

A Simulation Method to Analyze Chemo-Mechanical Behavior of Swelling-Induced Shape-Memory Polymer in Response to Solvent

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Received 28 December 2010; accepted 25 March 2011

DOI 10.1002/app.34597

Published online 9 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A network of thermally responsive shape-memory polymers (SMPs) could imbibe a quantity of solvent molecules to swell, and subsequently induces a chemical potential change in polymer. When an equilibrium is reached between the mechanical load and the chemical potential of polymer network and solvent, the SMP polymer usually swells with a field of inhomogeneous and anisotropic deformation, which is considered to be equivalent to a hyperelastic field. We implement this

theory in the free-energy function equation, and analyze examples of swelling-induced deformation and shape recovery behavior. This work may provide a powerful tool to study complex swelling-induced shape-memory behavior of SMPs in response to the immersing solvents. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1137–1146, 2012

Key words: chemo-mechanical; free-energy function; responsive; shape-memory polymer

INTRODUCTION

As is well known, stimulus-responsive shape-memory polymers (SMPs) have increasingly received considerable attention from scientific and engineering communities, due to their unique characteristic that is able to actively respond to a specific stimulus by means of significantly changing their shape and/or maneuvering accordingly. They are a class of unique macromolecules with the capacity of memorizing their original shape after undergoing a shape deformation.¹ The basic molecular architecture of SMPs is a polymer network underlying active movement. Almost all SMPs are incorporated of two segments, where one segment with relative higher elastic and transition temperature is defined as hard segment, and the other is able to remarkably reduce its stiffness in the presence of a particular stimulus.² The latter segment (relatively named as transition or switching segment) can be either a molecular switch or a stimulus-sensitive domain. On exposure to a specific stimulus, the switching/transition is triggered, which consequently results in the shape recovery. In addition, the transition temperature of hard segment is more 20°C than that of soft segment.

SMPs have a far higher recoverable strain (up to 400%), much lower density, more convenient processing and fabrication techniques, and more easily tailored properties (e.g., transition temperature, stiffness, bio-degradability, functional gradient) to better accommodate the requirements of a particular application.² Furthermore, one of the most notable features of these materials is that shape recovery of SMP can be triggered not only by directly heating, light,³ laser,⁴ electrical current,^{5–8} magnetic field^{9,10} but also can be induced by water¹¹ or solvent.^{12–14} These activation approaches have promoted researchers to utilize SMPs as sensors and actuators, deployable structures, drug-delivery systems, and biomedical devices.^{2,15}

Recently, we have identified a new approach to trigger the shape recovery of styrene-based SMP by solvent.^{12–14} Instead of heating, the SMP has been demonstrated to recover to its original shape by immersing it into solvent at room temperature, i.e., chemo-responsive shape recovery. The recovery is induced by the plasticizing effect of solvent molecules on polymer network, resulting in glass transition temperature (T_g) of the SMP indirectly declined. Hence, instead of heating the SMP above switching temperature, shape recovery can also be initiated by inductively lowering switching temperature through plasticizing effect.^{16,17} Flexible, long polymeric monomer could crosslink into a three-dimensional network. When the polymer is brought in contact

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with a solvent, polymer network imbibes solvent molecules and swells, resulting in solvent molecules aggregate known as a gel.^{18,19} The gel has characteristics of both a solid and a liquid: elastic deformation and viscous migration between the polymer network and solvent. The solvent-swollen polymer can undergo large deformation resulting from the long-range migration of the solvent molecules, making both shape and volume of solvent-swollen polymer changed, to reach the equilibrium with both the mechanical load and the external solvent. Therefore, these effects could be utilized to trigger shape recovery of SMP through lowering internal energy by mixing with solvent.

This article deals with the presentation of the achieved equilibrium after a SMP network has been in contact with a solvent and swells. In the absence of longitude uniaxial force mechanical load or geometric constraint, a homogenous and isotropic network will equilibrate with the solvent by a homogenous and isotropic deformation. In subsequence, it shows the inhomogeneous field in a solvent-swollen polymer equilibrates with the solvent and longitude uniaxial force. We implement this theory in the free-energy equation to identify free and constraint swelling-induced shape recovery. And we hope that this work will enable to construct the chemo-mechanical behavior of SMP in response to solvent.

FREE-ENERGY CHANGE AND CHEMICAL POTENTIALS ON MIXING POLYMER AND SOLVENT

A polymer dissolves or swells in a solvent if, at constant temperature and pressure, the total Gibbs free-energy decreases along with mixing. Therefore, it is necessary that the following hold²⁰:

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0, \quad (1)$$

where ΔG_m is the Gibbs function on mixing, ΔH_m is the enthalpy change on mixing, T is the temperature and ΔS_m is the entropy change on mixing. For most polymers, the enthalpy change on mixing is negative. This necessitates that the change in entropy be sufficiently positive if mixing is to occur.

The classical Flory–Huggins theory assumes at the outset that there is neither a change in volume nor a change in enthalpy on mixing a polymer with a low molecular-weight solvent.^{20–22} Thus, the calculation of the free-energy change on mixing at a constant temperature and pressure could be simplified into a calculation of the change in entropy on mixing. This latter quantity is determined under the help of a lattice model with formulas from statistical thermodynamics.^{22,23} As shown in Figure 1, an empty lattice begins with the number of ways, (Ω) , of arranging n_1 solvent molecules and n_2 polymer molecules in the

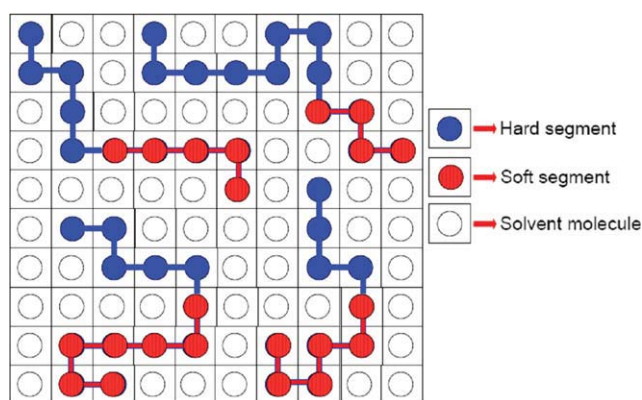


Figure 1 Schematic diagram of a polymer molecule on a two-dimensional lattice [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

$n_0 = n_1 + mn_2$ lattice sites, wherein each polymer molecule occupies m sites. As previously presented, the molecular structure of SMP contains two segments. One is highly elastic segment, the other is transition segment. Actually, the m sites occupied by each polymer molecule are incorporated of two parts, one is for elastic segment, and the other is for transition segment. Therefore, the m divides into m_1 plus m_2 , where m_1 sites are occupied by elastic segment, m_2 sites are occupied by transition segment. The m can be given by $m = m_1 + m_2$. Because the heat change on mixing is assumed to be zero in the simulation, each arrangement has the same energy and probability to occur. The only restriction is imposed by the connectivity of polymer chain segments.²⁰ It must be ensured that the interconnected polymer segments lie on the nearest neighboring lattice sites. Once the number of ways, (Ω) , is known, the entropy S_m of the mixture is given by $k \ln \Omega$, where k is the Boltzmann's constant.

