



# Programmed shape-dependence of shape memory effect of oriented polystyrene: A molecular dynamics study



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## ABSTRACT

Oriented polystyrene (PS) has attracted attention due to its capability of sequential self-folding behaviors by infrared (IR) light heating. It has been seen that temporal changes of the shape and properties of PS are affected by its pre-defined molecular structure. In this study, full atomistic molecular dynamics (MD) simulations are carried out to study the effect of initially applied strain on the thermoelastic properties and shape recovery behaviors of the oriented PS. The shape memory creation procedure (SMCP) is described by long-time simulation and initial strains between 15% and 100% are applied by in-plane tensile loadings. As the extent of pre-stretching increases, the anisotropy of elastic modulus and linear coefficient of thermal expansion (CTE) increase primarily due to the molecular alignment. The shape fixity ratio increases by up to 24% and the recovery ratio decreases by up to 32% by increasing the initial strain. In particular, the shape recovery ratio is mainly affected by the orientational order parameter of the oriented PS. The rate of the recoveries of the thermomechanical properties and shape reduce for a more pre-stretched PS. The retardation of conformational transformation comes from a reduction in the sizes of free volume elements. The results demonstrate a microstructure-property relationship which is important in designing the self-folding behaviors of oriented PS.

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## 1. Introduction

Stimuli-responsive shape memory polymers (SMPs) are promising smart materials that can change their shape and properties by exposure to light [1–4], temperature [5,6], pH [7], and electric [8,9] and magnetic [10] fields. Compared with other shape memory materials, SMPs have attractive features such as a wide elastic range, high recovery strain, enhanced processibility, light weight, and low cost. These smart polymers are used for self-deploying structures [11], sensors [12], self-healing [13,14], and smart fabrics [15]. Among them, thermal-responsive SMPs have been widely investigated and used because of their relatively simple actuation. Thermally-sensitive shape memory behaviors can be realized with certain conditions. The structural key elements for shape memory effect (SME) are net-points and molecular switches [16]. The net-points which can involve physical entanglement and covalent crosslinking fix the permanent shape. Molecular switches such as reversible crystallization and glass transition enable the shape

recoveries. Besides the molecular architecture, a cyclic thermo-mechanical procedure is required that consists of sequential steps [17]. First, the temporary shape is formed at above the transition temperature (glass transition temperature ( $T_g$ ) or melting temperature ( $T_m$ )) by applying an external load. Then, the desired shape is fixed by cooling with constant strain and stress relaxation. Under the stress-free condition, the pre-programmed shape recovers to the original shape by heating to above the transition temperature. These recoveries are induced by the entropy-driven elasticity of the polymer chains.

Pre-oriented polystyrene (PS) is also capable of thermally-induced shape memory behaviors. Many researchers have synthesized styrene-based SMPs incorporated with carbon nanotubes (CNTs), nanofibers (CNFs), and nanocarbon particles [9,18,19]. Recently, these commonly used polymers have attracted attention in the area of smart polymer research due to the capability of self-folding behaviors [20–23]. The soft self-folding structures are attractive because they can be utilized as biomedical containers, robotic actuators, and sequential packaging [20,24,25]. Liu et al. [21] realized the self-folding behaviors of the Shrinky-Dinks®, a commercial toy composed of the pre-oriented PS with black ink

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patterns by infrared (IR) light heating. The self-folding is driven by the localized light absorption on the patterned regions and accompanying in-plane shrinkage. This approach enables 2D patterns to be converted to 3D objects without complex fabrication steps. In order to manufacture more complicated structures, the precise prediction and design of sequential self-folding behaviors are required.

Many researchers have proposed computational approaches to describe the mechanical response of SMP with consideration of the molecular mechanism. Liu et al. [26] investigated a thermo-mechanical constitutive model with the assumption that the polymer is a mixture of frozen and active phases. The model can monitor the evolution of stress during the thermomechanical cycle. Nguyen et al. [27] implemented a thermoviscoelastic model for finite element frameworks with experimentally characterized parameters. Molecular dynamics (MD) simulation is a powerful technique to predict the change of the thermoelastic properties of polymers during thermal transition. Diani et al. [28] used full atomistic MD simulations to study the strain storage and energy evolution during the shape memory behavior of an amorphous polyisoprene model. Ghobadi et al. [29,30] constructed the atomistic modeling schemes of the shape memory creation procedures of poly(L-lactide) and investigated the effect of water uptake on the SME. Abberton et al. [31] elucidated the effects of phase fraction and temperature on the shape recovery of copolymer system with coarse-grained potentials using a two-phase molecular model. Yang et al. [32] investigated the thermomechanical properties and shape memory behaviors of the SMP with varying curing agent contents and Davidson et al. [33] studied the molecular origins of the SME in crosslinked polymers using MD simulation. Choi et al. [34] discussed the filler-size effect on the glass transition and the thermoelastic behaviors of epoxy-based nanocomposites. Ozmaian et al. [35] investigated the variation of static and dynamic properties with the glass transition of hydrated nafion. In the case of polystyrene, some experimental and computational studies on the shape memory behavior and design of the sequential self-folding have been conducted. Chivers et al. [36] found that the shape memory and stress relaxation behaviors of mono-dispersed PS are affected by the strain rate of uniaxial deformation. Zhang et al. [37] revealed the relation between the crosslinking agent contents and shape memory effect of PS by experimental analysis. Mailen et al. [38] proposed a nonlinear finite element model predicting the self-folding behaviors of pre-strained PS. Several MD simulations of the uniaxial deformation and strain-hardening mechanisms of PS have also been reported [39,40]. However, few studies have been carried out that deal with the relationship between the molecular state and the macroscopic changes of oriented PS during shape recovery behavior.

