Journal of the Mechanics and Physics of Solids 59 (2011) 2259–2278

Contents lists available at SciVerse ScienceDirect

Journal of the Mechanics and Physics of Solids

journal homepage: www.elsevier.com/locate/jmps

Mechanics and chemical thermodynamics of phase transition in temperature-sensitive hydrogels

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ARTICLE INFO

Article history:
Received 12 May 2011
Received in revised form
27 August 2011
Accepted 29 August 2011
Available online 1 September 2011

Keywords:
Elastomer
Phase transition
Temperature-sensitive hydrogel
Large deformation

ABSTRACT

This paper uses the thermodynamic data of aqueous solutions of uncrosslinked poly-(*N*-isopropylacrylamide) (PNIPAM) to study the phase transition of PNIPAM hydrogels. At a low temperature, uncrosslinked PNIPAM can be dissolved in water and form a homogenous liquid solution. When the temperature is increased, the solution separates into two liquid phases with different concentrations of the polymer. Covalently crosslinked PNIPAM, however, does not dissolve in water, but can imbibe water and form a hydrogel. When the temperature is changed, the hydrogel undergoes a phase transition: the amount of water in the hydrogel in equilibrium changes with temperature discontinuously. While the aqueous solution is a liquid and cannot sustain any nonhydrostatic stress in equilibrium, the hydrogel is a solid and can sustain nonhydrostatic stress in equilibrium. The nonhydrostatic stress can markedly affect various aspects of the phase transition in the hydrogel. We adopt the Flory–Rehner model, and show that the interaction parameter as a function of temperature and concentration obtained from the PNIPAM–water solution can be used to analyze diverse phenomena associated with the phase transition of the PNIPAM hydrogel. We analyze free swelling, uniaxially and biaxially constrained swelling of a hydrogel, swelling of a core–shell structure, and coexistent phases in a rod. The analysis is related to available experimental observations. Also outlined is a general theory of coexistent phases undergoing inhomogeneous deformation.

1. Introduction

A network of covalently crosslinked, long, and flexible polymer chains can aggregate with water to form an elastomeric hydrogel. When the hydrogel equilibrates with a surrounding aqueous solution, depending on the functional groups along the polymer chains, the amount of water in the hydrogel can be affected by many stimuli, including forces (Doi, 2009), temperature (Otake et al., 1990), pH (Marcombe et al., 2010), ionic concentration (Tanaka et al., 1980), and electric field (Shiga, 1997; Osada and Gong, 1998). The significance of mechanochemical interaction in hydrogels is vividly illustrated by the following example. In superabsorbent diapers, the granules of a hydrogel need to absorb water many times their own weight. The swollen diapers need to feel dry under the weights of babies (Masuda, 1994).

Stimuli-responsive hydrogels are being developed for diverse applications, such as microvalves (Richter et al., 2004), actuators (Carpi and Smela, 2009), and sensors (Lee and Braun, 2003). Many such applications require hydrogels to swell

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doi:10.1016/j.jmps.2011.08.008

under the constraint of surrounding materials, or under external forces. For example, Steinberg et al. (1966) developed a mechanochemical engine, involving a collagen fiber swelling and shrinking in two baths of aqueous solutions of different ionic concentrations, while lifting a weight. As another example, Hu et al. (1995) used a temperature-sensitive hydrogel to fabricate a hand-like device, gripping or releasing objects by changing the temperature.

These and many other applications have motivated recent development of the nonlinear field theory of hydrogels (e.g., Baek and Srinivasa, 2004; Dolbow et al., 2004; Hui and Muralidharan, 2005; Li et al., 2007; Hong et al., 2008, 2009, 2010; Doi, 2009; Marcombe et al., 2010; Chester and Anand, 2010; An et al., 2010; Baek and Pence, 2011). The theory is formulated on the basis of the kinematics of network deformation, kinetics of water migration, and thermodynamics of swelling.

The field theory of hydrogels, however, involves multiple fields and nonlinear functions; quantitative comparison between theoretical predictions and experimental observations has been challenging. This paper takes advantage of a large number of available experiments of a particular polymer: poly(*N*-isopropylacrylamide) (PNIPAM). Specifically, we use the thermodynamic data of aqueous solutions of PNIPAM to analyze the behavior of PNIPAM hydrogels under various mechanical forces and constraints. At a low temperature, uncrosslinked PNIPAM can be dissolved in water and form a homogenous liquid solution (Fig. 1a). When the temperature is increased, the solution separates into two liquid phases with different concentrations of the polymer (Fig. 1b). Covalently crosslinked PNIPAM, however, does not dissolve in water, but can imbibe water and form a hydrogel. When the temperature is changed, the hydrogel undergoes a phase transition: the amount of water in the hydrogel in equilibrium changes with the temperature discontinuously (Fig. 2).

While the aqueous solution is a liquid and cannot sustain any nonhydrostatic stress in equilibrium, the hydrogel is a solid and can sustain nonhydrostatic stress in equilibrium. The nonhydrostatic stress can markedly affect various aspects of the phase transition in the hydrogel. Consequently, it is significant to show that the interaction parameter obtained from the solution can predict diverse phenomena associated with the phase transition of the hydrogel under nonhydrostatic stress.

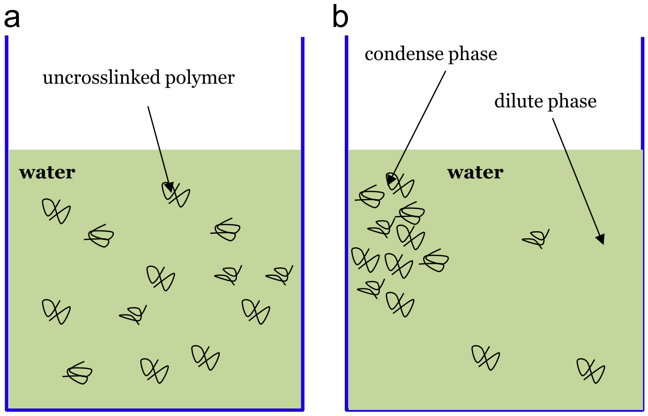

Fig. 1. Schematics of a temperature-sensitive polymer solution. (a) At a low temperature, the uncrosslinked polymers dissolve in water and form a homogenous solution. (b) At a high temperature, the solution separates into two liquid phases with different concentrations of the polymer.

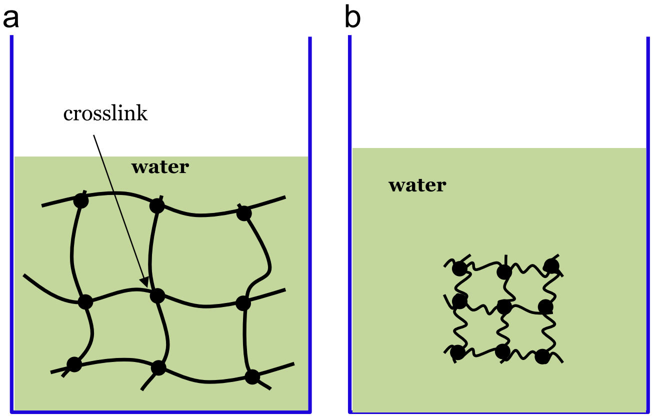

Fig. 2. Schematics of a temperature-sensitive hydrogel. (a) At a low temperature, the network absorbs a large amount of water, and the hydrogel is in the swollen phase. (b) At a high temperature, the network absorbs a small amount of water, and the hydrogel is in the shrunk phase.