To calculate the change in entropy that occurs from the mixing process, it is first arranged to reserve all the polymer macromolecules on the lattice. The identical solvent molecules are placed thereafter. Having arranged all of the polymer molecules, the number of ways of filling all of the indistinguishable solvent molecules in the remaining lattice sites is exactly one. As a result, the total number of ways of placing all the polymer and solvent molecules on the lattice is given by eq. (2):

$$S_m = k \ln \Omega. \quad (2)$$

It is evident that n_1/n_0 equals the volume fraction of the solvent ϕ_1 , and mn_2/n_0 equals the volume fraction of the polymer ϕ_2 .²¹ Thus,

$$S_m = -k \ln [n_1 \ln \phi_1 + n_2 \ln \phi_2]. \quad (3)$$

Then, the change in entropy on mixing n_1 moles solvent molecules with n_2 moles polymer molecules

can be calculated by multiplying the right-hand side of eq. (3) with the Avogadro's number, namely,

$$\begin{aligned} S_m &= -Nk \ln[n_1 \ln \phi_1 + n_2 \ln \phi_2] \\ &= -R \ln[n_1 \ln \phi_1 + n_2 \ln \phi_2], \end{aligned} \quad (4)$$

where R is the universal gas constant, as well as n_1 and n_2 now represent numbers of moles. Note that if m equals unity, ϕ_1 and ϕ_2 would equal the mole fractions. And eq. (3) could be treated as entropy change equation of mixing ideal molecules.^{23,24}

On the other hand, it is known that the enthalpy change ΔH_m equals to the internal energy change ΔU on mixing, when the change in volume on mixing is zero.²⁰ Thus, the enthalpy change on mixing can be expressed as,

$$\Delta H_m = kT\chi_1 n_1 \phi_2. \quad (5)$$

This expression reveals that the enthalpy change ΔH_m depends on the nature of both the solvent and the solute, and is the only Flory-Huggins interaction parameter χ_1 function in the model. Submitting eqs. (4) and (5) into, (1) we obtain,

$$\Delta G_m = kT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_1 n_1 \phi_2]. \quad (6)$$

The chemical potential could be defined as a partial molar Gibbs free-energy, and the fact that,

$$\Delta G_m = \Delta G_{\text{mixture}} - G_1 - G_2, \quad (7)$$

so that

$$\begin{aligned} \Delta G_{\text{mixture}} &= G_1 + G_2 \\ &+ RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_1 n_1 \phi_2], \end{aligned} \quad (8)$$

Differentiating eq. (8) with respect to n_1 and n_2 , in turn, gives the following,

$$\begin{aligned} \mu_1 &= \frac{\partial G_{\text{mixture}}}{\partial n_1} = g_1 \\ &+ RT \left[\ln \phi_1 + \frac{n_1}{\phi_1} \frac{\partial \phi_1}{\partial n_1} + \frac{n_2}{\phi_2} \frac{\partial \phi_2}{\partial n_1} + \chi_1 \phi_2 + \chi_1 n_1 \frac{\partial \phi_2}{\partial n_1} \right], \end{aligned} \quad (9)$$

$$\begin{aligned} \mu_2 &= \frac{\partial G_{\text{mixture}}}{\partial n_2} = g_2 \\ &+ RT \left[\frac{n_1}{\phi_1} \frac{\partial \phi_1}{\partial n_2} + \ln \phi_2 + \frac{n_2}{\phi_2} \frac{\partial \phi_2}{\partial n_2} + \chi_1 n_1 \frac{\partial \phi_2}{\partial n_2} \right], \end{aligned} \quad (10)$$

where g_1 and g_2 are the molar free energies of the solvent and polymer, respectively. Recognizing that $\phi_1 = \frac{n_1}{n_1 + mn_2}$ and $\phi_2 = \frac{mn_2}{n_1 + mn_2}$, gives the following,

$$\frac{\partial \phi_1}{\partial n_1} = \frac{\phi_2}{n_1 + mn_2}, \quad (11)$$

$$\frac{\partial \phi_1}{\partial n_2} = -\frac{m\phi_1}{n_1 + mn_2}, \quad (12)$$

$$\frac{\partial \phi_2}{\partial n_1} = -\frac{\phi_2}{n_1 + mn_2}, \quad (13)$$

$$\frac{\partial \phi_2}{\partial n_2} = \frac{m\phi_1}{n_1 + mn_2}. \quad (14)$$

Equations (11)–(14) are submitted into eqs. (9) and (10), and simplifying gives²³

$$\frac{\mu_1 - \mu_1^0}{RT} = \ln(1 - \phi_2) + \phi_2 \left(1 - \frac{1}{m} \right) + \chi_1 \phi_2^2, \quad (15)$$

$$\frac{\mu_2 - \mu_2^0}{RT} = (1 - \phi_2)(1 - m) + \ln \phi_2 + \chi_1 m(1 - \phi_2)^2, \quad (16)$$

in which g_1 and g_2 have been relabeled μ_1^0 and μ_2^0 , respectively. The preceding two equations can now be used for examining phase equilibrium.

Based on eq. (16), $\mu_2 - \mu_2^0/RT$ function with respect to ϕ_1 can be expressed as,

$$\frac{\mu_2 - \mu_2^0}{RT} = \phi_1(1 - m) + \ln(1 - \phi_1) + \chi_1 m \phi_1^2. \quad (17)$$

If we mix n_1 moles solvent molecules with n_2 moles polymer molecules, with molecular weight ratio of 1 : m , the change in chemical potential of the polymer on mixing can be calculated from eq. (17). For a fixed χ_1 , we can easily plot the curve for $\mu_2 - \mu_2^0/RT$ function against to ϕ_1 . By changing χ_1 and repeating this procedure, we would get a family curves for chemical potential change, because there is a one-to-one correspondence between χ_1 and $\mu_2 - \mu_2^0/RT$. Such a plot is shown in Figure 2 for m equaling 1000, taken from the work of Flory. Note that increasing χ_1 is equivalent to making it more difficult to mix polymer molecules with solvent molecules.