The effects of the deformation-induced changes of polymer structures should be considered to improve the accuracy of models that predict complex self-folding behaviors. This is because the shape memory behaviors of polymer structures are significantly affected by the thermomechanical history during the pre-stretching process [38]. Notably, the self-folding behaviors of PS sheets are basically induced by the variations in microscopic ordering of the polymer chains. A degree of initial orientation of the molecules can be controlled by the amount of deformation for fixing the pre-programmed shape. Accordingly, the extent of initial stretching can be a design variable for handling the SME of pre-strained PS. Also, the anisotropies in the Young's modulus and linear coefficient of thermal expansion can be controlled by deformation-induced molecular alignment. Because these thermoelastic properties are used as model parameters for continuum-based finite element formulation, their temporal changes during shape recovery should be implemented to reflect the underlying

molecular mechanisms.

In this study, we carried out all-atom MD simulations to examine the performance of the shape recovery behaviors and property changes affected by the initial orientational order of the amorphous PS domains. Although coarse-grained models with reduced degrees of freedom can reduce the computational time and are less limited by the temporal and spatial scales, we adopted all-atom-based MD simulations. These incur massive computational cost compared with simplified models. However, chemically realistic microscopic conformations can be obtained with the energetically rigorous force-fields. We constructed models to describe the shape memory creation process of pre-oriented PS and investigated the changes of microscopic chain orientation and polymer conformation during the shape recovery. Moreover, the correlation between the microstructural changes induced by pre-stretching and the macroscopic thermoelastic and shape memory properties were examined. The present study provides insight into the structure-property relationship of the polystyrene SMPs and engineering design of controllable self-folding behaviors.

## 2. Computational approach

Atomistic modeling of the initial unit cell is conducted using the Amorphous Cell Tools of Materials Studio 5.5 (Accelrys, Inc.), which use the Theodorou-Suter method [41] to describe the well-relaxed amorphous polymers. All MD simulations of the sequential shape memory creation processes are performed using the LAMMPS code developed by Sandia national laboratory [42]. A polymer consistent force field (PCFF) [43] is adopted for describing both the covalent and non-bonded interactions between atoms. The PCFF has well-defined parameters that are based on the experimental properties of organic compounds and it satisfactorily reproduces the thermomechanical and phase transition behaviors of polymeric materials. The atom-based summation with a cutoff distance of 9.5 Å is used in treating the non-bonded van der Waals interaction. The distance-dependent dielectric method with the dielectric value of 2.6 [44] is adopted to calculate the Coulombic potential. These simulation settings have been used to calculate various properties of the organic and composite materials [34,45,46].

### 2.1. Modeling of an amorphous unit cell

Prior to applying the thermomechanical treatment, a non-oriented amorphous unit cell is constructed. The conformational form of the PS considered in this study is atactic, whereby phenyl groups are randomly attached to both sides of the hydrocarbon chains. Random positioning of the aromatic rings prevents crystallization. The representative cell consists of two atactic PS chains ( $M_w = 41,662.8$  g/mol), and the periodic boundary conditions are assigned along all directions to describe the bulk system. The molar mass of chains is chosen to be much larger than the entanglement molecular weight ( $M_e = 19,000$  g/mol) to ensure entanglements between the chains. The physical crosslinking in our model plays a role as a net point for fixing the original shape. The unit cell is relaxed via stepwise equilibration consisting of conjugated gradient minimization, the NVT ensemble for 500 ps at 300 K, and the NPT ensemble for 2.5 ns at 300 K and 0.1 MPa. The time step of simulations is 1.0 fs. Fig. 1(a) and (b) show the representative fragment of the atactic PS chain and the atomistic configuration of the relaxed structure of an amorphous cell, respectively. Each PS chain in the unit cell consists of 400 repeating styrene units.

To validate our model, its thermoelastic properties and phase transition behavior are investigated. The elastic modulus of the relaxed unit cell is calculated using the Parrinello-Rahman fluctuation method [47] during the additional NσT runs for 600 ps at

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