

State Diagram of Phase Transition Temperatures and Solvent-Induced Recovery Behavior of Shape-Memory Polymer

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ABSTRACT: In this study we analyzed the phase and state transitions of shape-memory polymers (SMPs)/solvent mixtures using the Flory–Huggins (FH) theory by extension of Vrentas and the Couchman–Karasz theory for glass transition, as well as Clausius–Clapeyron relation for melting transition. Using scaling relations of model parameters, we have obtained a theoretical prediction of state diagrams of the phase transition temperature and solvent-induced recovery in SMPs. The inductive decrease in transition temperature is identified as the driving force for the solvent-induced shape-memory effect in SMPs. Consequently, the thermodynamics of the polymer solution and the relaxation theory were employed to characterize the dependencies of shape recovery time on the FH parameter and the ratio of the molar volume of solute to solvent. With the estimated model parameters, we constructed the state diagram for SMP, which provides a powerful tool for design and analysis of phase transition temperatures and solvent-induced recovery.

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INTRODUCTION

Thermo-responsive shape-memory polymers (SMPs) have increasingly received considerable attention from the scientific and industrial fields.¹ They are polymeric smart materials that have the ability to return from an imposed shape to their original shape after undergoing a shape deformation.² The basic molecular architecture of SMPs is expressed as polymer network undergoing active movement. Currently, two distinct types of SMPs are most widely studied. The first kind of “one way” SMP features a chemically or physically crosslinked structure that is capable of memorizing its permanent shape. A second type of shape-memory phenomenon for polymers exists, termed “two-way shape-memory,” wherein mechanical activity occurs during both heating and cooling process.^{3,4} Generally, the network structure of SMP contains at least two separate segments. One is hard segment, to remember the permanent shape of the polymer. The switching segment, on the other hand, is the segment with the ability to soften past a certain transition temperature (T_{trans}). To enable the shape-memory feature, another essential factor in a special architecture is consists of net points and/or molecular switches that are sensitive to an external stimulus. Net points can be realized by covalent bonds or intermolecular interactions and play a role in connecting the hard-segment and the soft-segment in a macromolecule chain.

According to the nature of their permanent net points and the thermal transition related to the switching domains,⁵ thermo-responsive SMPs with dual shape capability can be classified into four different categories, i.e., chemically crosslinked amorphous polymers, chemically crosslinked semicrystalline polymers, physically crosslinked thermoplastic with $T_{\text{trans}} = T_g$ and $T_{\text{trans}} = T_m$. Here, T_g and T_m are the glass transition temperature and melting transition temperature of SMP, respectively.⁶ SMPs have plenty of advantages over their well-investigated metallic counterpart, shape-memory alloys (SMAs).⁷ The inherent advantages of SMPs exist in their maximum strain (up to 400%, in contrast to only about 8% by SMAs),⁶ low density, ease of processability, low cost, adjustable transition temperature, and potential biocompatibility, and biodegradability.⁸ Atop of these, perhaps the most notable feature of SMPs is their wide variety of actuation stimulus. In addition to direct temperature heating, depending on the material used, possible stimuli may include light,⁹ electricity,^{10,11} or an alternating magnetic field.^{12,13}

Recently, we have identified a new approach to trigger the shape-memory effect (SME) of styrene-based SMPs by interacting solvents based on the outcomes of water-driven polyurethane SMPs.¹⁴ Chemical plasticizing effect and physical swelling effect have been identified to quantitatively separate the

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solvent-induced SMPs.^{15–20} Consequently, many works have been conducted to construct the theoretical relationship between polymer and solvent molecules.^{19,20} There we have shown that it is very instructive to represent the solvent-induced SME within the state diagram. The state diagram is a very useful, semi-quantitative map depicting the different physical states of a SMP as functions of temperature and solvent content. The state diagram is an extension of the phase diagram often used in physics, only now supplemented with metastable states like the glassy state or rubbery state. The different regions in the diagram are separated by (phase) transition lines. Often, phase transitions are used to create or stabilize new phases. Therefore, the recovery behaviors of SMP materials can be conveniently be depicted by processing paths through the state diagram.

A good first step in the direction of quantitatively understanding the physics of recovery behavior is the prediction of (phase) transition lines in the state diagram. In this article we will pursue that for SMP/solvent mixtures. This is a reasonable model for many types of systems, including amorphous, crystalline, semi-crystalline, and other liquid crystalline SMPs. Subsequently, we employed the relaxation theory and the FH theory of polymer solution to analyze the dependencies of recovery behavior on the FH interaction parameter and the ratio of the molar volume of solute to solvent. With the estimated model parameters we can predict the shape recovery for SMPs, which can be used as a quantitative tool for design and analysis of phase transition temperatures and solvent-induced recovery behavior of SMPs.

EXPERIMENTAL

The styrene-based shape-memory resin (Veriflex®S, VF62) purchased from Cornerstone Research Group (CRG), Dayton, OH, with a density of 0.92 g/cm³ was used as the matrix. The resin matrix was polymerized with dibenzoyl peroxide (as a paste) at a fixed proportion of 24 : 1 (in weight). The cured Veriflex VF62 polymer was engineered with a glass transition temperature (T_g) of 62°C. When heated above its T_g , it changes from a rigid plastic state to an elastic rubber state, and thus it can be twisted, compressed, bent, and/or stretched easily. *N,N*-Dimethylformamide (DMF) solvent (purchased from Tianjin Benchmark Chemical Reagent, Tianjin, China) was used as the interactive solvent. Before the SMP specimens were immersed in solvents for immersion tests, they were dried in a vacuum oven at 120°C for 2 h to remove the remaining moisture coated on the surface of the samples.