FLORY-REHNER FREE-ENERGY FUNCTION

A network of polymers immersed in a solvent and subject to mechanical loads

A cubic SMP block is immersed in a solvent to be studied. In the referenced state, no external loadings are applied on the block, and no solvent molecules are absorbed inside the block with dimensions of $L_1 L_2 L_3$. Exposing the polymer to solvent, the polymeric block is assumed to imbibe solvent molecules that diffuse into the interstitial space of the polymer chains. It is assumed that weights applied on the six surfaces of the block results in the dimensions of polymeric block changed to $l_1 l_2 l_3$.²⁵ Denote the stretches of the block by,

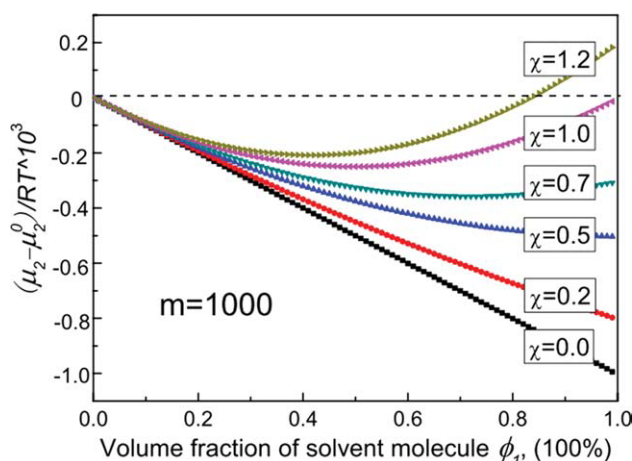


Figure 2 Polymer chemical potential as a function of solvent volume fraction for $m = 1000$. The value of χ_1 is indicated on each curve [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

$$\lambda_1 = \frac{l_1}{L_1}, \quad \lambda_2 = \frac{l_2}{L_2}, \quad \lambda_3 = \frac{l_3}{L_3}. \quad (18)$$

The six weights apply neat forces F_1 , F_2 , and F_3 to the block in three directions. Define the nominal stresses S_1 , S_2 , and S_3 in the polymer by,

$$S_1 = \frac{F_1}{L_2 L_3}, \quad S_2 = \frac{F_2}{L_3 L_1}, \quad S_3 = \frac{F_3}{L_1 L_2}, \quad (19)$$

The weights may allow the polymer to deform without constraint, and the small molecules to diffuse into the polymer. Denote the true stresses by $\sigma_1 = F_1/(l_2 l_3)$, $\sigma_2 = F_2/(l_3 l_1)$, and $\sigma_3 = F_3/(l_1 l_2)$, which relate to the nominal stresses by $S_1 = \sigma_1 \lambda_2 \lambda_3$, $S_2 = \sigma_2 \lambda_3 \lambda_1$, and $S_3 = \sigma_3 \lambda_1 \lambda_2$.²⁶

Let C be the number of the solvent molecules in the polymeric network, and M denote the nominal concentration of the small molecules by²⁰

$$C = M / (L_1 L_2 L_3). \quad (20)$$

It is assumed that both polymer molecules and solvent molecules are incompressible, as well as there is no void space inside the polymer block. Let v be the volume of per solvent molecule. When the M solvent molecules are diffused into polymer, the volume of the polymer changes from $L_1 L_2 L_3$ to $l_1 l_2 l_3 = L_1 L_2 L_3 + vM$. Dividing this expression by $L_1 L_2 L_3$, we obtain that

$$\lambda_1 \lambda_2 \lambda_3 = 1 + vC. \quad (21)$$

The polymer, the solvent and the weights, together constitute a thermodynamic system. Let W be the free-energy of the polymer in the current state

divided by the volume of the polymer in the referenced state, characterized by the generalized coordinates $\lambda_1, \lambda_2, \lambda_3$, and three control parameters F_1, F_2, F_3 . The free-energy of the system, of which the sum of that of the polymer, is given by,²⁶

$$G = W(\lambda_1, \lambda_2, \lambda_3) L_1 L_2 L_3 - F_1(l_1 - L_1) - F_2(l_2 - L_2) - F_3(l_3 - L_3). \quad (22)$$

Thermodynamics dictates that the left-hand free-energy reaches to a minimum value as the system gets a stable state. When the generalized coordinates vary slightly from $(\lambda_1, \lambda_2, \lambda_3)$ to $(\lambda_1 + \delta\lambda_1, \lambda_2 + \delta\lambda_2, \lambda_3 + \delta\lambda_3)$ the free-energy of the system varies by²⁶

$$\begin{aligned} \frac{\partial G}{L_1 L_2 L_3} = & \left[\frac{\partial W}{\partial \lambda_1} - S_1 \right] \delta\lambda_1 + \left[\frac{\partial W}{\partial \lambda_2} - S_2 \right] \delta\lambda_2 \\ & + \left[\frac{\partial W}{\partial \lambda_3} - S_3 \right] \delta\lambda_3 + \frac{\partial^2 W}{\partial \lambda_1^2} \delta\lambda_1^2 + \frac{\partial^2 W}{\partial \lambda_2^2} \delta\lambda_2^2 + \frac{\partial^2 W}{\partial \lambda_3^2} \delta\lambda_3^2 \\ & + \frac{\partial^2 W}{\partial \lambda_1 \partial \lambda_2} \delta\lambda_1 \delta\lambda_2 + \frac{\partial^2 W}{\partial \lambda_2 \partial \lambda_3} \delta\lambda_2 \delta\lambda_3 + \frac{\partial^2 W}{\partial \lambda_1 \partial \lambda_3} \delta\lambda_1 \delta\lambda_3. \end{aligned} \quad (23)$$

In equilibrium, the coefficients of the first variations vanish,

$$S_1 = \frac{\partial W}{\partial \lambda_1}, \quad S_2 = \frac{\partial W}{\partial \lambda_2}, \quad S_3 = \frac{\partial W}{\partial \lambda_3}. \quad (24)$$

In deriving eq. 24, we have regarded S_1, S_2, S_3 as the loading parameters set by the weights. Therefore, S_1, S_2, S_3 are also regarded as the functions of the generalized coordinates $(\lambda_1, \lambda_2, \lambda_3)$. As a result, the free-energy function of the polymer, $W(\lambda_1, \lambda_2, \lambda_3)$ is determined by the generalized coordinates $(\lambda_1, \lambda_2, \lambda_3)$. Furthermore, to ensure that a state $(\lambda_1, \lambda_2, \lambda_3)$ minimizes G , the sum of the second-order variations must be positive for arbitrary variation of $\delta\lambda_1, \delta\lambda_2, \delta\lambda_3$.²⁶

