation with observations when both experimental dependencies $Q(pH)$ and $Q(\theta)$ are provided, and (iii) to develop phenomenological relations that describe the effect of ϕ_m, ρ_i, and ρ_c on adjustable parameters in the model.

The novelty of the present study consists in the following: (i) it is demonstrated that the effect of molar fraction of salt on degrees of ionization of anionic and cationic gels is described by different equations, and (ii) structure-property relations are established for a cationic gel that allow its equilibrium degree of swelling Q to be predicted for a given composition (total molar fraction of monomers in a pre-gel solution, concentration of ionized functional groups, and concentration of a cross-linker). The latter is of essential importance for design of pH-sensitive gels with required swelling abilities.

The exposition is organized as follows. Governing equations for equilibrium unconstrained swelling of a cationic gel are reported in Section 2. A detailed derivation of these relations is presented in Supporting Information. Validation of the model