Demonstration and Repeatability of Solvent-Induced SME

Figure 1 shows the shape change of a piece of styrene-based SMP upon immersion into DMF solvent. The flat (permanent shape) specimen with the dimensions of 68 × 10 × 3.5 mm³ was bent into a “Z”-like shape (temporary shape) at 85°C ($T_g + 20^\circ\text{C}$), and kept this shape during its cooling back to 45°C ($T_g - 20^\circ\text{C}$). No apparent recovery was observed even after the deformed SMP sheet was left in air for 6 h. After which, the recovery demonstration of the SMP sample was performed in 45°C DMF solvent and recorded with a camera. The recovery was small in the first 40 min, but became more significant afterward. The shape recovery speed in the timeframe from 100 to

120 min was relatively faster than that in other time ranges. Approximately 95% recovery was achieved after 140 min of immersion, i.e., the SMP could not fully regain its original flat shape. This recovery loss resulted from the plasticizing effect between solvent and polymer molecules, causing a reduction in the stored strain energy in polymer. Furthermore, it must be noted that the rate of shape recovery strongly depended on the ambient temperature and solvent characteristics based on the theory of polymer solution when the dimensions and chemical structure of the tested SMP were fixed.

As known, a DMF solvent molecule contains covalent bonding of C=O, which reacts with the C=O group in styrene-based SMPs through conjugation reaction or electrostatic interaction.¹⁸ Conjugation reaction is an interaction that functions in covalent bonding with other chemical groups attached by covalent bonds. This chemical interaction results in the electron distribution being shifted in a covalent bonding, or even broken up completely. An electrostatic interaction is the electrostatic force between two charged bodies. We can judge the repeatability of SME by the interaction approach occurring between the polymer and the solvent. If the interaction is reversible, the recovery of the SMP can be repeated. For example, the water-driven recovery of polyurethane SMP is repeatable, because the water molecules absorbed into the polyurethane SMP can be completely removed at a certain temperature.¹⁴ The polymer will also repeatedly recover after the polymer is subjected to the water/moisture again. However, for the styrene-based SMP, there are two approaches to drive the recovery by the plasticizing effect, namely chemical polar interaction and the physical swelling effect. We found that the recovery driven by the former approach can be partially repeated. The recovery driven by the latter effect can not be repeated, due to there being a volume change along with the shape recovery. Even if, the solvent molecules in a swollen polymer could be completely removed, the volume of the swollen polymer cannot recover to its original state.

The shape recovery of styrene-based SMP is driven by the DMF solvent through chemical polar interaction. We attempted to remove the solvent molecules from the polymer system by a “heat and replace” interaction (another solvent that could dissolve the initial solvent in the polymer/solvent system). Till now, we have not found a proper manner to realize the repeatable recovery of styrene-based SMPs driven by the DMF solvent. The solvent molecules need to be completely removed from the system, while at the same time, leaving the chemical and physical properties of SMP unaltered. Similarly to the water/moisture driven polyurethane SMP, the solvent-driven recovery behavior of styrene-based SMPs is also repeatable even if it is repeatedly subject to its plasticizers.

Influence of Immersion Time on the Transition Temperature

SMP specimens measuring 10–15 mg in weight were prepared for a differential scanning calorimeter (DSC 2920, TA Instruments) test. All experiments were performed with a constant heating and cooling rate of 20°C/min, in a nitrogen atmosphere at a flow rate of 40 mL/min. The samples were measured in the temperature range from –20 to 120°C. Each sample was heated to 120°C, then cooled down to –20°C, and again warmed up

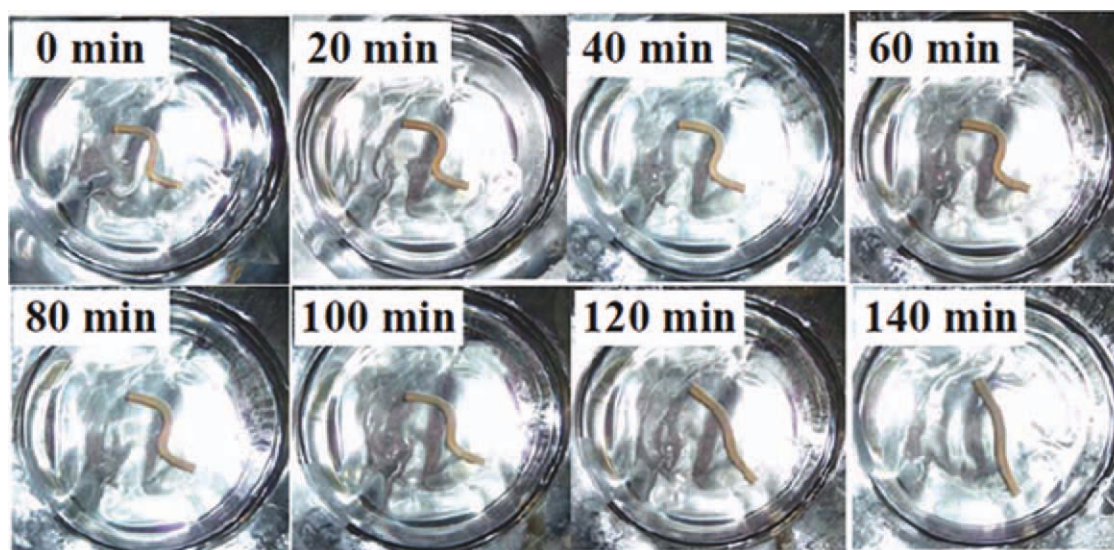


Figure 1. Shape recovery of polystyrene SMP sheet sample with dimensions of $68 \times 10 \times 3.5 \text{ mm}^3$ in DMF solvent. (Reproduced from Ref 15, with permission from Wiley). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to 120°C . Whenever a maximum or minimum temperature was reached in the testing program, this temperature was kept constant for 2 min. Each group of samples with the same immersion time was repeatedly tested three times. The T_g was determined from the second heating cycle. The T_g defined in such a way was 70.2 , 68.0 , 60.0 , 58.9 , and 56.3°C , respectively, as shown in Figure 2. This experimental result reveals that the T_g decreases significantly with an increase in immersion time.¹⁵

Another method to determine the effect of solvent molecule on the transition temperature of SMP was performed using dynamic mechanical analysis (DMA, DMA Q800, TA Instruments). All experiments were conducted in the three-point bending mode at a constant frequency of 1.0 Hz and a heating rate of $5^\circ\text{C}/\text{min}$, as well as temperature interval from 25 to 120°C . Tangent delta is defined as the ratio of the loss modulus over the storage modulus, and the temperature corresponding to the peaks of these tangent delta curves gives an alternative T_g . The T_g determined by DMA were 84.29 , 74.04 , 65.30 , 60.72 , and 55.05°C for the SMP samples with immersion times of 0 , 10 , 30 , 60 , and 120 min , respectively, as shown in Figure 3. It reveals that the tangent delta curves reach their maximum at lower temperature with the immersion time increase.¹⁵