Homogeneous state of deformation for free swelling

Based on above-mentioned, in a case when a non-ionic solvent-swollen polymer is subject to a solvent and stresses are applied, there are three contributions to the free-energy of the solvent-swollen polymer and they are: stretching free-energy, mixing free-energy and polarizing free-energy. The following equation can be used to account for it.²³

$$W = W_s + W_m + W_c. \quad (25)$$

To systematically explain and substantiate the applicability of eq. (25), the following part will present the respective effect of three contributions on the free-energy function. At first, the polarizing potential

sometimes is assumed as zero. The free-energy equation should be rewritten as

$$W = W_s + W_m. \quad (26)$$

The free-energy of stretching a network of polymers is taken to be (Flory, 1953),²³

$$W_s(\lambda_1, \lambda_2, \lambda_3) = \frac{1}{2}NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - 2 \log \lambda_1 \lambda_2 \lambda_3), \quad (27)$$

where N is the number of chains in the polymer divided by the volume of the polymer block in the referenced state, and kT is the temperature in the unit of energy.

When the polymers are not cross-linked, the polymers and the small molecules can form a solution. The mixing free-energy is taken to be (Flory, 1942; Huggins, 1941),²³

$$W_m(C) = -\frac{kT}{v} \left[vC \log \left(1 + \frac{1}{vC} \right) + \frac{\chi}{1 + vC} \right], \quad (28)$$

Here vC is the volume of the solvent molecules in the network divided by the volume of the polymers. Thus, the expression²⁶ can be substantiated by,

$$W = \frac{1}{2}NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - 2 \log \lambda_1 \lambda_2 \lambda_3) - \frac{kT}{v} \left[vC \log \left(1 + \frac{1}{vC} \right) + \frac{\chi}{(1 + vC)} \right]. \quad (29)$$

Considering a cubic solvent-swollen polymer without constraint to be stretched in three directions, and the stretches of polymer to a fixed value, namely $\lambda_1 = \lambda_2 = \lambda_3 = \lambda$. Thus, the $1 + vC$ can be calculated by inputting λ into eq. (21), namely $1 + vC = \lambda^3$. Equation (29) can be rewritten as,

$$W = \frac{3}{2}NkT(\lambda^2 - 1 - 2 \log \lambda) - \frac{kT}{v} \left[(\lambda^3 - 1) \log \left(\frac{\lambda^3}{\lambda^3 - 1} \right) + \frac{\chi}{\lambda^3} \right]. \quad (30)$$

We denote this free-swelling stretch by λ , which relates to the chemical potential μ , and the differential change of polymer is equal to the negative value of solvent. For example, in the case of "1," the molar numbers of polymer and solvent are x_1^1 and x_2^1 in the system (where $x_1^1 + x_2^1 = 1$), respectively. In the case of "2," the molar numbers of polymer and solvent are x_1^2 and x_2^2 in the system (where $x_1^2 + x_2^2 = 1$), respectively. From case "1" to "2," the change in the mole of solvent is $x_2^2 - x_2^1 = dC$. While the change in the mole of polymer is $x_1^2 - x_1^1 = (1 - x_2^2) - (1 - x_2^1)$

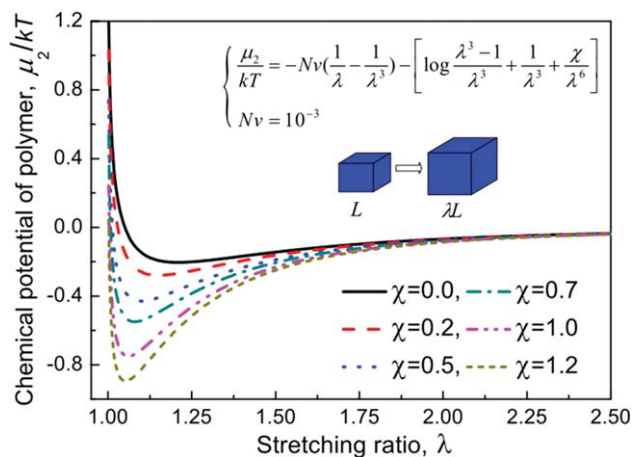


Figure 3 The free-swelling stretch of a solvent-swollen polymer is plotted as a function of the chemical potential of the solvent molecules with representative χ values [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).].

$= -(x_2^2 - x_2^1) = -dC$. So the change in chemical potential of polymer μ_2 can be expressed as,

$$\mu_2 = \frac{\partial W}{\partial(-C)} = -\left(\frac{\partial W_s}{\partial C} + \frac{\partial W_m}{\partial C} \right). \quad (31)$$

$$\mu_2 = \frac{\partial W}{\partial(-C)} = -\left(\frac{\partial W_s}{\partial C} + \frac{\partial W_m}{\partial C} \right) = -NkTv \left(\frac{1}{\lambda} - \frac{1}{\lambda^3} \right) - kT \left[\log \frac{\lambda^3 - 1}{\lambda^3} + \frac{1}{\lambda^3} + \frac{\chi}{\lambda^6} \right]. \quad (32)$$

So, the eq. (32) can be rewritten as,

$$\frac{\mu_2}{kT} = -Nv \left(\frac{1}{\lambda} - \frac{1}{\lambda^3} \right) - \left[\log \frac{\lambda^3 - 1}{\lambda^3} + \frac{1}{\lambda^3} + \frac{\chi}{\lambda^6} \right]. \quad (33)$$

We will normalize the chemical potential by kT . A representative value of the volume per solvent molecule is $v = 10^{-28} \text{ m}^3$. The Flory–Rehner free-energy function introduces two dimensionless material parameters: Nv and χ . Where the Nv is given the range $Nv = 10^{-4} : 10^{-1}$.²⁵ In the numerical examples below, we will take the value $Nv = 10^{-3}$. The parameter χ is a dimensionless parameter to measure enthalpy change of mixing, with representative value χ ranged from 0 to 1.2. For applications that prefer solvent-swollen polymer with large swelling ratios, materials with low values are used. The chemical potential as a function of swelling stretch with representative χ values is shown in Figure 3.