PREDICTION OF THE STATE DIAGRAM BY THE FH THEORY

FH Theory for T_g

FH solution theory is a mathematical model of the thermodynamics of polymer solutions, which takes account of the great dissimilarity in molecular sizes in adapting the usual expression for the entropy of mixing. Generally, the FH theory is capable of predicting the thermodynamics of polymer solutions, polymer blends, and mixed solvents. In this study, the FH theory is introduced to investigate the thermodynamic behavior of polymer solutions. Furthermore, we analyze the phase and state transitions of polymer solution using the free volume extension of the FH theory by Vrentas theory, combined with the Couch-

man-Karasz theory for glass transition. In general, FH theory holds only above the T_g of the polymer. For temperatures below the glass transition, FH theory has been extended by Vrentas theory²¹ using free-volume theory. This FH free-volume theory has reasonable success in predicting the behavior of synthetic polymer systems and some biopolymer systems-like dextrin and keratin solutions.^{22,23}

In previous works, the free-energy function has been introduced to qualitatively separate the solvent-induced recovery of SMPs. When a polymer is subject to a solvent, there are four contributions to the free-energy function (W), i.e., stretching free-energy (W_s), mixing free-energy (W_m), and polarizing free-energy (W_p).²⁴

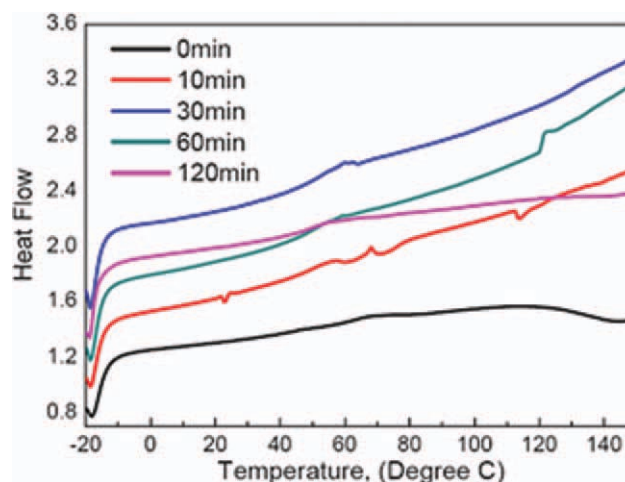


Figure 2. DSC results of SMP specimens with different absorbed DMF content. The glass transition temperature is 70.2 , 68.0 , 60 , 58.9 , and 56.3°C for the specimen with immersion time of 0 , 10 , 30 , 60 , and 120 min , respectively. (Reproduced from Ref 15, with permission from Wiley). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

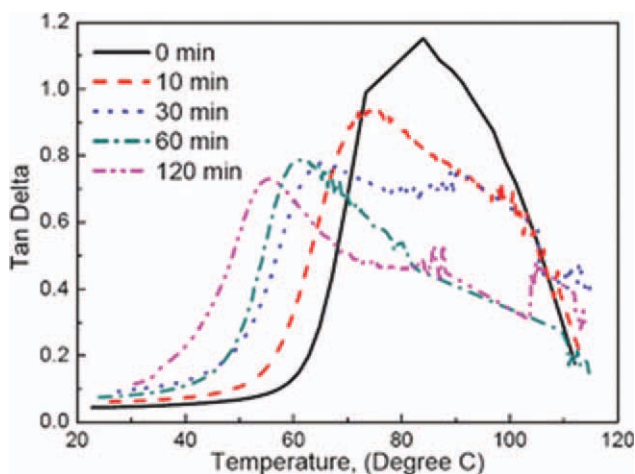


Figure 3. Loss tangent of SMP specimens with different absorbed DMF content versus temperature. The glass transition temperature is 84.29, 74.04, 65.30, 60.72 and 55.05°C for the specimen with immersion time of 0, 10, 30, 60, and 120 min, respectively. (Copyright reserved from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$W = W_s + W_m + W_p \quad (1)$$

The stretching free-energy and mixing free-energy of a network of a cubic polymer are taken to be,²⁵

$$\begin{cases} W_s(\lambda_1, \lambda_2, \lambda_3) = \frac{1}{2}NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - 2 \log \lambda_1 \lambda_2 \lambda_3) \\ W_m(C) = -\frac{kT}{v} \left[vC \log \left(1 + \frac{1}{vC} \right) + \frac{\chi}{1+vC} \right] \end{cases} \quad (2)$$

where C is the nominal concentration of the solvent molecules in polymer network and v is the volume per solvent molecule. For the free-energy of polarization, it is assumed that the polymer has a dielectric energy with a constant permittivity ϵ ,²⁶

$$W_p = \frac{1}{2} \epsilon E^2 \quad (3)$$

The permittivity of the polymer solution in general is a function with respect to permittivity ϵ and the true electric field is E . Because of the difference in the dielectric properties between the solvent and the polymer molecules, the permittivity of the gel in general is a function of the solvent concentration $\epsilon(C)$. A simple estimate would be the volumetric average among the solvent and the polymer, as follows,

$$\epsilon(C) = \frac{\epsilon_p + vC\epsilon_s}{1 + vC} \quad (4)$$

where ϵ_p and ϵ_s are the permittivity of the polymer and the solvent, respectively. In combination of eqs. (3) and (4), we may get the polarizing free-energy as,

$$W_p = \frac{1}{2} \epsilon(C) E^2 \quad (5)$$

By combining the eqs. (1), (2), and (5), the free-energy function can be rewritten as,

$$W = W_s(\lambda_1, \lambda_2, \lambda_3) + W_m(C) + \frac{1}{2} \epsilon(C) E^2 \quad (6)$$

On the basis of the expression of eq. (6), it can conclude that the thermodynamic behavior of solvent-induced recovery in SMP has a strong relationship with stretches ($\lambda_1, \lambda_2, \lambda_3$) of polymer network and the nominal concentration of the solvent (C) in the mixture.

For the prediction of the glass transition of polymer-solvent mixtures, we first list the different phases of solvent and polymer that can coexist. A solvent can be in the liquid state. A polymer can be in either a rubbery or a glassy state. The solvent absorbed by the glassy polymer may be in the glassy state too. From the thermodynamic point of view, the glass transition cannot be defined as a phase transition, but must be viewed as an immobilized liquid or rubbery state, and can be generalized as the amorphous state. For the freezing or boiling phase transition, the polymer needs to be in the rubbery state for the required mobility of the solvent phase (or in the liquid state). The polymer solution is a metastable state with the polymer molecules coexisting in both glassy and rubbery phases. The liquid state of a solvent will be indicated with W . The glassy and rubbery states of the polymer will be indicated with X and S , respectively. The different phases of the polymer will be used as an index for the chemo-potential. Fully gelatinized polymer, in the rubbery state is indicated as W/S , meaning “solvent dispersed in polymer.” Together with the thermodynamic condition for the coexisting phases, the possible phase transition of the polymer solution can be expressed by a mathematical relationship of (W/S) to ($W/S + W$), where the chemo-potential of the solvent is assumed to be “0” ($\mu_w \approx 0$). The chemo-potentials of rubbery polymer and liquid solvent, μ_s and μ_{ws} respectively, follow from the FH theory. Furthermore, FH theory allows polymer solutions in the rubbery state to phase-separate into a solvent rich and a polymer rich phase (e.g., via spinodal decomposition). Whether this occurs for polymer/solvent mixtures is not known. But if this occurred, the thermodynamic condition for the phase transition is that $\mu_w \approx 0$, which is a valid approximation for polymers with long chain lengths. The FH theory states that,²⁵

$$\begin{aligned} \frac{\mu_w}{RT} &= \ln(1 - \phi) + \left(1 - \frac{1}{N} \right) \phi + \chi \phi^2 \\ \frac{\mu_s}{RT} &= N \left[\ln \left(\frac{\phi}{N} \right) - \left(1 - \frac{1}{N} \right) (1 - \phi) + \chi (1 - \phi)^2 \right] \\ &= (1 - \phi)(1 - N) + \ln \phi + \chi N (1 - \phi)^2 \end{aligned} \quad (7)$$

where ϕ is the volume fraction of a polymer in a polymer solution, χ is the FH interaction parameter, R is gas constant, T is the absolute temperature, and $N = v_s/v_w$ is the ratio of the molar volume of polymer and solvent, v_s and v_{ws} respectively.

The glassy phase of a polymer is thought not to absorb a solvent. However, in a polymer, the glassy phase does contain solvent molecules, which do not contribute to the chemo-potential of liquid solvent μ_w . Hence, the polymer volume fraction ϕ represents only the fraction of polymer in the rubbery state, and is equal to,

$$\phi = \frac{(1 - \zeta)y_S/\rho_S}{(y_W - y_{W,X})/\rho_W + (1 - \zeta)y_S/\rho_S} \quad (8)$$

where ζ is the volumetric ratio between glassy polymer and rubbery polymer, y_W and $y_S = 1 - y_W$ are the mass fractions of the solvent and polymer, respectively, ρ_W and ρ_S are the mass densities of the solvent and polymer, respectively, and

$$y_{W,X} = \frac{1}{m} \cdot \frac{M_W}{M_U} \zeta y_S \quad (9)$$

where $y_{W,X}$ is the amount of the imbibed solvent. M_W and M_U are the molar weights of the solvent and polymer, respectively. The factor $1/m$ is due to the molar volume ratio of the imbibed solvent molecules to the polymer molecules in one lattice unit cell.

To obtain a good estimate of the FH interaction parameter, and represent the state diagram as an a_W vs. T diagram, we will investigate the solvent molecules sorption over the whole range of the volume fraction, $0 \leq \phi \leq 1$, and analyze the sorption isotherms with the FH free-volume theory. The solvent activity following this theory is²⁷:

$$\frac{\ln a_W}{RT} = \frac{\mu_W}{RT} = \ln(1 - \phi) + \left(1 - \frac{1}{N}\right)\phi + \chi\phi^2 + F(\phi) \quad (10)$$

With the free-volume term being equal to

$$F(\phi) = \begin{cases} 0 & \text{if } T \geq T_g \\ M_W y_W^2 \frac{\Delta C_{p,W}}{RT} \frac{dT_g}{dy_S} \frac{T - T_g}{T_g} & \text{if } T < T_g \end{cases} \quad (11)$$

Here, $\Delta C_{p,W}$ is the change in the specific heat capacity at the glass transition of the polymer, which is used in the Couchman–Karasz theory presented below. T_g is the solvent content-dependent parameter of the polymer solution, which can be obtained via the theory of Couchman and Karasz²⁸:

$$T_g = \frac{y_W \Delta C_{p,W} T_{g,W} + y_S \Delta C_{p,S} T_{g,S}}{y_W \Delta C_{p,W} + y_S \Delta C_{p,S}} \quad (12)$$

where $T_{g,W}$ and $T_{g,S}$ are the glass temperatures of solvent and dry polymer, and $\Delta C_{p,W}$ and $\Delta C_{p,S}$ are the difference in specific heat of solvent or polymer across the glass transition. For the solvent-induced SME, the temperature range of $T \geq T_g$ will be more significant. Therefore, the parameter of $F(\phi)$ is always going to be considered “0.” Then, the eq. (10) can be rewritten as,

$$\frac{\ln a_W}{RT} = \frac{\mu_W}{RT} = \ln(1 - \phi) + \left(1 - \frac{1}{N}\right)\phi + \chi\phi^2 \quad (13)$$

Using Couchman–Karasz theory, we can compute the derivative in the free-volume term of the FH free-volume theory²⁹:

$$\frac{dT_g}{dy_S} = - \frac{\Delta C_{p,S} \Delta C_{p,W} (T_{g,W} - T_{g,S})}{(y_S \Delta C_{p,S} + y_W \Delta C_{p,W})^2} \quad (14)$$