Homogeneous state of deformation for solvent-swollen polymer rod equilibrated with a solvent and a uniaxial force

When a solvent-swollen polymer rod is subject to a uniaxial stress along the longitudinal direction, the

solvent-swollen polymer would be equilibrated in a solvent of chemical potential and uniaxial stress. The state of deformation can be characterized by the longitudinal stretch λ_1 and two transverse stretches $\lambda_2 = \lambda_3$. The schematic depiction of stretches for the solvent-swollen polymer is shown in Figure 4. In this case, the eqs. (21) and (29) would be expressed as,

$$\begin{cases} 1 + vC = \lambda_1 \lambda_2^2 \\ W = \frac{1}{2} NkT (\lambda_1^2 + 2\lambda_2^2 - 3 - 2 \log \lambda_1 \lambda_2^2) \\ -\frac{kT}{v} \left[vC \log(1 + \frac{1}{vC}) + \frac{\chi}{(1+vC)} \right] \end{cases} \quad (34)$$

The stresses in the transverse directions vanish, so that eq. (31) gives,

$$\begin{aligned} \mu_2 &= \frac{\partial W}{\partial(-C)} = -\frac{\partial W}{\partial(C)} = -\left(\frac{\partial W_s}{\partial C} + \frac{\partial W_m}{\partial C} \right) \\ \Rightarrow \frac{\mu_2}{kT} &= -Nv \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_1 \lambda_2^2} \right) \\ &\quad - \log \left(1 - \frac{1}{\lambda_1 \lambda_2^2} \right) - \frac{1}{\lambda_1 \lambda_2^2} - \frac{\chi}{\lambda_1^2 \lambda_2^4} \end{aligned} \quad (35)$$

Equation (35) gives the equilibrium chemical potential of the solvent-swollen polymer when it is subject to a longitudinal stress. The left-hand side of equation corresponds to the stretch ratio λ_1/λ_2 and parameter χ , and these relationships are identified in Figure 5. Figure 5(a) and (b) characterize the relationship between μ_2/kT function and stretch ratio λ_1/λ_2 . For a given parameter, say $\chi = 0$ or $\chi = 0.5$, the μ_2/kT function sharply reaches to a constant maximum value, when longitudinal stress was applied to make solvent-swollen polymer stretched to a proper value. With further stretching solvent-swollen polymer, the μ_2/kT function gets smaller as the given stretch ratio is reached. On the other hand, with parameter χ increases from 0 to 0.5, the maximum value of μ_2/kT function is shifted to higher maximum. As it is known, when the parameter χ is increased, it is more difficult to mix the polymer with solvent. The chemical potential of solvent-swollen polymer is increased indirectly resulting from the increase in enthalpy and Gibbs free-energy, as shown in eqs. (5), (6), and (11).

Figure 5(c) and (d) show the effects of the parameter χ on μ_2/kT as a function of stretch λ_1 , for a given stretch ratio λ_1/λ_2 . The function μ_2/kT has a different maximum with respect to parameter χ . At first, the μ_2/kT firstly sharp increases with the stretch λ_1 increases. Then it gradually decreases with parameter λ_1 further increases. That's because the stretches change of the solvent-swollen polymer subjected to a solvent is critically determined by stress applied on the system at the beginning, and then is seriously determined by the stretching free-energy and mixing

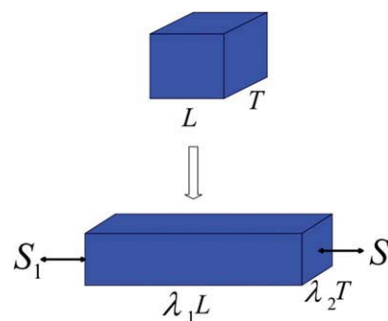


Figure 4 A SMP in contact with a solvent and subject to a uniaxial stress [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

free-energy. On the other hand, with the parameter χ increases, it is difficult for solvent-swollen polymer to be mixed with solvent, the stretch change has a more stronger relation with stress. Here, higher stress is needed to help the stretch ratio λ_1/λ_2 to reach the fixed constant.

Combining eqs. (24) and (34) could relate the longitudinal stress to the stretches:

$$\begin{aligned} \frac{vS_1}{kT} &= \frac{v}{kT} \cdot \left(\frac{\partial W}{\partial \lambda_1} \right) = Nv \left[\lambda_1 \left(1 + \frac{2}{B^2} \right) - \frac{3}{\lambda_1} \right] \\ &\quad + \left[\frac{3\lambda_1^2}{B^2} \log \left(1 - \frac{B^2}{\lambda_1^3} \right) + \frac{3}{\lambda_1} + \frac{3\chi B^2}{\lambda_1^4} \right]. \end{aligned} \quad (36)$$

For a prescribed parameter $\lambda_1/\lambda_2 = B$ (where B is a given constant), this part of equation provides the equilibrium relation of stress vS_1/kT , using the χ and λ_1 as parameters.

Equation (36) gives the equilibrium of vS_1/kT function for the solvent-swollen polymer being subject to a longitudinal stretch and solvent. The left-hand side of each curve corresponds to λ_1 , λ_2 , and parameter χ . The characteristic of vS_1/kT , using the χ and stretch ratio λ_1/λ_2 as parameters is plotted in Figure 6. Figures 6(a) and (b) plot the relation between vS_1/kT function and stretch ratio λ_1/λ_2 . For a given parameter, say $\chi = 0$ or $\chi = 0.5$, the vS_1/kT function gradually decreases with increasing values of stretch, λ_1 . On the other hand, with stretching ratio λ_1/λ_2 increases from 2 to 3, the vS_1/kT function decreases more slowly. This numerical result reveals that the higher stretching ratio, the stress reaches to a constant value with higher stretch λ_1 . And a decrease in vS_1/kT is more slow.

Figures 6(c) and (d) show the effects of the parameter χ on vS_1/kT as a function of stretch λ_1 , for a fixed stretch ratio λ_1/λ_2 . As a fixed level of the stretch ratio λ_1/λ_2 , the function vS_1/kT gradually increases with respect to λ_1 . With the parameter χ increases, the vS_1/kT also increases. That's because if mixing solvent-swollen polymer with solvent becomes more difficult, the contribution of stress