Equation (14) gives the equilibrium of the dT_g/dy_S function for the polymer/solvent mixture being transferred from a glassy to a rubbery transition. The right-hand side of the equation corresponds to the $\Delta C_{p,S}$, $\Delta C_{p,W}$, $T_{g,W}$, $T_{g,S}$, y_S , and y_W parameters. Here, the relation between the specific heat of polymer and solvent across the glass transition is assumed to be constant, $\Delta C_{p,S}/\Delta C_{p,W} = n$. In addition, the mass fraction of solvent is $y_W = 1 - y_S$. At this time, the left-hand side of the dT_g/dy_S parameter can be simplified as,

$$\frac{dT_g}{dy_S} = - \frac{n(T_{g,W} - T_{g,S})}{[(n - 1)y_S + 1]^2} \quad (15)$$

Now, the left-hand side parameters dT_g and dy_S correspond to the n , $(T_{g,W} - T_{g,S})$, and y_S parameters. We can then calculate the relationships among $(T_{g,W} - T_{g,S})$, n , and y_S , as follows,

$$(T_{g,S} - T_{g,W}) = \exp\left(\frac{n}{n - 1} \cdot \frac{1}{(n - 1)(1 - y_W) + 1}\right) + C, \quad (0 \leq y_W \leq 1) \quad (16)$$

where C is a constant. The characteristics of $(T_{g,W} - T_{g,S})$, using the n and y_S as parameters is plotted in Figure 4. Figure 4(a) plots the relation between the $(T_{g,S} - T_{g,W})$ function and mass fraction of polymer, y_S . For a given parameter, saying $n = 2$, $n = 3$, $n = 5$, or $n = 10$, the $(T_{g,S} - T_{g,W})$ function gradually decreases as the mass fraction of the polymer y_S increases. On the other hand, the $T_{g,S}$ of the polymer is gradually decreased as the mass fraction of the polymer y_S increases in the polymer solution. This numerical pattern reveals that the $T_{g,S}$ of a polymer does gradually decrease during the process of mixing polymer and solvent. Figure 4(b) plots the relation between the $(T_{g,W} - T_{g,S})$ function and the specific heat of polymer to solvent, n . For a given parameter, say $y_S = 0.0$, $y_S = 0.2$, $y_S = 0.4$, or $y_S = 1.0$, the $(T_{g,W} - T_{g,S})$ function gradually decreases as the specific heat of polymer to solvent n increases. On the other hand, the $T_{g,S}$ gradually increases as the specific heat of polymer to solvent n increases. This trend reveals that as the mass fraction of polymer y_S becomes larger, the $T_{g,S}$ decreases more rapidly at the same volumetric ratio of polymer to solvent. Also, the T_g between polymer and solvent becomes larger as the specific heat of polymer to solvent n increases.

The aforementioned FH theory and their numerical reveals have proven that the imbibed solvent molecules decrease the T_g .

FH Theory for Melting Transition Temperature

The chemo-potential of a crystalline polymer is given by the Clausius–Clapeyron relation,²⁹ which states,

$$\frac{\mu_X}{RT} = \frac{\Delta H_X}{R} \left(\frac{1}{T_{m,0}} - \frac{1}{T} \right) \quad (17)$$

where $T_{m,0}$ is the melting point of the polymer, and ΔH_X is the molar enthalpy of the melting of polymer. As for polymer the molar weight is not exactly known. It is more convenient to express the chemo-potential μ_U of the rubbery polymer phase per mole of the monomeric unit. The chemo-potential of the rubbery polymer becomes,

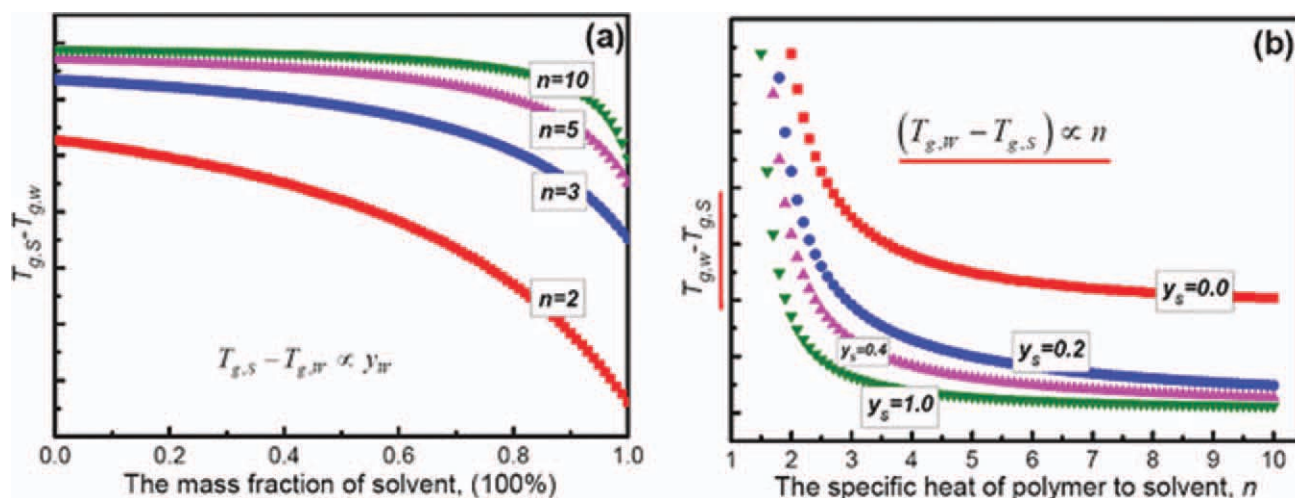


Figure 4. Dependences of glass transition temperature of polymer on (a) the mass fraction of solvent and (b) the specific heat of polymer to solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\frac{\mu_U}{RT} = \frac{v_U}{v_W} \frac{\mu_S}{NRT} = -\frac{v_X}{v_W} \left[(1 - \phi) - \chi(1 - \phi)^2 \right] \quad (18)$$

where $v_X/v_W = N$ is the ratio of molar volumes of the polymer repeating unit and solvent molecule. Combining eqs. (17) and (18) yields the following expression for the relation between T_m and solvent content,

$$\left[\frac{1}{T_m} - \frac{1}{T_{m,0}} \right] = \frac{R}{\Delta H_U} \frac{v_U}{v_W} \left[(1 - \phi) - \chi(\phi)(1 - \phi)^2 \right] \quad (19)$$