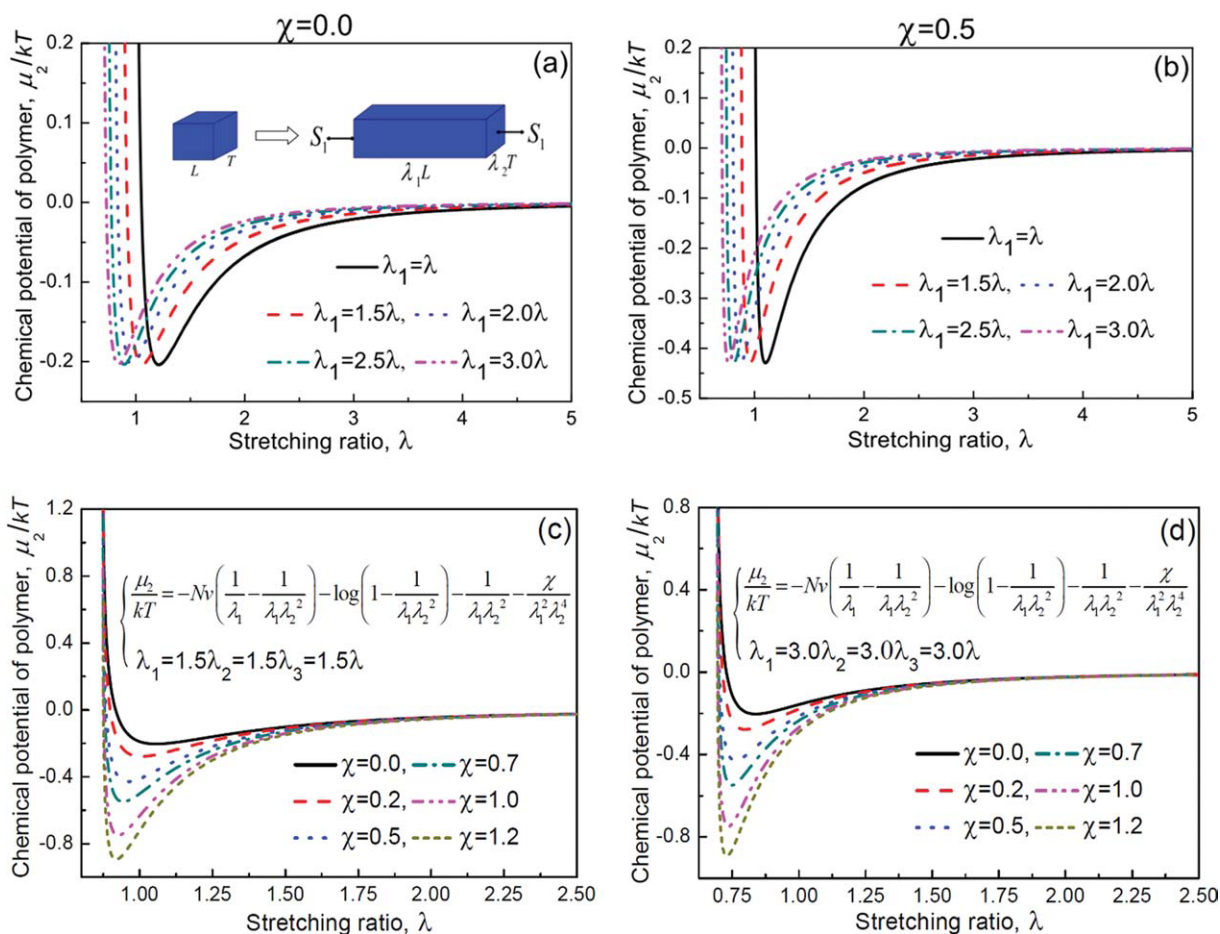


Figure 5 Numerical results for the constraint swelling of a SMP immersed in a solvent. (a) Relation of μ_2/kT function with λ_1/λ_2 , for a given parameter $\chi = 0$. (b) Relation of μ_2/kT function with λ_1/λ_2 , for a given parameter $\chi = 0.5$. (c) Relation of μ_2/kT function with χ , for a given parameter $\lambda_1/\lambda_2 = 1.5$. (d) Relation of $\nu S_1/kT$ function with χ , for a given parameter $\lambda_1/\lambda_2 = 3$ [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

should be increased to make the solvent-swollen polymer stretched to the same state.

Effect of swelling-induced chemical potential on shape-memory behavior of SMP

Shape-memory effect of SMP obeys with the relaxation theory, and the relationship between relaxation time and activation energy can be expressed by Eyring equation as,^{14,27}

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{RT}\right), \quad (37)$$

where τ is the relaxation time (is analogous to shape-memory recovery time), ΔE is the activation energy of chain mobility, R is the gas constant, T is the absolute temperature and τ_0 is a given constant. As presented in eq. (37), it is found that the shape-memory recovery time either can be determined by internal activation energy of polymer or sample temperature. Based on previous study,¹⁴ there is an

internal energy change in polymer when it is subject to a solvent on mixing. Therefore, the shape-memory behavior is inductively affected. And the relation between chemical potential and relaxation time can be expressed as,

$$\tau = \tau_0 \exp\left[\frac{\Delta E + \Delta U}{RT}\right], \quad (38)$$

where the $U = N\mu_2$, and N is the Avogadro's number. Equation (38) presents the behavior of one molar polymer. As presented in eqs. (32) and (35) the chemical potential of solvent system is given for free-swelling and constraint swelling. In contrary, the negative value of chemical potential in solvent system is considered as the corresponding chemical potential of polymer inside polymer system. Based on the eq. (38), the relation between relaxation time change and chemical potential can be obtained. As presented in eq. (38), the internal activation energy is determined by the internal energy of polymer. Thereafter, the

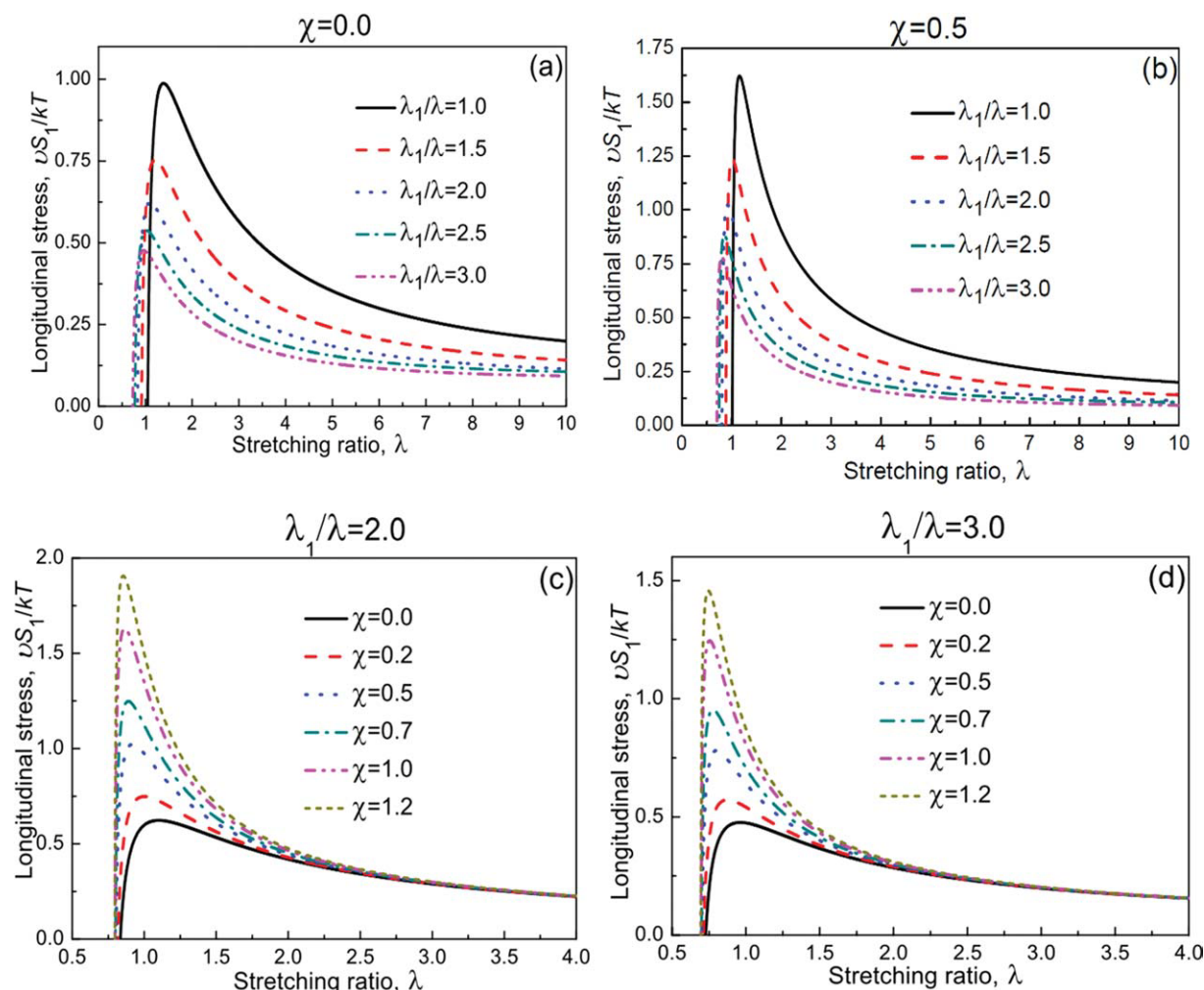


Figure 6 Numerical results for the constraint swelling of a SMP immersed in a solvent. (a) Relation of vS_1/kT function with λ_1/λ_2 , for a given parameter $\chi = 0$. (b) Relation of vS_1/kT function with λ_1/λ_2 , for a given parameter $\chi = 0.5$. (c) Relation of vS_1/kT function with χ , for a given parameter $\lambda_1/\lambda_2 = 2$. (d) Relation of vS_1/kT function with χ , for a given parameter $\lambda_1/\lambda_2 = 3$ [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).].

change in internal energy will influence the internal activation energy. Finally, the change in chemical potential indirectly or inductively influences the internal activation energy, which determines the shape-memory effect of SMP, as shown in eq. (39).

$$\tau = \tau_0 \exp \left[\frac{\Delta E + (-N\mu_2)}{RT} \right], \quad (39)$$

Combining eqs. (33) and (35) with (39) the effect of chemical potential on relaxation time can be written,

$$\begin{cases} \frac{\tau}{\tau_0} = \exp \left(\frac{-N\mu_2}{RT} \right) = \exp \left(\frac{-\mu_2}{kT} \right) = \exp \left\{ Nv \left(\frac{1}{\lambda} - \frac{1}{\lambda^3} \right) + \left[\log \frac{\lambda^3 - 1}{\lambda^3} + \frac{1}{\lambda^3} + \frac{\chi}{\lambda^6} \right] \right\} \\ \frac{\tau}{\tau_0} = \exp \left(\frac{-N\mu_2}{RT} \right) = \exp \left(\frac{-\mu_2}{kT} \right) = \exp \left\{ Nv \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_1 \lambda_2^2} \right) + \log \left(1 - \frac{1}{\lambda_1 \lambda_2^2} \right) + \frac{1}{\lambda_1 \lambda_2^2} + \frac{\chi}{\lambda_1^2 \lambda_2^4} \right\} \end{cases}, \quad (40)$$

As shown in Figure 7, the τ/τ_0 function of SMP decreases at the beginning of mixing, whatever the shape recovery of SMP is achieved by homogenous deformation or inhomogeneous deformation. However, with stretches of SMP further increase, the τ/τ_0 function

increases with respect to λ_1 . When the parameter χ increases, the solvent-swollen polymer becomes difficult to mix with solvent, resulting in τ/τ_0 function seriously decreased before the stretches are obviously changed. All these results could be accounted by the experimental

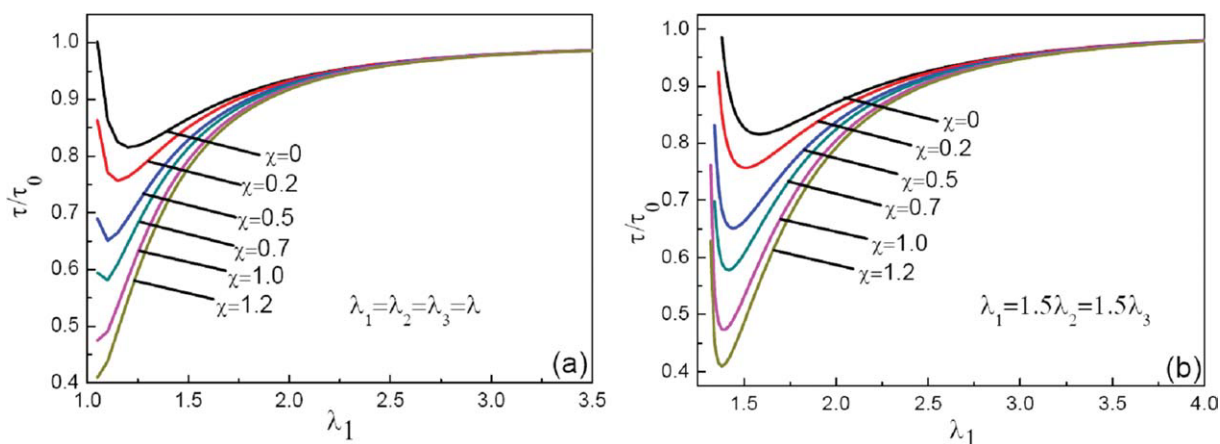


Figure 7 Numerical results for the free and constraint swelling of a SMP immersed in a solvent. (a) Relation of τ/τ_0 function with χ , for a free swelling with $\lambda_1 = \lambda_2 = \lambda_3 = \lambda$. (b) Relation of τ/τ_0 function with χ , for a constraint swelling with $\lambda_1 = 1.5\lambda_2 = 1.5\lambda_3$ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

phenomena,^{12–14} rubber elastic theory,¹⁶ polymer solution theory,¹⁷ and free-energy function.^{20–24}