Here ϕ is the volume fraction of the polymer in the rubbery phase, and is computed using eq. (8). The FH interaction parameter χ is related to the parameter ϕ . To better correspond to the melting point in this study, the FH interaction parameter χ is assumed to be independent of ϕ . Equation (19) can be therefore written as,

$$\left[\frac{1}{T_m} - \frac{1}{T_{m,0}} \right] = \frac{R}{\Delta H_U} \frac{v_U}{v_W} \left[(1 - \phi) - \chi(1 - \phi)^2 \right] \quad (20)$$

Because the $R/\Delta H_U$ and v_U/v_W are constants, the polymer and the solvent are confirmed. The characteristics of $\left[\frac{1}{T_m} - \frac{1}{T_{m,0}} \right]$, using the FH interaction parameter χ and the volume fraction of the polymer in the rubbery phase ϕ are plotted in Figure 5. Figure 5(a) plots the relation between the $\left[\frac{1}{T_m} - \frac{1}{T_{m,0}} \right]$ function and the volume fraction of the polymer ϕ . For a given parameter, $\chi = 0.0$, $\chi = 0.2$, $\chi = 0.4$, $\chi = 0.6$, or $\chi = 0.8$, the $\left[\frac{1}{T_m} - \frac{1}{T_{m,0}} \right]$ function decreases as the volume fraction of the polymer ϕ increases. On the other hand, the T_m gradually decreased as the volume fraction of the polymer ϕ decreased in the polymer/solvent mixture. This pattern reveals that the T_m of polymer decreases as the volume fraction of the solvent $(1 - \phi)$ increased in the process of mixing polymer and solvent. Figure 5(b) plots the relation between the $\left[\frac{1}{T_m} - \frac{1}{T_{m,0}} \right]$ function and the FH interaction parameter χ . For a given parameter, $\phi = 0.0$, ϕ

$= 0.2$, $\phi = 0.4$, $\phi = 0.6$, or $\phi = 0.8$, the $\left[\frac{1}{T_m} - \frac{1}{T_{m,0}} \right]$ function gradually decreased as the FH interaction parameter χ increased. On the other hand, the T_m is gradually decreased as the FH interaction parameter χ decreased. This numerical result reveals that as the FH interaction parameter χ gets smaller, the T_m of the polymer decreases more significant at the same volume fraction of the polymer ϕ or volume fraction of the solvent $(1 - \phi)$.

On the basis of the aforementioned numerical results, it is found that the transition temperature of the polymer will be decreased by mixing the solvent. Therefore, we can demonstrate that the SME of thermo-responsive SMPs can be inductively induced by the solvents from the FH theory, through lowering T_g or T_m indirectly furthermore lower the switching temperature of the SMPs.

PREDICTION OF THE SOLVENT-INDUCED RECOVERY BEHAVIOR OF SMP

When a polymer is subject to an interactive solvent, there is a change in enthalpy in the mixing process, which results in equilibrium for the change in free-energy (ΔF_m) for a polymer. As the solvent system is considered to approach infinity, the change in free-energy of the solvent is assumed to be zero. Therefore, the mixing free-energy change of solution system (ΔH_m) is equal to the mixing free-energy of the polymer (ΔF_m). It is assumed that there is no change in volume of the polymer. Here, the decrease in internal energy of the polymer is equal to the change in chemo-potential. As it is known, the change in free-energy is always negative if the mixing process occurs. Therefore, the mixing chemo-potential is always lower than zero.

$$\Delta H_m = \Delta F_m = RT[\kappa_S \ln(1 - \phi) + \kappa_W \ln \phi + \kappa_S \chi \phi] \quad (21)$$

where κ_S and κ_W are the number of moles of solvent and polymer, respectively. ϕ is the volume fraction of polymer (the volume fraction of solvent is $1 - \phi$), and χ is the FH interaction parameter (also meaning the difference in energy of polymer macromolecule and solvent molecule).

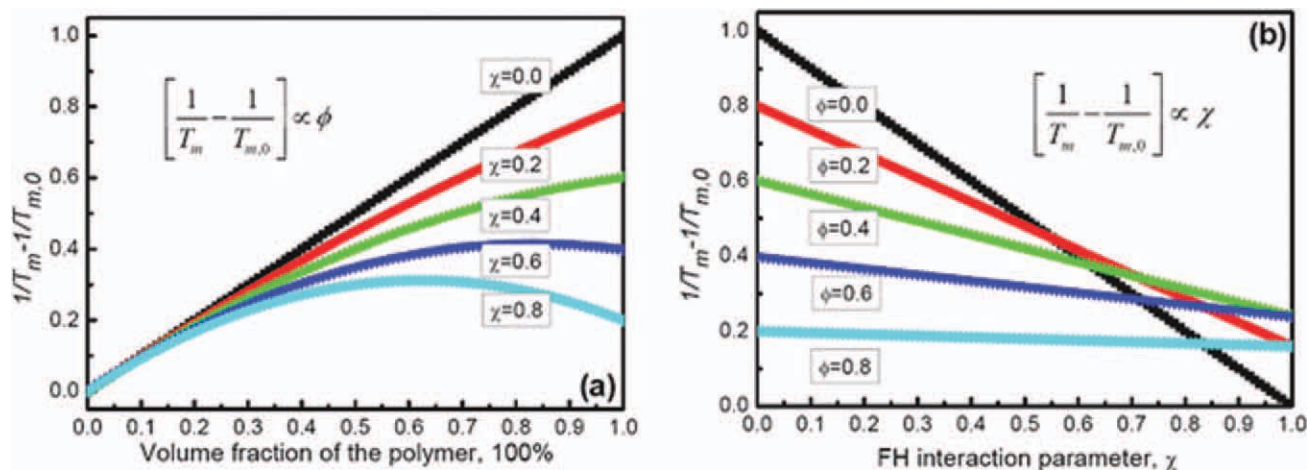


Figure 5. Dependences of melting transition temperature of polymer on (a) the volume fraction of the polymer and (b) the FH interaction parameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