Subsequently, it is desired to achieve chemo-mechanical shape-memory recovery actuation by

swelling-induced decrease in chemical potential on mixing, instead of increasing sample temperature. On this motivation, demonstration of shape recovery actuation of styrene-based SMP induced by free

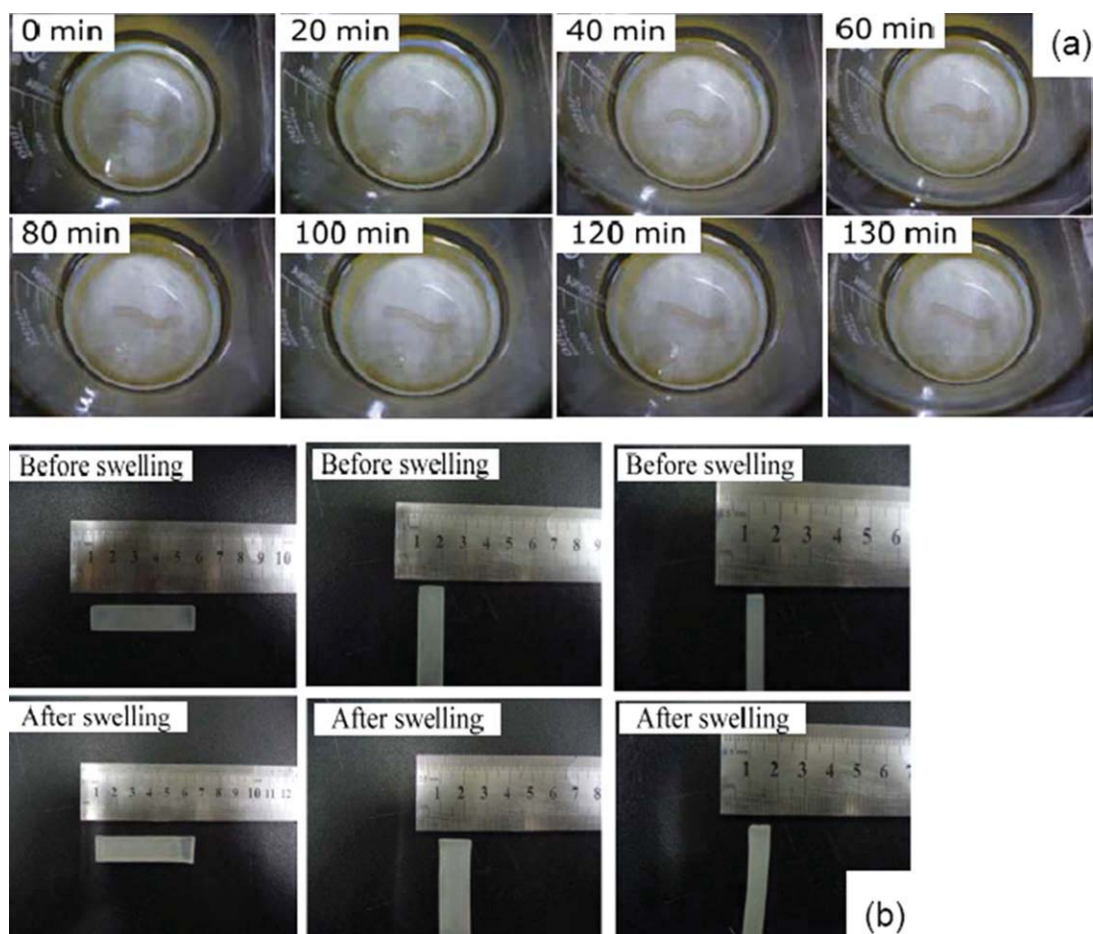


Figure 8 (a) Shape-memory recovery of styrene-based SMP induced by free swelling. (b) Dimensions change of tested sample before and after swollen by solvent [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

swelling was conducted out in toluene solvent. The straight (original shape) SMP sheet sample with dimension of $46 \times 11 \times 5$ mm was bent into a "N"-like shape at 85°C ($T_g + 20^\circ\text{C}$), and then retained this shape during cooling back to the temperature of 45°C ($T_g - 20^\circ\text{C}$). No apparent recovery was found after the deformed sheet was kept in air for more than 6 hours. However, after immersion in toluene at a temperature of 45°C for 40 min, the deformed SMP sample started to return to its original shape. As shown in Figure 8(a), a change in shape from deformed shape to original shape occurred within 40 min. After another 90 min immersion, the tested SMP sample almost regained its straight shape. Additionally, the dimensions of the SMP sample were swollen to $53 \times 13 \times 7$ mm, as shown in Figure 8(b).

As it is known, there is no polar group in toluene solvent molecules having chemical reaction with styrene-based SMP macromolecules. Therefore, only swelling-induced shape recovery actuation could be used to account for these experimental results. It is expected that the toluene solvent molecules diffuse into polymer network, the internal energy of polymer network is indirectly depressed resulting from stretching and mixing behaviors. Finally, the relaxation time of SMP is significantly decreased as expected from eq. (40).

CONCLUDING REMARKS

This article formulates the phenomenon of swelling-induced actuation of SMP by immersing it into a solvent and subject to chemo-mechanical loads. It is shown that the stretching and mixing processes result in the change in chemical potential of polymer, leading to relaxation time decreased. In subsequence, the swelling-induced shape-recovery actuation is inductively achieved when the internal energy of polymer is reduced to a proper level. Using free-energy function, we show that the field in the equilibrated SMP has a critical relationship with stretches, stretch ratio, Flory–Huggins parameter χ , and chemo-mechanical loads. We implement this free-energy function in the Eyring equation. This implementation enables us to use various two- and three-dimensional elements, and analyze diverse phenomena accompanying swelling-induced shape-memory actuation. It is hoped that this approach will help to recognize the mechanism and model the chemo-mechanical behavior of swelling-induced SMP in response to solvent (or solution). The chemo-mechanical model has been developed to simulate the performance and predicts the respon-

sive deformation of SMP. To solve the model consisting of multiple coupled fields, the free-energy function and polymer physics are employed. The model has been examined for its efficiency by comparing with numerically simulated data and experimental phenomena.

This work has been financially supported by "the Fundamental Research Funds for the Central University (Grant No. HIT.NSRIF.201157)".

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