On the basis of the aforementioned statements, the change in chemo-potential of per mole polymer molecule being subjected to solvent can be written as,³⁰

$$\Delta\mu_W = \left[\frac{\partial(\Delta H_m)}{\partial\kappa_W} \right]_{T,P,\kappa_S} = RT \left[\ln \phi + \left(1 - \frac{1}{N}\right)(1 - \phi) + \chi(1 - \phi)^2 \right] \quad (22)$$

where $N = v_x/v_W$ is the ratio of molar volumes of the polymer repeating unit and solvent molecule. Before discussing the effect of mixing chemo-potential on the recovery time of SMPs, the relaxation theory and Eyring equation should be addressed at first. The recovery behavior of temperature-responsive SMP agrees with the relaxation theory, and the relationship between relaxation time and internal energy can be expressed by the Eyring equation as,^{20,21}

$$\tau = \tau_0 \exp(\Delta E/RT) \quad (23)$$

where τ is the relaxation time (analog to shape recovery time), ΔE is the internal 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. (23), it is found that the relaxation time can be shortened by either reducing internal energy or increasing sample temperature. Thus, in this study, the effect of mixing chemo-potential on the recovery time maybe attributed to the former.

With the above analyses, it is found that the change in internal energy plays a critical role in influencing the relaxation time. The effect of mixing chemo-potential on the decrease in internal energy of the polymer molecules should be figured out in order to describe the relation between mixing chemo-potential and relaxation time. There are two essential suppositions that must be presented. First, there is no change in temperature when the mixing process occurs between polymer and solvent. Secondly, the volume of solvent is temporarily regarded as infinite. These two suppositions result in the temperature being kept as a constant, and the mixing chemo-potential being equal to the decrease in internal energy of the SMP. So, eq. (23) can be presented as

$$\tau = \tau_0 \exp\left(\frac{\Delta E + \Delta\mu_W}{RT}\right) \quad (24)$$

In combination of eqs. (13) and (24), it can relate the relaxation time with the decrease in chemo-potential as follows,

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{RT}\right) \exp\left(\frac{\Delta\mu_W}{RT}\right) = \tau_0 \exp\left(\frac{\Delta E}{RT}\right) \times \exp\left[\ln \phi + \left(1 - \frac{1}{N}\right)(1 - \phi) + \chi(1 - \phi)^2\right] \quad (25)$$

Equation (25) implies that the relaxation time is related by the volume fraction of polymer ϕ , FH interaction parameter χ , and the ratio of the molar volume of solute and solvent N . Therefore, the effect of the χ and N on recovery behavior will be studied in the following sections.

Dependence of Relaxation Time on FH Interaction Parameter

FH solution theory is a mathematical model for the thermodynamics of polymer solutions and takes into account the great dissimilarity in molecular size in adapting the usual expression for mixing entropy. The Hildebrand solubility parameter provides a numerical estimation of the degree of interaction, and can be a good indication of solubility, particularly for polymer materials. Polymers with similar values of solubility parameters will be able to interact with each other, resulting in salvation, miscibility, or swelling. The FH interaction parameter relates to the difference of solubility parameters with mixing entropy, and is a measurement of interactions between polymer and solvent.

Figure 6 qualitatively shows the effect of the FH parameter on the relaxation time. With a fixed value of the volume ratio between polymer molecule and solvent molecule [also named volume dissimilarity, $N = 2$ in Figure 6(a) and $N = 10$ in Figure 6(b), respectively], the relaxation time is gradually decreased as the volume fraction of the SMP molecule decreases in the solution system. From these curves, it is found that with a decrease in the volume fraction of SMP molecule, the mixing chemo-potential initially increased, and subsequently decreased. Alternatively, with the FH interaction parameter becoming

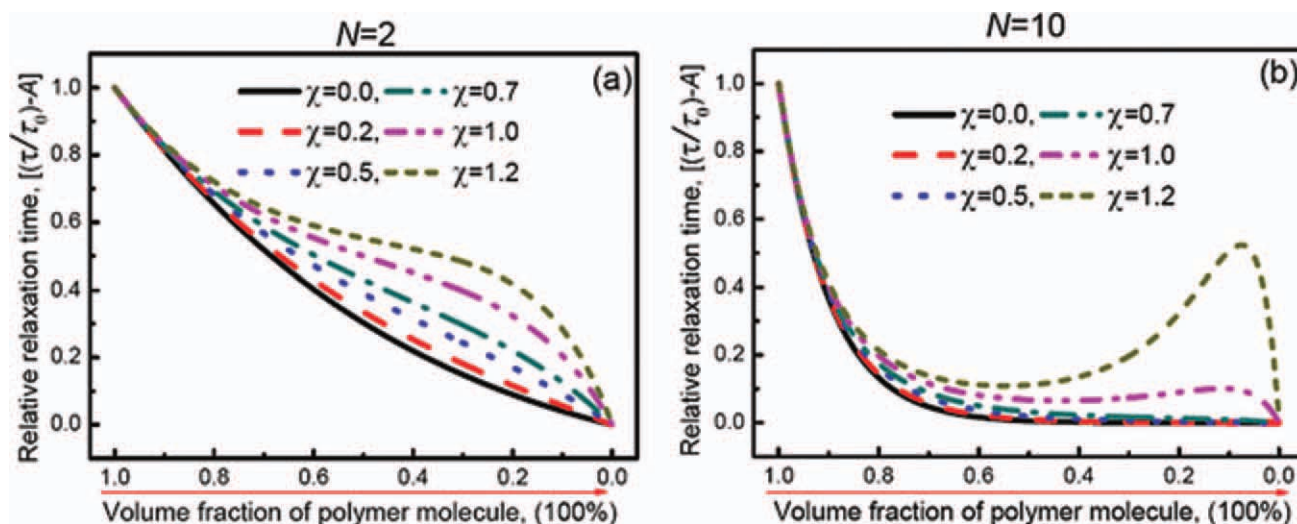


Figure 6. Solvent responsive shape recovery time of polymer as a function of FH interaction parameter with the ratio of the molar volume of solute and solvent: (a) $N=2$, and (b) $N=10$, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

large, the mixing entropy and chemo-potential will be increased. An increase in mixing chemo-potential results in an increase in the energy released from the polymer. Therefore, the internal energy of the SMP is subsequently decreased and the transition temperature is indirectly lowered. There is an essential point for the SME in SMPs that is addressed here to provide further clarification of this mechanism. At an elevated temperature for SMP materials, deformation caused by applied load can be fixed during cooling back to room temperature. Here, the work performed on the SMP material can be stored as latent strain energy as the recovery of the polymer molecules is prohibited by vitrification, crystallization, or other means. When the internal energy is lowered to a critical level, the stored strain energy in the molecules is subsequently released. This finding visually describes the shape recovery behavior of SMP driven by inductively reducing T_g through the plasticizing effect. Furthermore, these expressions theoretically depict the recovery behavior of

solvent-induced SMPs. We can utilize this chemo-responsive ability to widen the potential applications of SMPs.

Dependence of Relaxation Time on Volume Ratio of Polymer to Solvent Molecule

As stated in polymer solution theory and relaxation theory, the internal energy and the relaxation time is either determined by the FH interaction parameter, or by the volume dissimilarity between the SMP and solvent molecule. It is derived from the relationship between the entropy change and the volume dissimilarity. For a real synthetic polymer, there is a statistical distribution of chain lengths, so N would be an average. It is assumed that individual polymer molecule and individual solvent molecule occupy sites on a lattice. Each site is occupied by exactly one molecule of the solvent or by one monomer of the polymer chain. As the volume dissimilarity of N decrease, the probability of a given lattice site occupied by polymer molecules

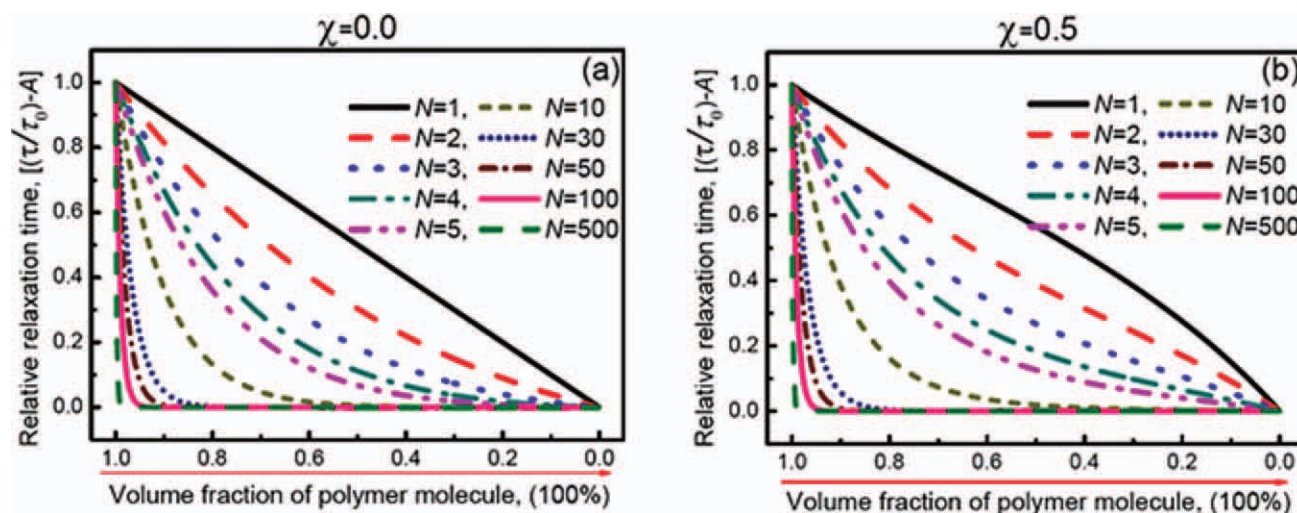


Figure 7. Solvent responsive shape recovery time of polymer as a function of the ratio of the molar volume of solute and solvent with the FH interaction parameter: (a) $\chi = 0.0$, and (b) $\chi = 0.5$, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreases. In return, the probability of a given lattice site being occupied by solvent molecules is increased. The volume fraction of solvent molecules in the mixture system that is incorporated of lattice sites would be high. As shown in Figure 7, the loss in internal energy is gradually increased with a decrease in volume fraction of polymer molecules. The relaxation time will be therefore shortened. As shown in Figure 7(a,b), the relative relaxation time significantly decreases as volume dissimilarity N increases, at the same volume fraction of polymer molecule in the polymer–solvent system over the entire range. It could be summarized that, when the volume ratio between polymers to solvent molecule is increased, the mixing entropy change is more difficult to reduce in the mixing process. Additionally, for a given SMP having the same average value of N , the relaxation time is also gradually reduced with a decrease in volume fraction of the polymer molecule. Also, it should be noted that it is necessary to account for the energy of these very favorable contacts when inserting a solvent molecule between them in the first step of mixing, for the systems characterized by strong interactions between two monomeric units via hydrogen bonds.^{31,32} In this case, the integral interaction parameter and FH interaction parameter should be amended.³³ The other parameters are consistent with that of polymer–solvent systems.

CONCLUSIONS

To conclude, this study has shown that both transition temperature and recovery behavior of the SMP/solvent mixture can be described very well by using the FH theory, complemented with the Vrentas, Couchman–Karasz theory, Clausius–Clapeyron relation, and relaxation theory. SME of thermo-responsive SMPs is affected not only by increasing the temperature, but also by the inductively lowering the transition temperature of the polymer. For the amorphous SMP, state transition from glassy to rubbery is solved by integrating the FH theory with Couchman–Karasz theory. The melting transition, or by extension, phase transition is solved by integrating the FH theory with Clausius–Clapeyron relation for the crystalline SMPs. The recovery behavior of the solvent-induced SMP is well predicted by integrating FH theory with relaxation theory, and characterized with the FH interaction parameter, and the ratio of the molar volume of solute to solvent. The predictive power of these theories makes transition temperature diagrams and recovery behavior a more quantitative and useful tool to analyze the solvent-induced SME in thermo-responsive SMPs.

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